The wetting film drainage and rupture at titania surfaces of different hydrophobicity

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The drainage of the film between a colliding bubble and a solid surface followed by this film rupture is essential for the three phase contact formation. The rate of film drainage as well as the film stability is governed by the properties of the interacting interfaces, such as degree of solid surface hydrophobicity, surface charges of solid/liquid and liquid/gas interfaces, surface roughness and hydrodynamic boundary conditions.

On the basis of the dynamic air bubble collisions with hydrophobised amorphous TiO_2 surfaces immersed into solutions at different pH values, we demonstrate that, even in the presence of the attractive electrostatic forces, the wetting film stays stable on hydrophilic titania surface (instantaneous water spreading, no finite contact angle). For an intermediate degree of hydrophobicity the stability of the wetting film formed under dynamic condition, as well as kinetics of the three phase contact (TPC) formation are governed by the interplay of surface electrical charge and surface hydrophobicity, with significantly faster TPC formation in the presence of the attractive electrostatic forces In the case of highly hydrophobic solids the effect of surface charge is negligible and surface roughness is the key factor determining the kinetics of the wetting film rupture and the three phase contact formation. The film ruptures via nucleation mechanism and the phenomena is shown in Fig 1. In addition, under the same conditions, the time of film drainage (t_d) and the time of the three phase contact formation (t_{TPC}), depend on size of the colliding bubble, with both t_d and t_{TPC} being significantly shortened with the decrease of bubble diameter.

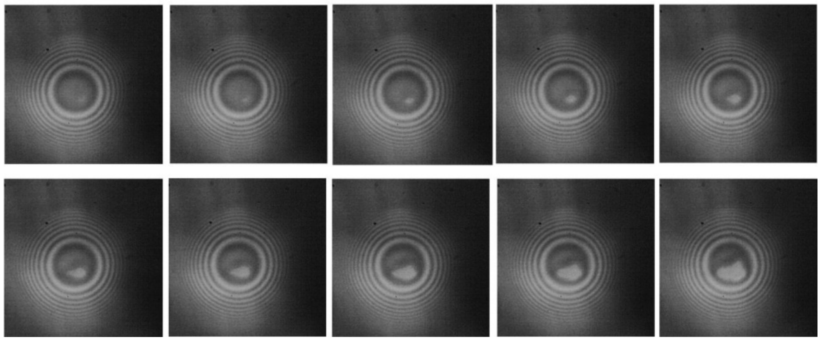

Fig. 1. Sequences of interferometric images presenting the wetting film rupture at hydrophobised (θ_{adv}=40°) titania. The rupture starts from one single hole in the film, and leads to a complete de-wetting of the whole film area within a few milliseconds. The time interval between subsequent images is 0.33 ms**.** pH = 5.8.

Acknowledgements:

We would like to acknowledge financial support from Polish Ministry of Sciences and Higher Education (Grant 1794/B/H03/2010/39).

Investigating electro-steric interactions of weak polyelectrolytes on particle surface through monitoring their aggregation kinetics

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The well-known use of polyelectrolytes[1, 2] to stabilize soap-free polymer particles is a very active area of industrial interest. The lack of quantitative kinetic model for fed-batch emulsion copolymerization processes with monomers of very different hydrophilicity and reactivity gives rise to a significant uncertainty about the detailed monomer distribution and architecture of the obtained particles. The synthesis of polyelectrolyte-covered particles using non-core-shell methods usually results in hydrophilic, pH- and salt-sensitive swellable layers of relatively small thickness, because they are used as additive in the material. This prevents the direct measurement of their physical properties using the usual techniques such as TEM or light scattering. It is therefore challenging to characterize the resulting particles and to predict trends in particle colloidal stability.

In this work, we use the particle aggregation kinetics obtained experimentally using various light scattering techniques as a tool to investigate steric interaction potential of weak polyelectrolytes on the particle surface. Our methodology is based on modelling of the measured Fuchs stability ratio, which links the aggregation kinetics to the interparticle potential. The interparticle potential is resulting from both charges and hydrophilicity of the polyelectrolyte layer. Therefore, modeling the potential using experimentally measured stability under various conditions provides a reliable insight into the mechanism of steric stabilization and general trends with polymerization conditions and particle composition. The investigated systems are various combinations of neutral acrylic monomers and weakly acidic acrylic monomers[3].

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Acknowledgements:

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Low-frequency shear viscoelastic relaxation in liquids

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Micro inhomogeneous structure of liquids has been suggested. It is assumed that the liquid structures are fluctuating clusters which form and break. High- and low-viscosity liquids have no fundamental difference. They differ in quantity, namely the lifetime of clusters which in simple liquids is much smaller than that of high-viscosity liquids.

The low-frequency relaxation process in liquids and slow relaxation process in amorphous polymers have analogy. The mechanism of low-frequency viscoelastic relaxation in liquids associated with the decay of the cluster, which is a multi-step process with a relatively long relaxation time.

The activation energy of the low-frequency viscoelastic relaxation and the number of kinetic units in the cluster has been estimated by the cluster modeling.

This work is concerned to studying of the low-frequency viscoelastic relaxation in liquids by an acoustic resonance method. The cluster model has been carried out for the interpretation of low-frequency viscoelastic relaxation in liquids. The study of low-frequency elasticity of liquids may be important for understanding of the boundary layers of liquids and their structural features, stability of colloids, for the theory of structural component of the disjoining pressure, etc.

Acknowledgements:

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Static and Dynamics of Capillary Bridges

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Capillary bridges (CB) are systems of liquid droplets wetting two other interfaces. Most popular CB variant is a droplet between two parallel plates. Even this relative simple system reveals number of interesting and non-trivial behaviors part of which are experimentally demonstrated and theoretically analyzed in the present study. The experimental setup consists of two plates parallel fixed at a micrometer with the help of which the two plates can be drawn nearer and apart. The processes taking part within BCs are recorded by a camera. Experiments are carried out with BCs of pure water between hydrophilic and hydrophobic surfaces. One of the most informative static parameters obtained from these measurements is the upper limit of distance at which a CB can be stretched, i.e. the upper CB's stability limit. These experimental data are interpreted from the viewpoint of Rayleigh stability theory. The CB's dynamic concerns the kinetics of capillary attraction. For that purpose the lower plate (the plate with the droplet on it) is mobile (not fixed) and when the upper plate touches the droplet cap, the droplet together with the adhered (lower) plate are set in motion. Actually the two plates are pressed together until a thin (less than 0.5 mm) liquid film between the plates is formed. The attraction kinetics is recorded and the corresponding rates are evaluated. The experimental data are interpreted as a balance of capillary inertia and viscose forces.

Adhesion improvement of electroless copper coatings by thixotropic additives

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The problem with the adhesion of metal coatings is well known, but its solution, especially at smooth substrate surfaces in great extend remains open till nowadays. The standard way for adhesion improvement is substrate roughening but there are objects, where the roughening is unsuitable or even impossible (e.g. glass, steel, decoration surfaces). Adhesion increasing in such cases requires other methods. Encouraging results in this respect shows addition of the so-called thixotropic substances in metallization solutions. In our experiments we have used ethyl cellulose (EC) and a polyzwitterion polymer poly(dimethyaminoethykmethacryloyl propanesulfonate) (PDMAPS) showing pronounced stickering properties. Utilized was a standard copper bath, pure and with added thixotropic substances. Metalized were smooth epoxy fiber glasses, glass and stainless steel substrates. The deposition rate was 2-3 □m/h and the deposition thickness about 0.1÷0.3 µm. The thixotropic additives changed not substantially the deposition rate, in the same time they have shown stabilizing action on the electroless bath. At al cases thixotropic additives improved substantially the adhesion especially on smooth surfaces. The sticking mechanism has been investigated via analysis of viscous, wetting, electrochemical properties and EPR-spectrums. Most interesting correlations have been shown with respect to the viscous and wetting properties. So for instance it has been found, a drastic increase of the relative viscosity (up to 236%) of the bath solution by adding EC. Not so drastic, but enough expressive influence has been observed by the wetting properties: the solutions with EC/PDMAPS additives have shown highest degree of three phase contact angle hysteresis, compared with the bath solutions without thixotropic additives. The experimental results are qualitatively, quasi-quantitatively interpreted and discussed.

Acknowledgements:

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Stability of foam films under dynamic conditions

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We have developed a new procedure, which allows us to form foam films, from a limited surface of surfactant solution. With this procedure we studied the stability of dynamic foam films, formed by rapidly stretching the solution surface (viz. under dynamic conditions). This procedure mimics the surface expansion of newly formed bubbles during foaming. This procedure was used to study the effect of surfactant type and concentration on the stability of dynamic foam films. The effect of some basic electrolytes (NaCl and $CaCl_2$) was also studied. The obtained results were compared to the foamability of the same surfactant solutions, as well as with the results from several other "classical" methods for studying foam films – vertical films withdrawn from large solution surface, capillary cell of Scheludko-Exerowa, and bubble under air-water interface. For most of the studied systems we observed a good correlation between the stability of the dynamic films and the foamability of the respective solutions. In contrast, no such correlation was seen with the results from the "classical" methods.

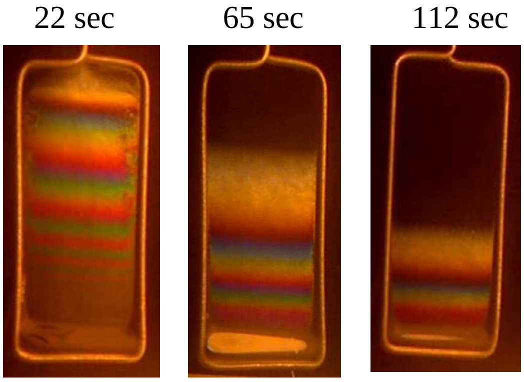

Fig. 1 Thinning of a foam film under dynamic conditions. This film ruptures 113 s after its formation, immediately after the third frame shown on the right-hand-side of this figure.

Disjoining pressure of core-shell particle stabilized thin films

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An analytical expression to determine the disjoining pressure(van der Waals interaction force per unit area) of a thin film stabilized by core-shell particles straddling a thin film interfaces is presented. The method used is similar to the Hybrid -Hamaker approach employed in Ref. [1] for Janus particle or bear particle stabilized films. The expression finds application in the stability of thin films for electronic devices and the stability against coalescence of drop in polymeric blends for producing advanced functional materials.

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Parabolic and Linear Growth Regime of PDADMAC/PSS Multilayers

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The buildup of polyelectrolyte multilayers is investigated in solution with multiple angle nullellipsometry. Polyanion poly(styrenesulfonate) (PSS) and polycation poly(diallyldimethylammonium) (PDADMAC) are adsorbed sequentially from 0.1 M NaCl solution. First the films grow parabolically. After N_{trans} deposited PDADMAC/PSS layer pairs a transition from a parabolic to a linear growth occurs.

For large molecular weight (M_w(PSS) > 25 kDa and M_w(PDADMAC) > 80 kDa), N_{trans} is fifteen, the thickness per layer pair in the linear growth regime is 12.3 nm. But if either the PDADMAC or the PSS molecular weight is decreased, N_{trans} either falls (down to 8) or rises (highest value observed 33), respectively. Simultaneously, in the linear growth region the thickness per layer pair decreases down to 4.3 nm or exceeds 25 nm. If the PSS molecular weight is decreased below 20 kDa, three growth regimes are observed: first exponential, then parabolic and finally linear. The opposite influence of PSS and PDADMAC molecular weight is attributed to different polymer conformations during adsorption. The data suggest that molecular weight provides a way to control growth and internal structure of polyelectrolyte multilayers.

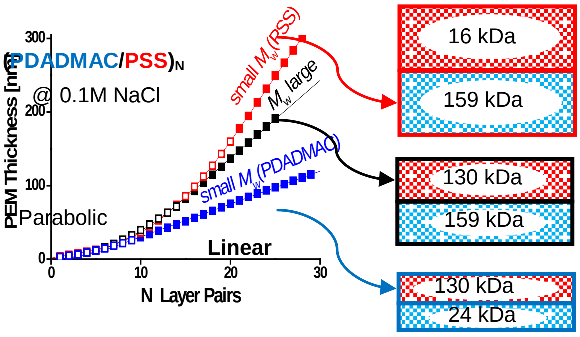

Fig. 1 Thickness of polyelectrolyte multilayer as function of the number of deposited layer pairs for three different combinations of PDADMAC/PSS molecular weight.

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The Effects of Reactive Oxygen Species on Single Polycation Layers

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Positively charged, branched polyethylenimine (PEI) adsorbed onto silicon wafers and silica surfaces are attacked by free hydroxyl radicals.[1] With AFM colloid probe technique, the surface forces between the PEI layers are measured.[2] Force profiles show that between freshly deposited PEI layers electrostatic repulsion dominates the surface forces. After radical attack both, surface potential and surface charge density, are reduced by a factor of about two, while the Debye length remains unchanged. Adsorbed gold nanoparticles and force volume measurements show a homogeneous distribution of the surface charge on length scales between 40 nm and 30 µm. For radical attacked PEI layers we find a 10 % decrease of saturation coverage of gold nanoparticles. This is consistent with the decreased surface charge density when the electrostatic three-body interaction is considered. Nevertheless, the NP adsorption kinetics is slowed down suggesting that the PEI layer is inhomogeneous on the nm-scale after radical attack.

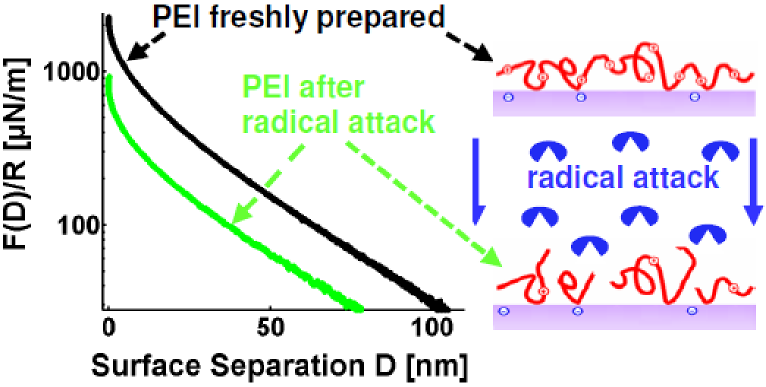

Fig. 1. Left: Surface Forces before and after exposure to free oxygen radicals. Right: Schematic of the partial decomposition of the surface layer.

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The Impact of water on a range of non-aqueous colloidal suspensions

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Water has for many years been known to have a significant impact on the behaviour of non-aqueous colloidal systems[1]. There are two potential impacts of water. It will either a. destabilise the system due to the formation of water bridges [2] and capillary action, or b. stabilise the system due to an increase in the surface potential of the particles resulting in repulsion [3]. The majority of the published research has focused on inorganic solids suspended in non-aqueous media, however there is growing interest within the pharmaceutical industry as much of primary processing (processes up to the isolation of the pure active pharmaceutical ingredient – API) is carried out in non-aqueous systems where the water levels may vary.

The aim of this work was to investigate correlations between the physical properties of the solid and the suspending media and the impact water has on the suspension properties. A range of solvents have been investigated with varying water miscibility and dielectric constants, coupled with a range of APIs with varying hygroscopic nature, wettability and solubility. Additionally lactose (a more wettable organic compound) and Calcium carbonate (a comparably wettable inorganic compound) have been investigated. A relative prediction of the impact of water on the colloidal properties is suggested with reference to the physical properties of both the solids and the liquids investigated.

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Surfactant transport onto a foam lamella

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The evolution of surfactant on a foam film interface determines the efficiency of separation obtained by a foam fractionation column used e.g. for purifying/enriching that surfactant. Therefore, a study of the surfactant evolution on the film surface coupled to lamellar film drainage has been carried out to understand the performance of a foam fractionation column. This study simulates the surfactant transport onto a lamella in a foam fractionation column with reflux, since such columns offer greater control over enrichment and recovery.

Assumptions made for the simulation are that the lamella is flat due to the bubble shape in a dry foam – a common situation in a foam fractionation column, the initial surfactant concentration on the film surface is uniform and the surfactant concentration at the Plateau border is held fixed at the value set by the reflux. Insoluble surfactant is assumed during the simulation as such surfactants derive more benefit from a reflux system. There are two terms involved in the equation for surfactant flux which are the Marangoni flow – from the Plateau border to the centre of the lamella – and the film drainage – which is directed from the centre of the lamella to the Plateau border. The extent of film drainage is bounded using two extremal assumptions of mobile [1] or rigid [2] interfaces. On a mobile interface, the film drainage dominates the Marangoni effect, while on a rigid interface, the Marangoni effect is dominant. The numerical simulation was carried out using a material point method [3] followed by a bookkeeping operation to regrid the film. Analytical solutions for the case of no drainage and for a (quasi) steady state for the case of a rigid film – in which Marangoni flows and drainage are balanced – as well as the asymptotic solution for the case of a mobile film – where there is a boundary layer near the Plateau border, were used to verify the numerical simulation. From the simulations, it can be concluded that the film drainage obtained using surfactant with a mobile interface is much faster than that modelled using surfactant with a rigid interface, meaning that surfactant is washed out of the film in the mobile case. The desirable condition in a foam fractionation column is however where the Marangoni flow dominates the liquid drainage which can be achieved when using surfactant that gives a rigid interface. The (quasi) steady state solution verifies the simulation result at later time for the case of film with a rigid interface. An asymptotic solution in the case of film with a mobile interface gives a good prediction of the surface concentration of surfactant at the centre of the film as well as that within the Boundary layer.

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Adsorption on solid surfaces: Effect of surfactant and calcium

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The surface energy of solids and the solid-liquid interfacial tension are two important characteristics, governing the behaviour of solid materials in practically important processes, such as adhesion and wetting. In the approach proposed by van Oss[1], the interfacial tension is decomposed into three components: Lifshitz-van der Waals (γ^{LW}), electron-acceptor (γ^{+}) and electron-donor (γ^{-}) components. To determine the aforementioned components for a given surface, one should measure the three-phase contact angles of at least three liquids with known surface properties. The major aims of the current study are: (1) to characterize the surface properties of a series of solid substrates by using van Oss approach and (2) to evaluate how these energies depend on the presence of surfactant and calcium ions in the liquid phase. To achieve our goals we determined γ^{LW}, γ^{+} and γ^{-} by measuring the contact angle of water, formamide and diiodomethane on the studied substrates. Then we examined the effect of surfactant concentration on the solid-water interfacial energy, as well as on the contact angle of oily drops placed on a given solid surface. The obtained results demonstrate that the contact angle of oily drops may pass through a maximum, whereas the surface tension may go through a minimum, with the increase of surfactant concentration for anionic surfactants in the presence of calcium ions. These unexpected results are explained with the competitive adsorption of the calcium ions on the surface of the anionic surfactant micelles and in the surfactant adsorption layer.

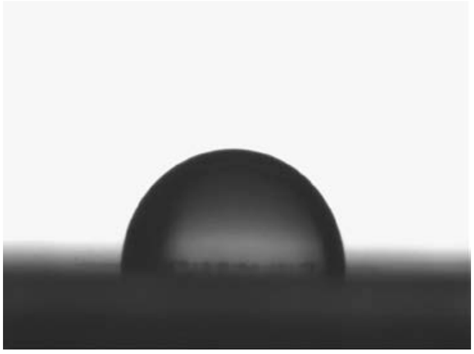

Fig. 1 Oily drop deposited on solid substrate in presence of anionic surfactant and calcium ions.

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Quantitative Evaluation of Surfactant Adsorption from Kinetic Interfacial Tension Data

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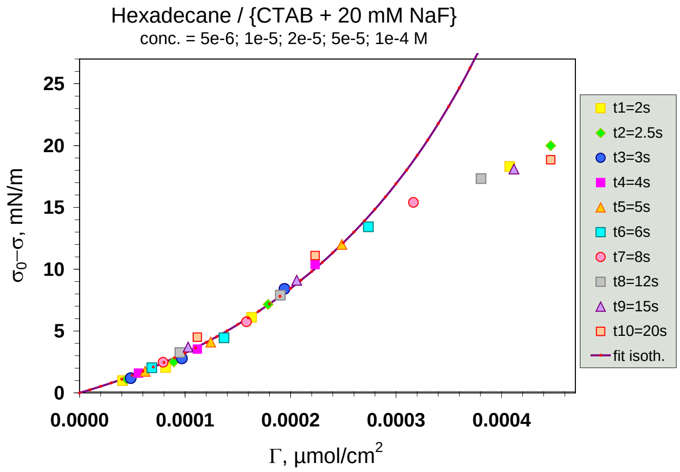
In this work we discuss experimental data for dynamic interfacial tension (O/W), measured at different surfactant concentrations, $\sigma(c,t)$. A procedure for interpretation of such data is proposed – we show how to determine the adsorbed amount per unit area (Γ), and obtain useful information for the surface equation of state and the time evolution of Γ. The method for data processing is based on the theory described in Ref. [1]; currently, it is applicable to relatively short times and/or low bulk concentrations. An example of results is shown in Fig. 1, for the cationic surfactant cetyl trimethylammonium bromide, in the presence of salt. One observes that the experimental points at different times and concentrations lie on a “master curve”; the latter can be fitted with a suitable equation of state. This gives values for some characteristic parameters, e.g., $\Gamma_\infty = 5.69\times10^{-4}$ μmol/cm^2 (the limiting adsorption). Another outcome from the processing operations is the time dependence of the adsorption, Γ (presented in Fig. 2). The calculations might be useful for analysis of measured data in the case of fast adsorption dynamics in undersaturated surfactant layers.



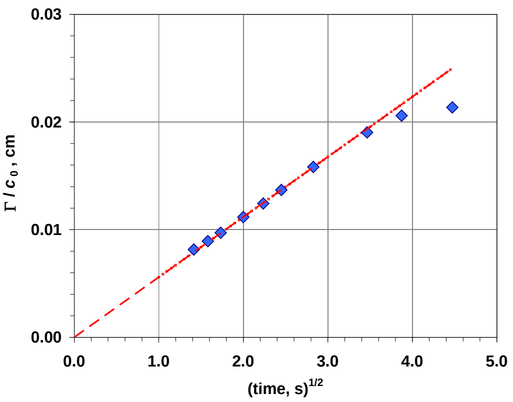


Fig. 1 Data for $\sigma(c,t)$, extracted from the kinetic curves and fitted with an isotherm.

Fig. 2 The short-time adsorption kinetics, obtained for the system in Fig. 1.

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Self-Assembled Bilayers from the Protein HFBII Hydrophobin: Nature of the Adhesion Energy

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The hydrophobins are a class of amphiphilic proteins, which spontaneously adsorb at the air/water interface and form elastic membranes of high mechanical strength as compared to other proteins [1]. The mechanism of hydrophobin adhesion is of interest for fungal biology and for various applications in electronics, medicine and food industry. We established that the drainage of free foam films formed from HFBII hydrophobin solutions ends with the appearance of a 6 nm thick film, which consists of two layers of protein molecules (Fig. 1), i.e. it is a self-assembled bilayer (S-bilayer), with hydrophilic domains pointing inward and hydrophobic domains pointing outwards. Its formation is accompanied with a considerable energy gain, which is much greater than that typically observed with free liquid films. The experiments at different pH show that this attraction between the “hydrophilic” parts of the HFBII molecules is dominated by the short-range hydrophobic interaction rather than by the patch-charge electrostatic attraction [2].

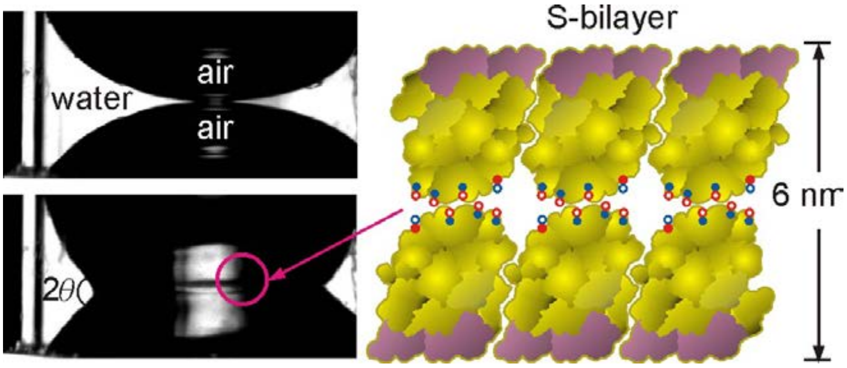

Fig. 1 Two photographs of the process of S-bilayer formation, and sketch of its structure.

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The effect of varying substrate wettability on the thermocapillary motion of droplets

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We study the two-dimensional dynamics of a droplet moving on a non-isothermal, inclined solid substrate, heated with constant temperature gradients. We use lubrication theory to derive a single evolution equation for the gas-liquid interface. Our model takes into account the presence of dynamically-varying substrate wettability brought about by local temperature variations. This important feature of the model has, to the best of our knowledge, not been taken into account by previous models in the literature in which the contact angles were typically kept constant. The evolution equation is solved numerically using the finite element method and an implicit Euler method in time. A full parametric study is carried out that focuses on the interplay between the effects of the magnitude of the substrate temperature gradient, substrate wettability, Marangoni stresses, and gravity. The results show that in the presence of temperature-induced wettability variations, the dynamics are rather complex. This is characterised by a non-monotonic dependence of the droplet centre-of-mass velocity on the magnitude of the substrate temperature gradient for horizontal substrates, and situations wherein, for inclined substrates, this monotonicity persists even when the thermal gradient is such that Marangoni stresses are expected to reinforce the action of gravity. We have also found evidence of 'stick-slip' contact line motion that arises in cases in which the initial contact angles are between the corresponding temperature-varying equilibrium values. These results show collectively that it is essential to account for variations of the substrate wettability in models of droplet motion over non-isothermal walls.

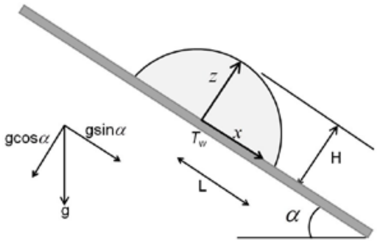

Fig. 1 Schematic diagram of the drop on an inclined plate. $T_w = T_o + \Gamma x$, where Γ is the constant temperature gradient applied at the solid wall

Acknowledgements:

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Dendritic nanofluids mediating surface forces: A combined SAXS and SFA study

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Fluids containing nano-sized structures are increasingly employed in modern technologies, ranging from cooling fluids to drug delivery systems. However, despite their numerous applications, our fundamental understanding of the surface forces mediated by nanofluids is still limited[1]. In particular, due to their nanosize and related characteristics, applicability of established surface force theories, such as the DLVO theory is unclear.

With several tunable parameters such as the size, surface and interior chemistry, dendritic macromolecules (or dendrimers), offer a unique model nanofluid for investigating the effect of nanostructures on classic colloidal phenomena– for instance, how they may mediate surface forces or interact with lipid mesophases. Recently we have performed complementary small angle X-ray scattering (SAXS) and surface force apparatus (SFA) measurements in aqueous solutions of anionic polyamidoamine (PAMAM) dendrimers to study their interactions in the bulk and when under nano-confinement. Furthermore, we have studied how the interactions mediated by the dendrimers would be modified by the presence of a number of ionic surfactants, including cationic surfactant dodecyltrimethylammonium bromide (DTAB) and anionic surfactant sodium dodecyl sulfate (SDS).

We find in the bulk that the presence of cationic surfactant DTAB, at concentrations just above its cmc, the adsorption of the surfactant monomers to the dendrimer surfaces leads to the formation of a new dendrimer-surfactant complex. Under nano-confinement in the SFA under similar conditions, we observe short range interactions between confining surfaces relating to structuring of the dendrimer-surfactant complexes. For anionic surfactant SDS which is similarly charged to the dendrimers, the dendrimers and surfactant remain non-interacting which leads to a binary depletion interaction between when confined in the SFA.

From these SAXS and SFA measurements, we have gained insight into the complex effects of nanofluids on surface interactions. Such interactions between nanofluids and soft matter structures bear fundamental relevance to how nanostructures interact with lipid mesophases encountered in complex biological tissue surfaces such as cell membranes, as well as to the design of drug delivery systems employing dendrimers where such interactions are an important consideration.

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Poisson-Boltzmann Description of Interactions and Aggregation in Charged Colloidal Suspensions in the Presence of Multivalent Ions

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The DLVO theory is able to explain the interactions between the charged colloidal particles in the presence of ions. From the interactions one can also predict the aggregation rates at different conditions and thus the stability of the suspensions [1,2]. Within the DLVO the interactions are explained as a sum of the van der Waals and electrostatic forces. The latter can be described by the Poisson-Boltzmann (PB) theory which usually involves a numerical solution of the non-linear differential equation. On the other hand Debye-Hückel (DH) approximation leads to a linear differential equation and therefore in many cases permits an analytical solution.

We numerically study the forces and aggregation rates between spherical colloidal particles in the presence of multivalent ions. The electrostatic interactions are treated at full PB level as well as within the DH approximation. The DH model is valid for weakly charged particles and in the presence of ions of low valence. Furthermore within this approximation the ionic composition is not important, because the ion valence enters in the equations only through the ionic strength. On the other hand, the full PB approach discriminates between electrolytes with different ion valence but the same ionic strength.

The DH approximation predicts the decrease of the critical coagulation concentration (CCC) with the square of the valence, z^{-2}, whereas in the case of the full PB approach the dependence of CCC on the valence is stronger and it enhances with increasing the surface charge of the particles. However even at unrealistically high surface charge densities the classical Schulze-Hardy rule, which predicts the z^{-6} dependence, is not recovered by PB.

For the prediction of the CCCs, the DH approximation can be used, because at CCC the diffuse layer potentials are small. We derive a simple analytical expression for calculating the CCCs within the DH approximation and compare it to the experimental results. By using the surface charge densities of the particles, that are calculated from the electrophoretic mobility data, very good agreement with the experimentally determined CCCs [2,3] is observed.

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Acknowledgements:

This research was supported by the Swiss National Science Foundation and the University of Geneva.

Emulsion (oil/water/oil and water/oil/water) Films from Polyoxyalkylated Dietylenetriamine Polymeric Surfactant Solutions: Molecular Structure Effect.

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The present study explores four polyoxyalkylated dietylenetriamine polymeric surfactants (A, B, C and D), products of Champion Technologies (USA). Surfactant A is an industrially applied agent, while surfactants B, C and D have been recently synthesized. The molecule of each polymer consists of two parts: a more hydrophobic one, where polypropylene oxide (PPO) blocks are predominant and a more hydrophilic one, where polyethylene oxide (PEO) blocks are predominant. Surfactants A, B, C have a similar structure and belong to the group of the so-called “star-like” polymers, differing only in the number of polymeric branches: 4, 6 and 9 in the mentioned order. Surfactant D is of a dendrites type and its molecule consists of 4 to 6 primary and 2-3 secondary branches. (Fig.1)

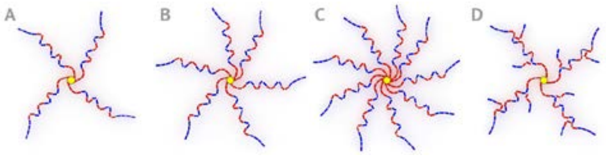

Fig.1 Sketch of Polyoxyalkylated Dietylenetriamine Polymeric Surfactants

The differences in surfactants’ ability to stabilize oil/water/oil and water/oil/water emulsion films are evaluated. Emulsion films stabilized by the surfactants also show different behaviour regarding some specific parameters such as surfactant concentration for obtaining a stable film, critical pressure of a single film rupture, etc.

These observations give reasons to believe that model studies can support a comprehensive understanding of how the change in polymeric surfactants’ molecular structure can impact the emulsion films properties. This may enable a target design of the macromolecular architecture depending on the polymeric surfactant purpose to stabilize or destabilize different types of emulsions.

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Wetting Properties of Ionic Liquids

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One of the interesting discoveries in the field of chemistry in the last two decades turns to be the room-temperature ionic liquids (RTIL). They are liquid salts at low temperature (room temperature or below), consist entirely of ions – organic cations and organic or inorganic anions, i.e. electrolytes without solvent. These liquids reveal many useful properties. In this study we investigated the wetting properties of series of six RTILs in contact with solid (glass) surfaces. Particularly, we studied the RTIL adhesion on glass via influence on the three-phase contact (TPC) hysteresis. This was carried out by means of two independent methods – the conventional small droplet on flat inclined plane (Fig.1a) and a method developed by us, named as „capillary tube method” here and afterwards (Fig.1b).

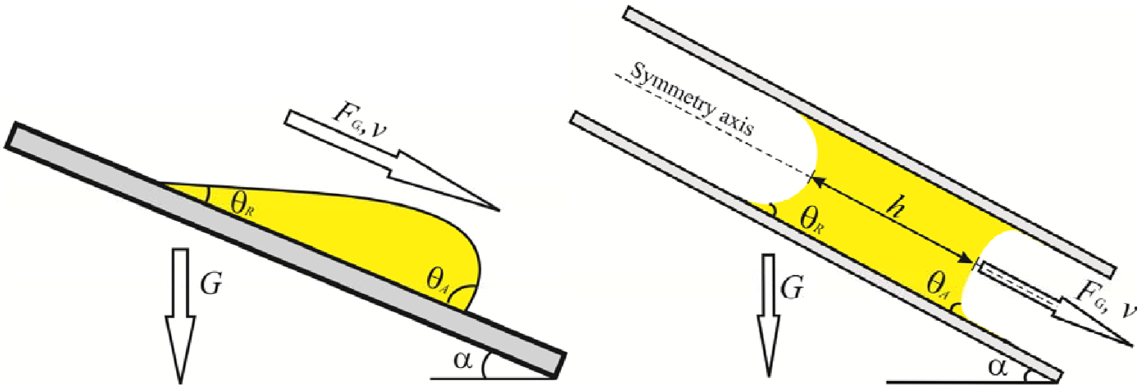

Fig. 1 Sketches of the measuring element of the methods used in this study**: Left:** droplet on flat inclined plane; **Right:** droplet in a capillary tube; *G* – the droplet weight; F_G – the driving force (projection of G along the plate surface/tube axis). *v* – the rate of propagation of the TPC line; $\theta_{A/R}$ – TPC advancing/rececing contact angle.

One of the most informative parameter, characterizing the TPC hysteresis is the so-called critical angle of inclination α_{cr}. This is the angle α_{cr} at which the droplet is set in motion.
Experimental results for both wetting statics and dynamics of ionic liquids and pure water hysteresis are given and discussed.

Impinging Jet Study of the Deposition of Colloidal Particles on Synthetic Polymer (Zeonor) and Glass Surfaces

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Adsorbtion, deposition and removal of colloidal particles and bioparticles on/off a solid/liquid interface is of a high scientific and industrial importance, e.g. for better understanding of filtration processes, water treatment, microfluidic devices construction, paper making, biofouling of membranes and artificial organs etc. For detailed and exact understanding of the latter mentioned phenomena well defined hydrodynamic and physicochemical conditions during experiments are required. These conditions are met in Impinging Jet technique . In our study, Impinging Jet deposition experiments were performed on microscopic glass and on synthetic polymer (Zeonor) original and by micro-embossing modified substrates with exactly defined topology as confirmed by AFM, SEM and TEM. Deposition experiments were performed at ambient temperature and at selected flow regimes (Re ranging from 10 to 20). As a particles deposited the PS 1,1 µm diameter particles (Sigma-Aldrich) were used having negative charge of -20 mV as observed by zeta potential experiments. There was found gradual increase of total number of deposited particles with time reaching steady state number. Obtained kinetic curves were fitted to the theoretical blocking model where characteristic time required to reach the steady state (blocking time) as well as steady state number of deposited particles were calculated.

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Acknowledgements:

Financial support from the Operational Program Research and Development for Innovations – European Regional Development Fund (Grant CZ.1.05/2.1.00/03.0058) and of internal grant of Palacky University in Olomouc (Grant Prf_2013_028) are gratefully acknowledged.

Co-adsorption of bovine serum albumin in n-dodecyl-β-D-maltoside foam films

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The co-adsorption of Bovine Serum Albumin (BSA) in *n*-dodecyl-β-D-maltoside ($C_{12}G_2$) foam films formed from mixed solutions with a composition (BSA:$C_{12}G_2$ = 1:7.5; 1:50; 1:100) was experimentally investigated. In order to answer the question which one of the surfactants or both of them is/are adsorbed on the film surfaces data for: (i) the kinetics of surface tension of the single surfactants and their mixtures; (ii) the AFM pictures of BSA surface layer and its mixed layers with $C_{12}G_2$; (iii) the viscosity in the foam film determined from its thinning before 100 nm; (iv) the kinetics behavior of foam films at pH = 4.9, 3.8; (v) the BSA concentration in the solution obtained by dissolving of a dry foam were obtained.

Data for the surface activity of investigated solutions showed that in the mixed adsorption layers from solutions with molar ratio BSA:$C_{12}G_2$=1:50 and 1:100 $C_{12}G_2$ molecules predominate. This conclusion is supported by AFM pictures. The lower viscosity calculated from the thinning of foam films stabilized by these mixtures than this for the films from individual BSA solution is explained with the less aggregation between albumin molecules due to their hydrophilization by bind $C_{12}G_2$ molecules. The stable foams produced from the above mixtures were dried to such an extent enough for black foam films formation in them. Quantitatively, it was found that the concentration of BSA in the solution obtained after dissolving of the dry foam is an order lower than the concentration of the solution drained from the foam during its drying.

The thinning evolutions of the films from pure and mixed solutions, recorded at pH = 4.9 showed that $C_{12}G_2$ films thin up to 90 nm, while the thinning of films from the mixture (1:100) depends on the time of film interfaces aging: the films with fresh interfaces have a similar drainage as the pure $C_{12}G_2$ films; the films with intermediate times of aging become unstable or stable ones when black spots (mobile or frozen) formed in them; the aged films thin fastest and they jump to NBF as the films from $C_{12}G_2$ solution but with pH =3.8 or with 10^{-1} M NaCl. It means that the films electrostatics stabilization is screened which can be due to BSA adsorption. This suggestion was checked by an estimation based on the surface charge density of the following interfaces: air/water; air/$C_{12}G_2$ solution and air/$C_{12}G_2$+BSA solution. It was found that the number of OH^- ions expelled by BSA is two orders smaller that those by $C_{12}G_2$. The values of films equilibrium thickness and surface potential in the case when pH of the mixed solution is 3.8 indicate that the films are common ones. This finding demonstrates again that BSA molecules adsorb on the film interfaces. At pH=3.8 BSA molecule is charged positively that is why the film interfaces are recharged.

Acknowledgment:

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Tensiometric investigation on adsorption of oil–soluble emulsifiers at w/o interfaces

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Polyglycerol polyricinoleate (PGPR) and distilled monoglycerides (DMG) are oil–soluble emulsifiers which are often used for emulsification of water droplets in triglyceride oils. PGPR and DMG adsorb at w/o interface and stabilize the droplets. Unhydrogenated vegetable fats (UVF), having relatively high melting temperature, are commonly used as ‘oil adsorbers’ and rheology modifiers, and are normally poor emulsifiers. Formation of good adsorption layers at w/o interface are especially required in w/o emulsions with high concentration of dispersed phase, such as low–fat spreads, where the water droplets are more susceptible to coalescence. The objective of this work was to investigate adsorption of PGPR, DMG and UVF at w/o interface, when used alone or as their mixtures. The oil phase was prepared by dissolving PGPR, DMG, UVF or their mixtures, at different concentrations, in sunflower oil. Deionized water was used as the water phase. Interfacial tension measurements were performed at 40 ^{o}C, and for selected compositions at 15 ^{o}C. PGPR and DMG adsorb at the w/o interface, as evidenced by decrease in interfacial tension. UVF is not surface active. Binary PGPR/DMG mixtures give lower interfacial tension when compared to the single component solutions, indicating a synergistic adsorption. Finally, ternary PGPR/DMG/UVF mixtures gives even lower interfacial tension, indicating that UVF influence properties of PGPR/DMG adsorption layers, even though it does not adsorb at w/o interface when used alone.

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Bubble-bubble interaction in aqueous β-lactoglobulin solutions

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The presented drop and bubble micro manipulator (DBMM, SINTERFACE Technologies, Berlin) is a new experimental tool for the quantitative analysis of the interaction between two drops or two bubbles or even between a single drop and a single bubble in a liquid medium [1]. We used DBMM to analyse the stability of bubbles, having protein absorbed on their surfaces. The stability of the liquid films between bubbles depends on the β-Lactoglobulin (BLG) solution concentrations, the ageing time [2] and the solution pH. A threshold concentration of BLG is required to prevent immediate coalescence. The longer the ageing time above this threshold concentration of BLG is the longer is the lifetime of the liquid film between the bubbles. The adsorbed amount of BLG determined as a function of time and concentration by bubble profile tensiometry correlates with the observed coalescence behaviour of the two contacting bubbles.

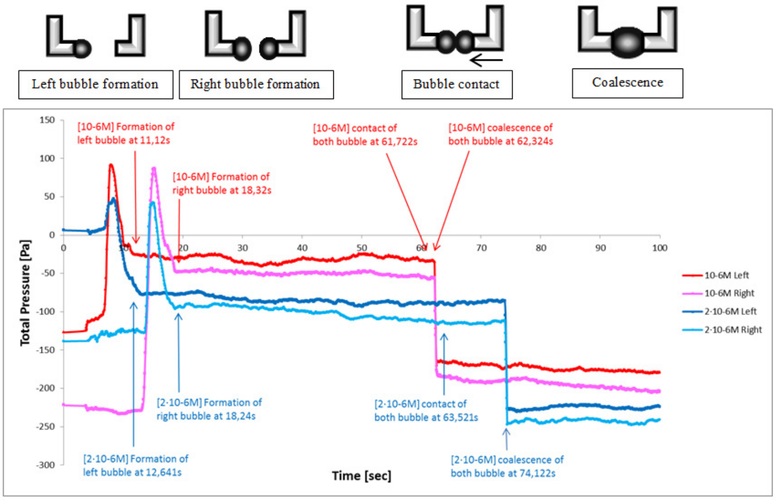

Fig. 1 Sudden pressure changes registered for both sides of DBMM and estimation of coalescence time for solutions of BLG concentrations of 10^{-6} M and 2×10^{-6} M at a fixed ageing time of 40 s

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Kinetics of the bubble collisions at hydrophilic fritted glass with controlled air presence – experiments and numerical simulations

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Kinetics and outcome of the rising bubble collisions with liquid/solid interfaces depends on many interconnected factors, like: bubble size, shape deformations, impact velocity, hydrophobic/hydrophilic properties of solid surfaces, solid surface roughness, air presence at solid surfaces, presence and state of adsorption layer at the interacting surfaces and properties of the liquid film formed during the collisions, etc. During the very short collision time (millisecond time-scale), the liquid film needs to drain to its critical thickness of rupture, otherwise a bubble rebounds from the surface. It is well known that the kinetic of the liquid film drainage depends mainly on its radius, kinetic energy and a size of the colliding bubble, solid surface roughness, mobility of the film interfaces, presence and state of the adsorption layer at the film interfaces. Moreover, recently we showed that air presence at solid surface in form of nano- and micro-bubbles affects significantly stability of the liquid films formed and the bubble attachment to hydrophobic surfaces.

The paper presents the computational fluid dynamics (CFD) simulations and experimental results on the bubble collisions with hydrophilic fritted glass filter immersed in distilled water. The filter was connected to a closed system consisting of: (i) syringe (ii) one-way valve and (iii) precise pressure analyser. The syringe was used to have an overpressure (< 1 kPa) in the system in order to force the presence of air in the pores and at surface of the hydrophilic fritted glass filter. The collision of the bubble with filter surface was monitored using high-speed camera (1000 Hz). The surface was immersed in the liquid either (i) with overpressure (case 1) or (ii) equilibrium (atmospheric) one (case 2). For case 2 the filter surface was additionally immersed several times (quite vigorously) in water to get rid of air, which could be potentially present at the surface. It was found that the outcome of the bubble collisions and dissipation of kinetic energy associated with its motion was significantly affected by the procedure of surface preparations. Comparison of variations in position of the bubble centre and local velocities during collisions showed that a characteristic phase-shift of the bubble oscillations period occurred. The period was shifted towards smaller values for case 1. For example in the air absence (case 2) the second collision occurred at $t = 23$ ms after the first one, while in the air presence (case 1) this time period was shortened to 19 ms. Additionally, the number and amplitude of the bubble bouncing was smaller for case 1. The results obtained indicate that rupture of water film formed by the colliding bubble and submicroscopic bubbles, present in pores of the fritted glass filter in case 1, was responsible for changes of the bubble bouncing kinetics. The CFD simulations results were compared to the experimentally obtained data. The bubble behaviour during collision with hydrophilic solid surface was calculated numerically by solving the governing equations, describing the conservation of momentum and mass of an incompressible liquid. Two cases were considered in numerical simulations: (i) collision of the bubble with smooth, hydrophilic wall, and (ii) collision of the bubble with the wall having a hole (80×160 μm) filled with air in a form of small bubble. The height of this micro-bubble was equal 31 μm. Very good agreement between the experimental data (phase shift, changes in the bouncing amplitude, the energy exchange rate) and the numerical results were found.

Influence of cationic surfactant on kinetics of the three phase contact formation at mica and Teflon surfaces

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Probability and kinetics of the three phase contact (TPC), gas-liquid-solid, formation and the bubble attachment to solid surface depends on many interrelated factors among which properties and drainage kinetics of the separating liquid film are the factors of crucial importance. Properties of the thin liquid film (TLF) formed by the colliding bubble are strongly affected by hydrophobicity and roughness of solid surface, the bubble impact velocity, size and degree of the bubble shape deformation, presence of surface active substances (SAS), properties of the SAS adsorption layers, and also on a dynamic architecture of the adsorption layer (DAL) formed. A preferential adsorption of ionic surfactant at surface of the colliding bubble can modify electrostatic interactions and stability of the TLF formed. It can either (i) lower or (ii) increase stability of the film formed. In the case (i) we should observe a facilitation of the TLF rupture and the TPC formation, while in the case (ii) the time of the TPC formation and the bubble attachment should be prolonged.

Results of studies on influence of n-hexadecyltrimethylammonium bromide (CTABr) on time of the TPC formation (t_{TPC}) at model surfaces; hydrophilic mica and hydrophobic Teflon, are presented. In the case of mica plate immersed in distilled water, both the solid and the bubble surface were negatively charged (zeta potentials: ca. -100 mV and -65 mV, respectively), what caused formation of stable thin liquid film due to electrostatic repulsion between similarly charged film interfaces. Presence of CTABr (cationic surfactant) in solution and its preferential adsorption at bubble surface caused electrical charge reversal at gas/solution interface from negative to positive. As a consequence, destabilization of the wetting film and attachment of the colliding bubble to mica surface occurred. The time-scale of this phenomenon depended on CTABr solution concentration and distance (L) between the mica surface the bubble formation point (capillary orifice). For example in the case of L= 100 mm, increase of the CTABr concentration, from $1 \cdot 10^{-6}$ M to $1 \cdot 10^{-5}$ M, resulted in shortening of time of the TPC formation (t_{TPC}) from 577± 121 ms to 365±127 ms. In the case of $1 \cdot 10^{-6}$ M, the t_{TPC} for different mica locations, i.e. L = 100 mm and L = 3 mm, was 577±121 ms and 161±97 ms, respectively. The obtained results clearly indicate the importance of the CTABr concentration the DAL formation over the bubble surface and for kinetics of the TPC formation at mica surface. In the case of the smooth Teflon surface (zeta potentials: ca. -40 mV), addition of CTABr should lead to shortening of the t_{TPC} due to mentioned above charge reversal of the bubble surface. However, opposite phenomena, for both studied distances, i.e. 3 and 250 mm, was observed. Increases of CTABr concentrations from $1 \cdot 10^{-6}$ M to $1 \cdot 10^{-5}$ M caused prolongation of the t_{TPC} from 90 ±17 ms to 260± 25 ms and from 141±14 ms to 240±36 ms, for L=3 mm and L=250 mm, respectively. Prolongation of the t_{TPC} on Teflon surface indicates that air, in a form of nano- and micro-bubbles, was attached to hydrophobic solid surface. Thus, preferential adsorption of CTABr on liquid/air interface led to prolongation of the t_{TPC} due to increased stability of foam films formed locally between colliding macro-bubble and air "captured" at the Teflon surface.

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Control of the bubble departure diameter by saw-tooth surfaces

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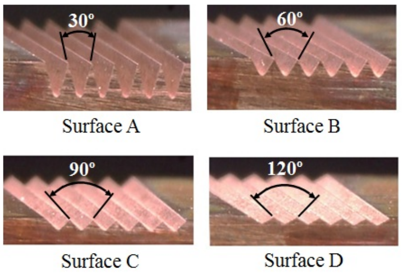
Controlling the bubble diameter departing from the wall is highly important for the performance improvement of the boiling systems, but the mechanism of the bubble detachment is still open issue due to the complexity of the phenomenon. In this study, the control of the bubble departure diameter is achieved by equipping saw-tooth surfaces, which can enhance the relative influence of the surface tension in the bubble detachment mechanism.

The bubble generation process in the liquid–gas micro mixing system is dominated by the surface tension and the pressure difference between two phases [1]. Although other forces such as the drag force due to the bubble growth and buoyancy force may attract the bubble detachment in boiling systems, it is anticipated that the surface tension may still have large influence on the phenomenon. Therefore, if the relative influence of the surface tension can be enhanced, the phenomenon may be considered to be dominated by the surface tension. Since the inner pressure of bubbles in microscale are considerably high and hence bubbles tend to form the spherical shape, four different microscale saw-tooth surfaces were fabricated in order to interfere the bubble to grow in a spherical shape at the nucleation site (Fig. 1).

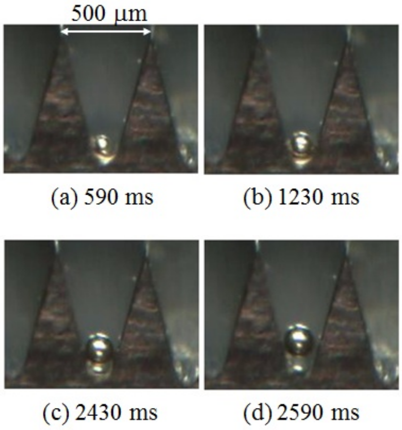


Surface A Surface B

Surface C Surface D

Fig. 1 Test surfaces fabricated by the wire-cut EDM. All the grooves have 500 μm width at their top and rounded bottom (less than R = 100 μm).

Carbonated water were chosen as the test liquid because of the similarity of the bubble generation process and the easiness of the experiment, and it was observed that the generated bubbles (Fig. 2a) immediately departed from the nucleation sites as they grew and touched the opposite wall (Fig. 2b). The bubbles then kept growing and slid the wall (Fig. 2c), and completely departed from the wall (Fig. 2d). The bubble departure diameters on Surface A were constant and they were altered when different saw-tooth surfaces were equipped. On the contrary, departure diameters were not constant for bubbles generated from a flat surface.



(a) 590 ms (b) 1230 ms

(c) 2430 ms (d) 2590 ms

Fig. 2 Successive images of the bubble growth on Surface A.

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Bacterial adhesion to metal surfaces.

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Interactions between bacteria and material surfaces play an important role in biology and different process technologies. The aim of this study is to investigate the influence of material surface roughness on the degree of bacterial adhesion. Two different stainless steel materials AISI 304 and AISI 316TI are used. The surface roughness is adjusted as needed by brushing, 3D polishing and electropolishing. The roughness, morphology and texture of the material surfaces was measured and evaluated by Atomic force microscopy (AFM) [1]. The adhered cells are stained and detected spectrophotometrically and consequently compared with the results obtained by scanning electron microscopy [2]. For experiments we will use one Gram-positive bacterium (Staphylococcus aureus) and two Gram-negative bacteria (Pseudomonas aeruginosa and Escherichia coli). Finally, the influence of bacterial shape on the adhesion will studied.

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Relation between surface rheological propertiesand foam film behavior of saponin solutions

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Saponins are natural surfactants, whose molecules are composed of hydrophobic steroid or triterpenoid group, and one or several hydrophilic oligosaccharide chains attached to the hydrophobic group. In our previous study[1] we found that the saponin extracts of Escin, Tea Saponin, Berry Saponin Concentrate and Ginsenosides exhibit very high shear elasticities and viscosities, Quillaja Dry has intermediate shear elasticity, whereas the other studied saponins with triterpenoid and steroid aglycone have zero shear elasticity and viscosity – these are Horse chestnut extract, Sapindin, Ayurvedic Saponin Concentrate, Tribulus terrestris and Fenusterols. The major aim of the current study is to characterize the foam film behavior of these saponins and to relate this behavior to the surface rheological properties of the saponin solutions. Foam films were studied in the Sheludko-Exerowa capillary cell at capillary pressure of 50 Pa. We measured the drainage time and the equilibrium thickness of the foam films, formed from the various saponin solutions. The obtained results show that all studied saponins with triterpenoid aglycon formed films which thin down more slowly than the films stabilized by typical low molecular-mass surfactants, whereas two of the three steroid saponins formed films with typical drainage behavior of low molecular mass surfactants. The comparison of the film drainage time and the surface rheological properties of the saponin adsorption layers showed that the saponins which lead to slowest thinning of the foam films are those with very high surface shear and dilatational elasticities - Escin, Berry saponins, Quillaja Dry 100 and Ginsenosides. Saponins with intermediate dilatational elasticity and zero shear elasticity showed intermediate drainage time. The fastest drainage is observed with saponins which exhibit no shear and dilatational elasticity.

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Effect of solid surface modification on the formation of supported lipid bilayers

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Supported lipid bilayers (SLBs) are commonly used as models of cell membranes with potential biotechnological applications such as biochips and biosensors. One of two main pathways, which are usually used to form SLBs is spreading of the small unilamellar vesicles (SUV) on the solid supports. It is an attractive and simple route to form thermodynamically stable bilayers on these substrates.

Our study aims at understanding how the modification of surfaces by adsorption of polyelectrolytes influences the process of vesicle adsorption and SLB formation on various supports. For the preparation of lipid vesicles following lipids were used: zwitterionic 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine, positively charged 1-palmitoyl-2-oleoyl-sn-glycero-3-ethylphosphocholine (chloride salt) and negatively charged 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (sodium salt). Small unilamellar vesicles were prepared by the extrusion method using polycarbonate membranes with the defined pore size of 100nm. For the characterization of the obtained lipid vesicles dynamic light scattering and zeta potential measurements were applied.

We examined the formation of SLBs by quartz crystal microbalance with dissipation monitoring (QCM-D), which provided information about the mass and the structure of adsorbed material during the deposition. We investigated the effect of polyelectrolyte multilayers of various thickness and surface charge, used for the modification of QCM crystal surface, on the vesicle fusion and the formation of supported lipid bilayers. Modification of sensors was done by using the layer-by-layer deposition of polyelectrolytes. Cushion thickness was regulated by the number of polyelectrolyte layers used and its surface charge – by the proper terminating layer: either positively or negatively charged.

Acknowledgements:

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Membrane emulsification as a method to form liquid core polyelectrolyte microcapsules

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The layer-by-layer adsorption of polyelectrolytes (PE) is considered as a convenient method to obtain microcapsules' shells on colloidal cores. Solid particles (polystyrene latex, silica, $CaCO3$) are most often used as cores for formation of capsules, which may contain some active ingredient. Alternatively the solid core can be dissolved to leave the hollow shell, which can be then refilled with the desired composition. The disadvantage of this method can be traces of the destructed core trapped in the capsule and low efficiency of loading the active substance into the hollow shells. Use of emulsions droplets as liquid cores provides possibility to encapsulate oil soluble active components with control of size and shell properties of obtained capsules, that opens perspectives for application in many fields such as cosmetic, medicine, pharmacy and food industry. Membrane emulsification is a two-liquid phase flow process, in which a dispersed phase is pressed through the membrane pores to a continuous phase. Droplets grow at the membrane pore, and after reaching a certain size, they are detached by the shear force of the continuous phase flow. Membrane emulsification has received increasing attention over the last 10 years, with potential applications in many fields where the monodisperse emulsions is required. One of them is the fabrication of monodisperse polymer microcapsules.

In this work we were focused on the preparation of o/w emulsion as cores for microencapsulation by sequential adsorption of polyelectrolytes (layer-by-layer method). The emulsions of squalene stabilized with AOT/PAH interfacial complex (AOT-Docusate sodium salt, PAH poly(allylamine hydrochloride)) were prepared on membrane emulsification unit. The influence of AOT and PAH concentration on the size and zeta potential of obtained emulsions was investigated. Size of the emulsion droplets was correlated with the dependence of the interfacial tension at squalene/water interface. The emulsion droplets were used as a cores for further layer-by-layer encapsulation within PAH/PSS (PSS-poly(styrene sulfonate) polyelectrolytes (up to 10 layers) using the saturation technique. A growth of the polyelectrolyte shell was followed with the electrophoretic mobility and light scattering measurements. A hydrophobic drug (Naproxen) and oil-soluble witamin D were encapsulated within the cores and their presence was confirmed by UV-vis measurements.

Acknowledgements:

This work was supported by the "Krakow Interdisciplinary PhD-Project in Nanoscience and Advanced Nanostructures", which is operated within the Foundation for Polish Science MPD Programme co-financed by the EU European Regional Development Fund, by NCN project N N209 757340 and the Marian Smoluchowski Krakow Research Consortium - a Leading National Research Centre KNOW supported by the Ministry of Science and Higher Education and the COST Action CM1101.

Co-Adsorption of the Proteins β-Casein and BSA in Relation to the Stability of Thin Liquid Films and Foams

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Set of complementary experimental methods is used to determine the properties of adsorption layers from solutions containing two proteins and to analyse qualitatively the impact of the individual components: Phase exchange experiments with (i) rising bubbles to determine the surface tension by the ADSA method, combined with surface dilatational rheology measurements; and (ii) thin films observations for determination of the film thickness and stability.

Two types of mixed adsorption layers and thin films are compared: (i) formed from mixed solutions, i.e. upon parallel adsorption; (ii) a protein initially adsorbed and afterwards exchanged in the bulk by another protein or a surfactant, i.e. by sequential adsorption.

The applied combination of experimental methods and techniques allows detailed analysis of the role of the individual components for the overall stability and surface properties of the mixed system[1], and could be further successfully applied to study many other protein and surfactant blends.

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Short-range Hydrophobic Attraction between Silanated Silica Surfaces and Solvophobic Attraction

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The origin of the hydrophobic attraction between macroscopic hydrophobic surfaces[1] has been under debate for a long time. Almost 10 years ago, it was shown that the bridging of nanobubbles attached to hydrophobic surfaces is attributable to be the origin of long-range attractive forces.[2,3] However, this bubble-bridging force is occasionally regarded as not being a 'true' hydrophobic force because it is not produced by surface hydrophobicity itself but rather by the bubbles attached to hydrophobic surfaces. To date, it is unclear whether there is an additional attractive force between hydrophobic surfaces when there are no bubbles on the surfaces.

In this study, the interaction forces between hydrophobised silica surfaces were examined in aqueous solutions using atomic force microscopy (AFM). To prevent the attachment of nanobubbles on the silanated surfaces when water is introduced between the surfaces, the AFM fluid cell was first filled with ethanol and the surfaces were then consecutively rinsed with several organic solvents. Finally, the electrolyte solutions were injected into the cell, and the approaching and retracting forces were measured.

In the approaching force curves, no anomalous long-range attractive force was evident; however, the surfaces jump into contact at a distance of 10–20 nm, which indicates the presence of an additional attractive force that is stronger than the van der Waals attraction. This demonstrates the existence of a 'short-range' hydrophobic attraction, i.e. a hydrophobic attraction independent of nanobubbles, between the surfaces. We also measured the interaction between fluorinated silica surfaces in organic solvents and found a similar short-range force that is also stronger than the van der Waals attraction; this force can be regarded as a 'solvophobic attraction'.

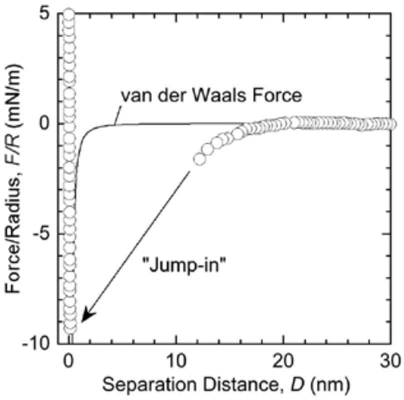

Fig. 1 Approaching force curve for silanated silica surfaces with a contact angle of 108° in 1 × 10^{-3} M $NaNO_3$ solution.

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Contact Angle Interpretation of CO_2-Water-Oil-Sandstone System by Surface Free Energy Analysis

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In reservoir engineering, it has been well recognized that interfacial interactions control flow behavior and displacement in porous media. Particularly, wettability is one of the most important factors determining residual saturations and capillary-pressure and relative-permeability functions [1]. Given the importance of the wetting properties of the rock, a correct description and interpretation of the contact angle is crucial. Of special interest are the pressure and temperature conditions where the CO_2 phase is supercritical. To describe the wetting properties of the rock surface as a function of pressure, we use surface-free-energy analysis based on an equation of state (EOS) [2]. Following this approach, we propose a modified equation of state to describe the contact angle of a liquid/gas/solid system at various pressures. The method is applied to experimental data for the water/CO_2/oil/sandstone system. The experiments were performed in a pendant-drop cell at typical in-situ reservoir pressures, up to 15 MPa. According to our experimental results, the modified EOS is able to reproduce the contact angle data within the range of the pressures studied (Fig. 1(a) and (b)). This modified EOS can only be applied if the solid phase is not altered due to swelling, chemical reaction or mineral dissolution. The equation-of-state method can be used to describe the wetting properties of a specific surface, if a number of reliable contact-angle and interfacial-tension data are available for a system of interest.

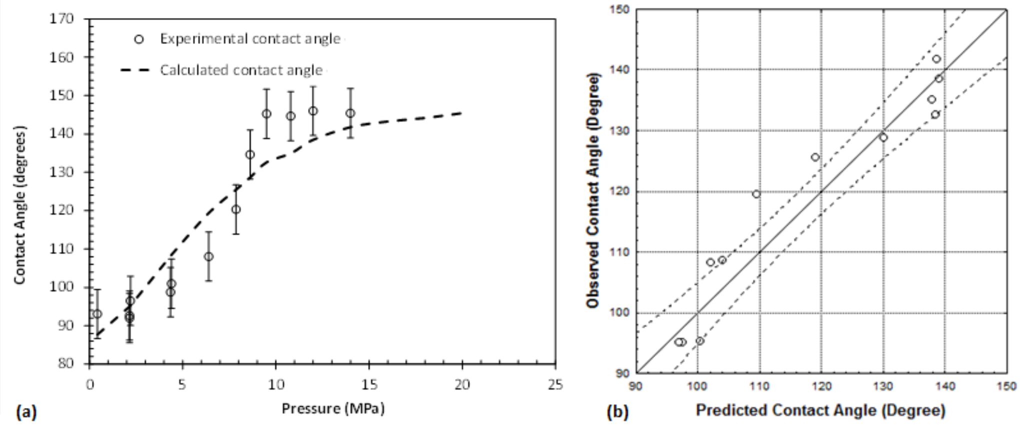

Fig. 1 (a) Contact angle as function of pressure for CO_2-Water-Oil-Sandstone system at a temperature of 318 K. (b) Point by point comparison. The dashed lines show the 95% confidence interval.

Acknowledgements:

The research reported in this paper is carried out as a part of the CATO2 project (CO_2 capture, transport and storage in the Netherlands).

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The pH Dependence of Cascade Partial Coalescence at Oil-Electrolyte Interfaces

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Determining the value of electric surface potential of liquid-liquid interfaces using currently available colloid methods is very challenging due to surface deformation.[1] Recent work from this group utilized a cascade partial coalescence phenomenon, where a “mother” droplet coalesces with the electrolyte-oil interface, while a stable “daughter” droplet is left behind, to overcome the issue of deformation. The number of partial coalescence events and final stable droplet size were employed to develop a simple method to infer the bounds of the absolute value of the surface charge of oil-electrolyte interfaces.[2]

The current work examines the effect of pH at various salt concentrations on the partial coalescence sequence. Fig. 1 depicts a toluene droplet interacting with a 10^{-2} M KCl/toluene interface at pH 4 and 5. The final stable droplet size for the same oil, but different pH and salt concentration differs significantly, most likely due to specific ion adsorption. Estimating the absolute value of the surface potential for a range of salt concentrations and pHs will provide insight into the behavior of oil-electrolyte interfaces and further improve our understanding of their charging mechanism.

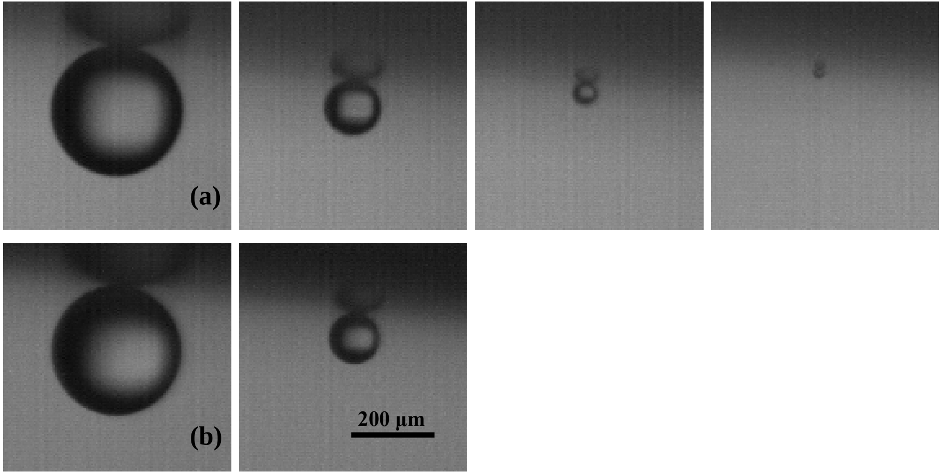

Fig. 1 Cascade coalescence process for purified toluene in 10^{-2} M KCl at (a) pH 4 and (b) pH 5.

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Surface dilatational properties of triterpenoid and steroid saponins on the air-water interface

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Saponins are a class of natural surfactants, with molecules composed of hydrophobic head group (triterpenoid or steroid) and hydrophilic oligosaccharide chains. In our previous study[1] we found that some of the studied triterpenoid saponins - Escin (ESC), Tea Saponin (TS), Berry Saponin Concentrate (BSC) and Ginsenosides (GS) possess very high shear elasticities and viscosities, Quillaja Dry (QD) has intermediate shear elasticity, whereas other studied saponins with triterpenoid and steroid aglycone have zero shear elasticity and negligible shear viscosity – these are Horse chestnut extract (HC), Sapindin (SAP), Ayurvedic Saponin Concentrate (ASC), Tribulus terrestris (TT) and Fenusterols (FEN). In the current study we compare the same saponins with respect to their behavior under dilatational deformation. To characterize the surface dilatational properties of these saponins, we used two methods: (1) Langmuir trough and (2) Oscillating drop method (ODM). Several types of experiments were performed – oscillatory experiments and deformation-relaxation experiments. The obtained experimental data were described by the Burgers model for both compression and expansion of the adsorption layers. From the best fit of deformation and relaxation stages we determined the two elastic moduli in the Burgers model (E_1, E_2**)** and the two related relaxation times of the layers (t_{R1} and t_{R2}). The ODM method provides complementary information about the surface dilatation moduli and their dependence on the surface deformation. The obtained results revealed that the adsorption layers of ES, TS, BSC and GS have extremely high dilatational and shear elasticities (200-1500 mN/m) at small deformations (ca. 0.1 %). The measured elasticities decrease steeply with increasing the surface deformation for these layers. In contrast, QD adsorption layers have high dilatational elasticity but intermediate shear elasticity which depend weakly on surface deformation, up to 5 %. The adsorption layers of HC, SAP, ASC, TT and FEN exhibit noticeable dilatational elasticity of 20-40 mN/m and negligible shear elasticities. The surface rheological properties of the latter saponins do not depend on deformation and on whether compression or expansion is applied. The lowest dilatational elasticity is measured for Foamation Dry (FD) (10 mN/m). The obtained results are discussed from the view point of the structure of adsorption layers.

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Electrohydrodynamic Instabilities in Emulsion Films

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Upon application of an electric field across a water-oil-water emulsion film, instability patterns were observed as small white dots in the film's microscopic image. The characteristic lengths of these instabilities were measured for constant electric fields of various strengths. The experimental characteristic lengths agreed reasonably well with theoretical predictions for dominant wavelengths based on linear stability model. The linear stability model used in this study took into account experimentally measured disjoining pressure and calculated Maxwell stress. The films were formed in a thin film apparatus (Sheludko-Exerowa cell) modified such that the oil film separated two aqueous phase compartments, each in contact with a platinum electrode. This modification allows measurements of film thickness while applying electric field and external pressure to the film. The films were formed from a solution of a block co-polymer Tegopren (Degussa, Germany) in decane. Electric polarization in the form of step function at various potentials was applied across the film below the critical voltage for film rupture. Electric field induced breakdown of thin films have various applications such as electric field induced dewatering (electrostatic desalting) of petroleum emulsions and electroporation of bilayer lipid membranes. While pore nucleation is a known mechanism for breakdown of bilayer lipid membranes, rupture mechanism of thicker films with substantial solvent core such as those observed in petroleum industry is not well understood yet. The reported results demonstrate that the formation of electro-hydrodynamic instabilities and their growth is a possible mechanism for breakup of thick emulsion films. DC polarization studies of single thin films are promising approach for understanding of electro-induced coalescence and stability mechanisms of W/O emulsions.

Langmuir monolayer properties of egg yolk lecithin with palmitic acid and hexadecanol

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Two-dimensional (2D) monolayers at the air-water interface were investigated for the physicochemical interactions of eggPC with PA, HD, and an equimolar PA/HD mixture. The only structural difference between PA and HD is their head group; their monolayer properties are very similar. Thus, in this study, the composition of the PA/HD mixture was kept constant at a 1:1 molar ratio. Our objective was to elucidate the miscibility, interactions, and phase behaviors of the binary and ternary mixtures. The interfacial behavior of eggPC with PA, HD, and their equimolar mixture in the monolayer state was evaluated by surface pressure (π)–molecular area (A) and surface potential (ΔV)–A isotherms on 0.15 M NaCl at 298.2 K. The excess Gibbs free energy of mixing was calculated from the isotherm data, and a 2D phase diagram was constructed from the monolayer collapse pressures. In addition, the phase behavior for the monolayers upon compression was examined using *in situ* fluorescence microscopy (FM). A new finding in the present study is that PA, HD, and the equimolar mixture of PA/HD were partially miscible with eggPC in the binary and ternary monolayer states. In a strict sense, they are considered to interact favorably both thermodynamically and morphologically with certain components containing fatty acid moieties, such as C16:0 in eggPC [1].

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Miscibility behavior of sphingomyelin with phytosterol derivatives by a Langmuir monolayer approach

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The miscibility behavior of palmitoyl sphingomyelin (PSM) with phytosterol derivatives of β-sitosterol (SITO), β-sitosteryl glucoside (SG) and β-sitosteryl glucoside palmitate (SGP) has been systematically investigated by the Langmuir monolayer. The surface pressure (π)–molecular area (A) and surface potential (ΔV)–A isotherms for the binary PSM/SITO, PSM/SG, and PSM/SGP systems on 0.02 M Tris buffer with 0.13 M NaCl (pH 7.4) have been measured as a function of molar fraction of PSM (X_{PSM}). Surface potentials (ΔV) of pure components were analyzed using the three-layer model proposed by Demchak and Fort 1). The contributions of the hydrophilic D-glucose moiety, the hydrophobic palmitoyl group, and sphingomyelin group to the vertical component of the dipole moment ($\mu_{\perp}$) were evaluated. The thermodynamic quantities based on π–A isotherms reveal that PSM interacts attractively with all the three phytosterol derivatives in the following order; SITO>SGP>SG. In addition, the two-dimensional phase diagram constructed on the basis of phase transition presure (π^{eq}) from a liquid-expand (LE) to liquid-condensed (LC) state and of collapse (π^{c}) pressure shows that all the two-component systems are miscible with each other. Miscibility manner between PSM/SG and PSM/SGP systems is found to be opposite at large X_{PSM} region, in which the interaction between the same molecules (PSM−PSM or SG−SG) is stronger than that between the different molecules (PSM−SG) in the PSM/SG system and vice versa in the PSM/SGP system. These results suggest that the incorporation of D-glucose and palmitoyl group to SITO molecule dramatically changes the miscibility behavior with PSM. The observations using fluorescence microscopy (FM) image also provide the miscibility behavior in the monolayer state.

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Specific effcect of glycyrrhetinic acid on lipid raft model membrane: A Langmuir monolayer study

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To elucidate an interfacial behavior of glycyrrhetinic acid (GA), which is aglycon of glycyrrhizin (GC), with lipid raft model consisting of equimolar ternary monolayers of *N*-palmitoyl-D-*erythro*-sphingosylphosphorylcholine (PSM), 1, 2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), and cholesterol (CHOL), Langmuir monolayer have been systematically investigated. The surface pressure (π)–molecular area (A) and surface potential (ΔV)–A for ternary PSM/DOPC/CHOL (1/1/1) monolayers on 0.02 M Tris buffer with 0.13 M NaCl (pH 7.4) containing different GA concentrations (0.1, 0.25, 0.5, 1.0, and 5.0 μM) have been simultaneously measured by an automated homemade Wilhelmy balance. The monolayer was directly visualized by a Brewster angle microscope (BAM) and a fluorescence microscope (FM) coupled with KSV Minitrough. The π–A and ΔV–A isotherms show that the GA molecules are penetrated from the subphase, and are squeezed out into bulk phase upon compression. Subsequent in situ morphological analysis by BAM and FM revealed that the microdomains corresponding to lipid raft domains become smaller as GA concentration increases. This result suggests that the LE network is promoted by the increment of GA. Interestingly, the distinct striped regions are formed at the 5.0 μM subphase concentration of GA. As the result, GA divides the ternary PSM/DOPC/CHOL (1/1/1) monolayers showing the stripe region in the FM image. Furthermore, the single-component (PSM, DOPC, and CHOL) and equimolar binary-component (PSM/DOPC, DOPC/CHOL, and PSM/CHOL) monolayer systems on 5.0 μM GA are studied. It was clarified that CHOL with GA plays an essential role in partitioning of monolayers. It is found that GA interacts more strongly with lipid raft model as compared with GC, which may suggest that the penetration of GA to the membrane regulates the exertion of numerous activities. The present study reveals the specific effect of GA on the lipid rafts model is more effective than the case of GC1).

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Kinetics studies of gold nanoparticle growth in the presence of metal ions studied by UV-vis spectroscopy and Atomic Force Microscopy (AFM)

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The gold nanoparticles were obtained either by classical Turkevich citrate synthesis or by modifying the method with the addition of europium (III), iron (III), copper (II) or silver (I) ions in the initial reaction mixture. At different temperatures we observe acceleration effect of every one of these ions. Particularly, we studied the kinetics of nanoparticles' growth at two different temperatures with or without metal ions by means of UV-Vis spectroscopy and Atomic Force Microscopy (AFM). We found that the kinetic curves obtained from the nanoparticles plasmon maxima coincide with the kinetic data (i.e. nanoparticles size evolution **Fig. 1**) extracted from a newly proposed experimental approach which involved AFM imaging[1]. The obtained nanoparticle growth profiles were fitted with the well established in literature Finke-Watzky model in order to describe the acceleration effect of the metal ions. From the experimental data and the theoretical fits we found that the citrate reduction of tetrachloroauric acid is accelerated by the addition of the metal ions. The addition of the ions at smaller temperatures has also led to an acceleration effect of the reaction rate. Using Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) we compared the morphology and the size distribution of the nanoparticles synthesized by Turkevich method as well as those obtained in presence of metal ions. The results of TEM and DLS were also used to validate the newly proposed experimental approach which involved AFM as a tool for studying the kinetics of gold nanoparticles' growth.

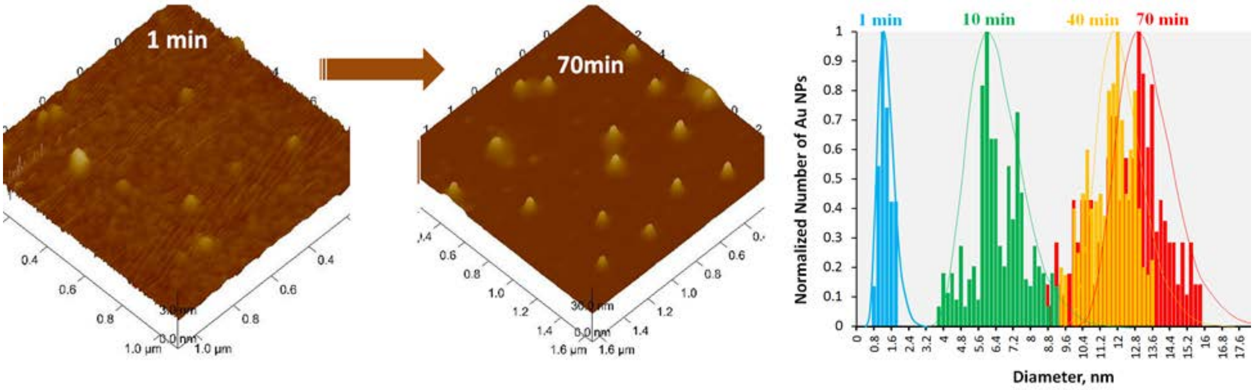

Fig. 1 AFM imaging and analysis of gold nanoparticles size evolution.

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Role of gold nanoparticles on the photocatalytic efficiency of ZnO films

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Semiconductor photocatalysis has important applications for achieving sustainable energy sources and for the environmental cleaning. ZnO is one of the most widely studied photocatalysts, but its application in practice suffers from low efficiency and narrow light response range. Hence, the research efforts are focused towards overcoming these limitations. One approach which has a prominent potential is the combination of ZnO with gold nanoparticles. Here we report for a simple and inexpensive method for preparation of ZnO/Au nanocomposites by dip-coating technique. It was found that Au deposition plays an important role on the optical and photocatalytical properties. Nanostructured zinc oxide films were obtained on glass substrate via sol-gel method. The sol was prepared using zinc acetate dehydrate as a starting reagent while the gold nanoparticles were obtained by classical citrate synthesis[1]. Thin ZnO and ZnO/Au films were characterized by Atomic Force Microscopy (AFM) and UV-Vis spectroscopy. The UV-Vis spectra of ZnO/Au films showed two maxima – first exiton peak of ZnO and second small peak due to surface plasmon resonance of gold nanoparticles (Fig. 1). The photocatalytic activity was studied by UV-vis spectroscopy in respect to the photocatalytic degradation of Malachite Green. The experiments were conducted upon UV and visible light illumination. The results showed, that ZnO/Au films have higher photocatalytic efficiency in degradation of the textile dye in comparison to the pure ZnO films.

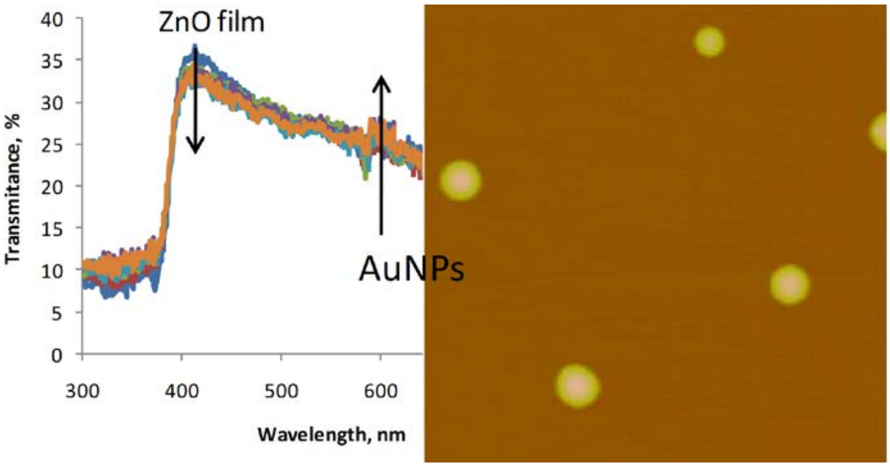

Fig. 1 Sample illustration: Transmittance spectra of zinc oxide nanoparticle films with increasing gold nanoparticle content and AFM image of gold nanoparticles.

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Acknowledgements:

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Evidence for electrostatic interactions mediating the affinity of phosphorylated lipid for TiO_2 surface

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Titanium dioxide nanoparticles are widely used in food industry[1-2], cosmestic[3] , etc. Their interaction with biological materials has been an important concern for scientists because of its safe use and potential environment impact[5]. Understanding this interaction will help to assess the behaviour of TiO_2 versus biomaterials. The aim of this study was to investigate the electrostatic interaction between TiO_2 particles with selected phospholipids (phophatidic acid, phosphatidylglycerol, phosphatidylserine, phosphatidylcholine, phosphatidylethanolamine and sphingomyelin) by using Langmuir trough technique coupled with Laser Doppler velocimetry. The pH ranges where the electrostatic interaction is expected to be either attractive or repulsive were deduced from the electrophoretic mobilities measured by Laser Doppler velocimetry. Based on these results, the surface pressure-area isotherms of phospholipid monolayers on subphase containing TiO_2 agglomerates were analysed at constant temperature and at various ionic strengths and pH values. The overall study revealed that the interaction between oxyde particles in aqueous suspension with phospholipids is essentially charge-dependent. It was found that two conditions are required to observe attractive interactions between TiO_2 samples and phospholipids: first, charge carried by inorganic particles must be opposite with that carried by phospholipid headgroup; second, both TiO_2 particles and phospholipid headgroup must be charged enough, defined as an absolute value of zeta potential higher than approximately 15 mV.

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Competitive adsorption of HFBII hydrophobin and surfactant: Sequential vs. parallel adsorption and effect of surfactant micelles

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Adsorption and displacement of HFBII by the ionic surfactant SDS is studied. The surface properties of solutions containing both HFBII and SDS are compared to those obtained by a consecutive adsorption of the individual components. Phase exchange (PhE) during measurement of the surface tension of a pendant bubble at the tip of a capillary by using the drop shape analysis (DSA) method is applied. The oscillating bubble method (OBM) is used to determine the surface dilatational elasticity and viscosity before and after the exchange. The obtained results show that the adsorption of HFBII is irreversible if the low molecular weight surfactant SDS is added after the HFBII molecules have adsorbed already on the water/air surface, and the effect did not depend on the SDS concentration, i.e. below or above CMC. The HFBII adsorption is irreversible also when it adsorbed from solution containing SDS below CMC. However when HFBII is present in a micellar solution of SDS the protein molecules are not detected to adsorb at the water/air surface: neither the surface tension nor the surface dilatational moduli indicate for possible presence of HFBII at the surface. This result is in agreement with the recently published data by Zhang et al., *Langmuir* 2011, 27, 11316–11323.

Foam flow behaviour through two parallel channels

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Flowing foams are used in many engineering and technical applications. For processes such as enhanced oil recovery and soil remediation, foam is injected into rock or soil in order to displace the fluid that initially saturates it or to mobilize pollutant chemical species. As both rocks and soils are both porous materials with inherently complex structures, a knowledge of how a foam will flow in a complex geometry is therefore of great importance.

A study into the behaviour of an aqueous two-dimensional foam flowing through two asymmetric parallel channels (Figure 1a) was carried out as a precursor to the study of foam flow through a porous material. The individual channel widths could be varied, but the total combined width of the two channels was kept constant. The velocity in each channel was measured, and it was found that the velocity ratio between the two channels was not uniquely determined by the ratio of the channel widths, as would be the case for a Newtonian fluid. Instead, there was a strong dependence of the flow behaviour on the foam structure within the narrow channel. In particular, discontinuities in the velocity ratios were observed when the foam structure in the narrow channel transitioned between double and single staircase and between single staircase and bamboo. A theoretical model accounting for the viscous dissipation at the solid wall [Cantat, 2004] and the capillary pressure across a film pinned at the channel outlet predicts the observed non-monotonic evolution of the velocity ratio as a function of the width ratio [Jones et al, 2013].

Following this initial study, preliminary studies have been carried out on foam flow through a simplified, random, two-dimensional porous media created using 7mm diameter obstacles (Figure 1b).

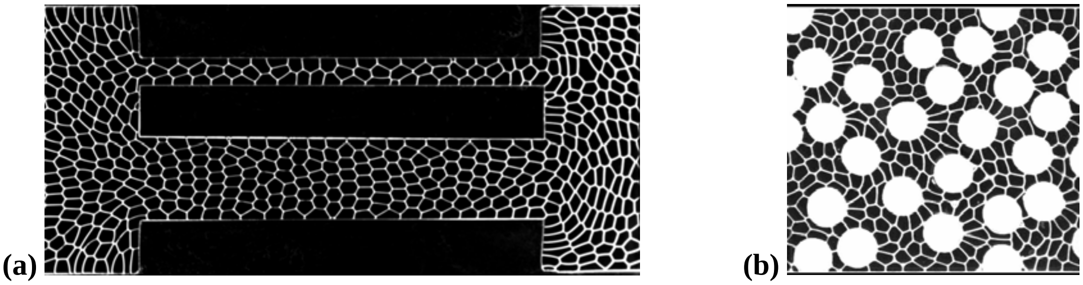

Fig. 1 Images of foam flowing through **(a)** two parallel, asymmetric channels and **(b)** a simplified two-dimensional porous media. In both cases, flow is from left to right.

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Solubility Limits and Phase Diagrams for Fatty Acids in Anionic (SLES) and Zwitterionic (CAPB) Micellar Surfactant Solutions

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The limiting solubility of fatty acids in micellar solutions of the anionic surfactant sodium laurylethersulfate (SLES) and the zwitterionic surfactant cocamidopropyl betaine (CAPB) is experimentally determined. Saturated straight-chain fatty acids with n = 10, 12, 14, 16 and 18 carbon atoms were investigated at working temperatures of 25, 30, 35 and 40 °C. The rise of the fatty-acid molar fraction in the micelles is accompanied by an increase in the equilibrium concentration of acid monomers in the aqueous phase. Theoretically, the solubility limit is explained with the precipitation of fatty-acid crystallites when the monomer concentration reaches the solubility limit of the acid in pure water. For ideal mixtures, the plot of the log of solubility limit vs. the chainlength, n, must be a straight line, which is fulfilled for n = 14, 16 and 18. For the fatty acids of shorter chains, n = 10 and 12, a deviation from linearity is observed, which is interpreted as non-ideal mixing due to a mismatch between the chainlengths of the surfactant and acid. The data analysis yields the solubilization energy and the interaction parameter for the fatty acid molecules in surfactant micelles. By using the determined parameter values, phase diagrams of the investigated mixed solutions are constructed. The four inter-domain boundary lines intersect in a quadruple point. The results can be applied for the interpretation and prediction of the solubility, and phase behavior of medium- and long-chain fatty acids and other amphiphiles that are solubilizable in micellar surfactant solutions, as well as for determining the critical micellization concentration of the respective mixed solution [1].

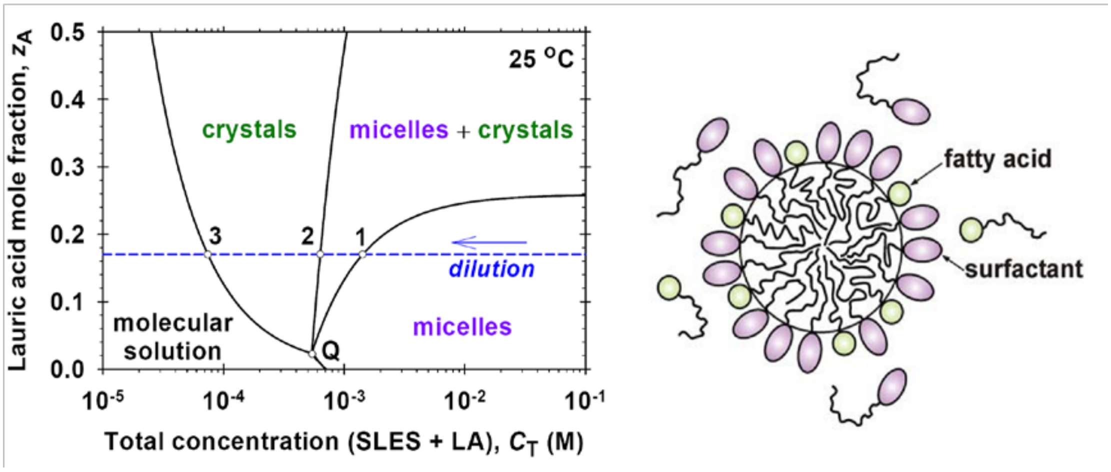

Fig. 1 Phase diagram of the aqueous solutions of anionic surfactant (SLES) and lauric acid (LA).

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Light-harvesting complex II monolayers in two conformational states

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The major light harvesting complex of photosystem II (LHCII) is an important regulatory protein in photosynthetic membranes (Gruszecki, 2010). In vivo it adopts trimeric form and is found either associated to the photosystem II complex or in LHCII-only containing domains (Dekker and Boekema, 2005). It was suggested that in native thylakoid membrane LHCII changes its conformation and macroorganization upon switching to photoprotective state (Johnson et al., 2011).

Monolayers of LHCII were investigated in nonprotonated (nLHCII), pH 7.8, and protonated state (pLHCII), pH 5.2, mimicking the physiological and photoprotective states of the protein. The organization and intermolecular interactions of LHCII trimers in the protein monolayers are studied at the air/buffer interface. The surface pressure/monomer area isotherms of nLHCII and pLHCII monolayers are smooth, without plateaus and kinks. The slow surface-pressure change with area indicates that the LHCII monolayers have a high compressibility and the particles are flexible. pLHCII particles occupy a smaller area and have higher inflection pressure as compared to nLHCII. The increased stability of the protonated monolayer is confirmed by comparison of the time dependencies of the monomer area at two constant surface pressures. Compression–expansion cycles of nLHCII and pLHCII monolayers suggest that during the pLHCII monolayer compression no phase transitions or conformational changes takes place, in contrast to nLHCII films where protein molecules at the air/buffer interface occupy much smaller area (by 500 $Å^2$) at expansion than at compression of the monolayer. The same value of the surface potential at the maximum monolayer density ΔV_{max}= 420 mV, achieved at the inflection points of the π/A curves, was obtained for nLHCII and pLHCII monolayers. Typical surface potentials obtained immediately after spreading range from 100 mV for pLHCII to 140 mV for nLHCII films, suggesting that at the same initial conditions after spreading LHCII complexes assume different molecular orientation and conformation at the interface. This study contributes to better understanding the LHCII conformations in light harvesting and photoprotective states.

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Fundamentals of Theory of Coagulation of Heterophilic Colloids (Beyond DLVO)

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In colloidal chemistry, regarding interfacial/surface tensions considered as homogeneous, one does introduce two extreme classes of colloids – lyophilic and lyophobic ones. Fundamental principles of their interaction, coagulation and stability are developed in classical model and theory of DLVO. However, interfaces/surfaces of all real systems are heterogeneous. A modern progress of science and technology demands to complete the classification of colloids with third class of heterophilic systems, i.e., systems with energetically heterogeneous interfaces/surfaces. In our talk, we will discuss fundamentals of theory of coagulation and dynamics of such systems, beyond the DLVO model. First, we will review the simplest initial models of interacting heterophilic particles in medium. On this basis, we can analyze a series of important phenomena missed in the classical approach, such as virtual cavitation, two-barrier nucleation, bubble-bridging, fluctuation capillary-hydrodynamic instability, sound resonances, etc. Then, we will discuss importance of surface statistics of heterogeneity in theory of coagulation and theory of surface forces and phenomena. In the frame of this approach, one can derive the exponential law of hydrophobic attraction of macroscopic particles/membrane in water solutions, as well as some other exponential laws in surface phenomena. On this way, the physico-chemical theory of micro-flotation has been advanced. Based on our theoretical estimations and experiments, we could establish possibility to improve a micro-flotation coefficient of selectivity of anthracite by its previous heterophilization with methods of radiation chemistry - up to 20%! In conclusion, one has to note, that completing the current classification of colloids (as lyophilic and lyophobic) with third class of heterophilic systems is the imperative of our time. Advanced theory of coagulation/dynamics of heterophilic colloids in media presents a new research paradigm in modern colloid interface science!

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Synthesis, Investigation and Use Aqueous Acrylic Dispersions

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The work at investigating and studying of a polymeric dispersion on the acrylic basis has been carried out for many years. The main objects of investigation in this work were copolymerization of unsaturated ethers with unsaturated acids, forming of a double electric layer and preventive covers around polymeric particles and regulating of properties of disperse medium.

With the application of diverse modifying monomers - unsaturated acids [1], mono- and di-(meth) acrylates of diatomic alcohols [2], methyl-α-acrylates [3], decylmethacrylate [4] the kinetics and mechanisms of emulsive polymerization have been investigated, the dispersions on the basis of basic industrial (meth) acrylic monomers (butylacrylat, metylacrylat, metyl(meth)-acrylat) have been synthesized, their colloidal chemical properties, astringent and film making ability have been investigated.

The application of unsaturated acids, mono(meth)acrylates of diatomic alcohols as the most polar monomers, which can be re-distributed between water and monomeric phases, gave the opportunity to involve them to forming preventive layers on the surface of polymeric particles together with emulsifying agents [1,2].

The regulation of pH synthesized dispersions of carboxyl containing polymers let have a great influence on the size of solvate covers and globular structure of macromolecules in the particles of dispersed phase [1]. The substantial increase of stability of the investigated colloidal systems, which was faced in the process, became the basis of developing of technology of synthesis of frost-resistant acrylic dispersions using the technology of non-coagulate polymerization, which was realized in industrial conditions at manufacturing [5]. The reconstruction of molecules structure in polymeric particles under the influence of pH let have a big effect on their interaction with organic additives, the molecules of which contained considerable hydrophobic parts [1]. It allowed regulate the distribution of water-insoluble organic dyes in dispersions and films and their optical properties [6].

The application of monohydric alcohols for regulating properties of disperse medium let have a great influence on rheological properties of dispersions and physical and mechanical properties of films received from them without copolymers structure change [7].

The investigations allowed develop effective film-forming compositions which have been synthesized at investigating manufacturing in Russia and Ukraine.

Acrylic dispersions synthesized at open joint stock company “Barva” have been successfully applied for purification of monuments surface during the restoration in Lviv [8].

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The Spreading Dynamics of Liquids on Rough Surfaces

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The phenomena of the spreading of liquid on a solid, particularly on rough surfaces are complex. Many industries of material processing require moving of the contact line in different substrates A computational fluid dynamics models (CFD), based on the volume of fluid technique (VOF) is applied to simulate the time evolution of spreading drop on solid surfaces (drop base radius and contact angle). Surface tension, wall adhesion and surface roughness phenomenon are included in the computational model. The influence of different factors, such as surface roughness, drop nature, and type of surface, on the temporal evolution of the drop base radius and contact angle is systematically investigated. The numerical results reproduce perfectly the several spreading regimes which occur during the time course of the drop. The calculated results compare very well with the experimental data for a large range of drops and surfaces.

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Stabilization Factors and Coagulation Kinetic of Polydisperse Positively Charged Alumina Sol

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Information about colloid-chemical properties and aggregate stability of disperse systems can be very useful at definition of optimal preparation conditions of the nanostructured materials in modern technologies. During dispersion process of the most of industrial dry nanopowders in liquid media the polydisperse systems containing both individual nanoparticles, and small aggregate, possessing sediment stability, are received. Undoubtedly, this fact has to have influence on properties of sols and slip compositions prepared on the basis of nanopowders, their aggregate stability, and, therefore, on density and homogeneity of the materials synthesized on their basis. Therefore, at synthesis of new materials using disperse systems it is necessary both to take into account initial sol polydispersity, and to have clear ideas of a role of the surface forces determining of interaction of nanoobjects, especially at the forming of fine microstructures.

In the present work γ-Al_2O_3 hydrosol, prepared on the basis of commercial powder «Aeroxide Alu C, Degussa» (particle size 26 nm, specific surface area 100±15 m^2/g) was chosen as the object of research. Coagulation kinetic of positively charged alumina sol at $4 < pH < 7$ were studied on the background of NaCl solutions (10^{-4} M – 2 M). Zones as well as thresholds of the fast ($C_{f.c.}$) and slow ($C_{s.c.}$) coagulation were defined by method of photometry. The changing of particle size and particle size distribution at the adding of electrolyte was controlled by the method of dynamic light scattering (DLS).

High stability of alumina sol in respect to electrolyte was observed ($C_{f.c.} > C_{f.c.}$ for typical liophobic colloids). This fact allows considering alumina sol as pseudoliophilic dispersion. It is proposed that main factors which could explain anomalous sol stability are presence of water boundary layers (BL) on the surface of oxide particles (structural component of particle interaction energy) and adsorption on a this surface of the aluminum polynuclear aquacomplexes that results in increase of surface hydration. The interaction potentials of oxide particles were calculated within the framework of the extended DLVO theory taking into account the initial polydispersity of sol and three possible types of the particle interaction: 1) nanoparticle aggregates (theirs size determined by DLS method); 2) the primary nanoparticles, and 3) the primary nanoparticles with aggregates. Parameters of structural component of particle interaction energy and effective Hamaker constant values for aggregates were estimated by means of the comparison of photometry data with calculation results.

It was established that observed kinetic of sol coagulation can be explained by two-stage non-simultaneous beginning of the coagulation of primary nanoparticles and aggregates as well as various mechanisms of their coagulation at rather high electrolyte concentrations. Coagulation of aggregates and particle aggregates with primary nanoparticles proceeds on the barrierless mechanism in the long-range potential minimum, caused by the predominance of dispersion forces of attraction on structural and ion-electrostatic repulsion forces. It is difficult to make definite conclusions about the mechanism of primary nanoparticles coagulation, because in this case there is a possibility of proceeding of the barrier coagulation with a fixation of particles in the primary minimum.

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Nanoscale Droplets and Thin Films of Ionic Liquids on Mica Surface

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Ionic liquids (ILs) are promising candidates for wetting study due to their non-volatility and tunable physical properties [1]. In our study, nanoscale droplets of ionic liquid [bmim][TFSI] were produced by depositing the solution of this ionic liquid (IL) and extracting the solvent (ethanol) through evaporation [2]. By imaging these tiny droplets using tapping mode AFM, we revealed the coexistence of solid and liquid phases of [bmim][TFSI] on mica, similar to what was previously reported for another IL [bmim][PF_6] [3]. The solid-like thin film between the tiny IL droplets was correlated with the precursor film in partial wetting and the possible autophobicity of this IL on mica. In addition, these nanoscale droplets of IL appeared to be nearly spherical (cap) on mica. By assuming an even distribution of this film, an attempt was also made to extract the line tension exhibited by these nanoscale droplets. The order of line tension obtained using the modified Young's equation is in agreement with theoretical approximations.

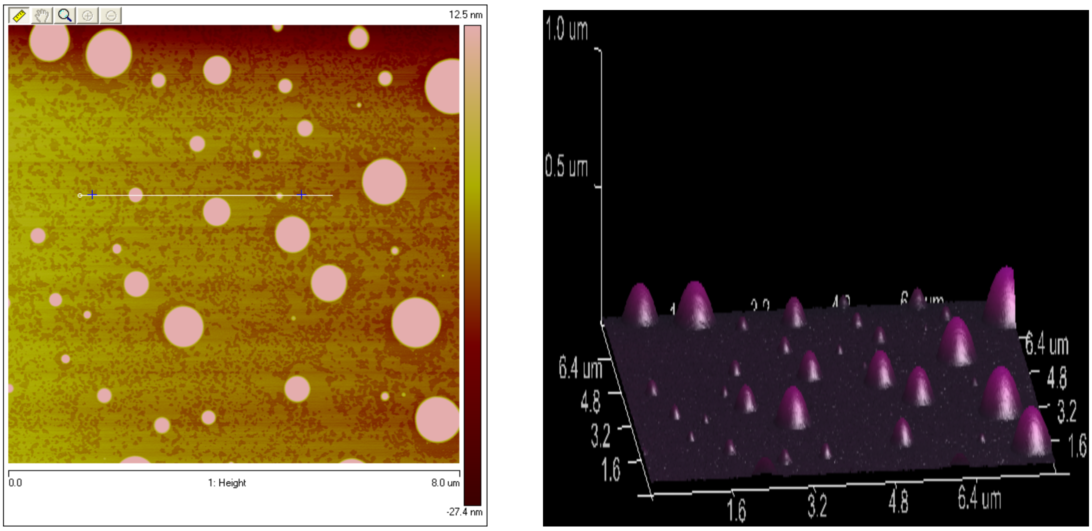

Fig. 1 2-D and 3-D images of [bmim][TFSI] droplets on mica surface from tapping mode AFM.

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Acknowledgements:

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Continuous Foam Fractionation: Influence of Operating Parameters on Bubble Size Distribution and Separation Efficiency

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Continuous foam fractionation is a technique to separate surface active molecules from aqueous solutions based on their affinity to adsorb at gas-liquid interfaces. By aerating a surfactant solution with gas interfaces are generated in form of bubbles where surface-active molecules can adsorb. The emerging foam, enriched with surface active molecules, is collected at the top of the column and liquefied to get an enriched product. Foam fractionation is regarded as a gentle and economical procedure for the separation and/or concentration of highly diluted protein mixtures, including active enzymes, which makes it applicable for the early stages of downstream processing [Merz, 2011].

The bubble size distribution in the generated foam is one of the important parameters for continuous foam fractionation, because the bubble size directly determines the available surface for the adsorption of the surface-active molecules. Consequently, the bubble size distribution considerably affects the separation efficiency. Hence, the influence of the operating parameters on the bubble size distribution should be investigated.

In this study, we initially introduce an image based method for optically measuring the distribution of bubble sizes in a device for continuous foam fractionation. The approach is based on the detection and subsequent analysis of spherical bubbles in digital images fusing a template matching technique [Zabulis, 2007]. The method is implemented in MATLAB® and consists of three steps: A template-based detection step, a validation step to remove false positives, and an evaluation step for estimating the size of the selected bubbles.

Based on the developed bubble size measurement method, the influence of different operating parameters such as the gas and feed flow rate on the bubble size distribution could be investigated for the model system β-casein. Furthermore, the feasibility of two different gas spargers (a porous glass frit and a perforated plate) to generate homogeneous bubble sizes is analyzed. Due to that, it is possible to determine the provided surface for the adsorption of the surfactants and to estimate the concentration of the target molecules in the collected foam.

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Acknowledgements:

1. Federal Ministry of Education and Research, Germany, “Technologie-Plattform: Innovative Downstream Prozesse”, FKZ:0315520

Self Assembly in a Magnetic Room Temperature Ionic Liquid (MRTIL)

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Magnetic room-temperature ionic liquids (MRTIL) are a specific class of RTIL where an ion confers a paramagnetic behavior to the liquid. The first occurrence of this new class of liquid media was discovered in 2004 [1, 2] based on the organic cation 1-butyl-3-methylimidazolium (bmim$^+$) and the anion tetrachloroferrate ($FeCl_4^-$). Thanks to the high spin $FeCl_4^-$, a small magnet is enough to modify the meniscus of the fluid, and stronger macroscopic effects are visible when the surface tension is reduced.

MRTIL can be used as a solvent for self assembly of surfactant systems which leads to structures like micelles, liquid crystals, macro- and microemulsions [3] that possess magnetic properties. In our experiments we studied such microemulsions that were formulated with the help of cationic surfactants of different alkyl chain length and decanol as a cosurfactant. The phase behavior was determined and the corresponding structures were determined by comprehensive SANS experiments. The analysis showed a generally similar behavior as in normal microemulsions but compared to aqueous systems the surfactants show much weaker amphiphilicity. New insights into the nature of self assembly by studying these water-free, aprotic systems are to be derived from these investigations.

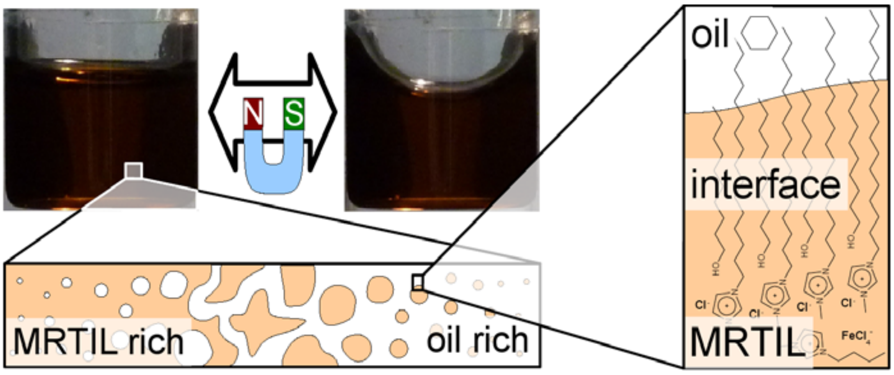

Fig. 1 Pictures of a paramagnetic microemulsion with a modified miniscus by exposing to a magnet and schematic draws of the structure [3].

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Step-by-step investigation of droplet breakup and release of water by coalescence in W/O/W multiple emulsions

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Multiple water-in-oil-in-water (W/O/W) emulsions are complex multiphase systems that consist of a water-in-oil emulsion dispersed in a second continuous water phase. There is a great interest in the production of multiple W/O/W emulsions for different applications ranging from separation / extraction, encapsulation of sensitive molecules for food, cosmetic and pharmaceutical products to fat reduction in food. However, the production of these structures is still a challenge and the processes are not fully understood.

One possibility to produce W/O/W double emulsions is by means of a two-step process. Therefore, first a so called inner water-in-oil emulsion is produced. In the second step this emulsion is taken as the dispersed phase of the double emulsion. The second step contains two main challenges. The droplets which have to be broken up show non-Newtonian flow behavior especially for high dispersed phase concentration of the inner emulsion. Moreover, instabilities like coalescence of the inner water droplets with each other or with the outer water phase may occur. Especially coalescence between inner and outer water phase is crucial as it leads to the release of inner water droplets and thus to a loss of functionality.

In order to investigate double emulsion droplet breakup and the release of water by coalescence we first conducted single droplet experiments in a 4-roll mill. This approach enabled the visual observation of the phenomena. We observed that droplet deformation and breakup are independent of the dispersed phase content of the inner emulsion for viscosity ratios smaller than one. The immobilization of the interface by the surfactant used is responsible for this behavior. Concerning coalescence of inner droplets with the outer water phase we found that this process is strongly dependent on the surfactants used. If coalescence occurred, it was independent of deformation of the droplets. This observation is in contrast to former visual observations by *Stroeve et al.* [1].

In order to quantify these visually observed phenomena we conducted emulsification experiments in a colloid mill. We characterized the droplet size distributions of the final double emulsions as well as the encapsulation efficiency (percentage of water still encapsulated in the inner droplets). We found a direct correlation between double emulsion droplet sizes and encapsulation efficiency. This dependency is strongly influenced by the dispersed phase content of the inner emulsion and by the droplet sizes of the inner droplets. We want to show and discuss a first geometrical approach to model this coalescence behavior.

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Acknowledgements:

We want to thank Prof. Gary Leal, University of California Santa Barbara for enabling the experiments in the 4-roll mill.

We acknowledge financial support by KHYS (Karlsruhe House of Young Scientists).

Activity of the lipase *Candida Antarctica* B in bicontinuous microemulsions

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Enzymes as catalysts provide excellent specifity and selectivity towards their substrates, allow for saving energy due to mild reaction conditions and open up new pathways in synthetic organic chemistry. A major challenge in the industrial application of biocatalysis is the accessibility of a hydrophobic substrate for an enzyme preferring a hydrophilic environment. In the last decade non-conventional reaction media have been proposed to overcome enzyme-substrate incompatibilities, these include heterogeneous two phase systems, immobilised enzymes in organic media, ionic liquids and microemulsions [1]. Each of these reaction media features different properties suitable for different applications. In this work we present a bicontinuous microemulsion to be used as reaction media for the enzyme-catalysed hydrolysis of hydrophobic substrates. Bicontinuous microemulsions offer a suitable microenvironment for water soluble or interfacially active enzymes combined with application-relevant substrate concentrations. Interpenetrating water and oil channels separated by a continuous surfactant monolayer allow confining enzyme and substrate to the same nanostructured motif. The high interface to volume ratio enhances the contact between enzyme and substrate, and provides a fast mass transfer [2]. High solubilisation capacity allows for high substrate concentrations. We chose the lipase *Candida Antarctica* B (Cal B) to investigate the activity of an enzyme introduced in this reaction media. Cal B is interfacially active and thus is able to adsorb to the surfactant monolayer present in the microemulsion where a hydrophobic substrate being solubilized in the oil channel can be converted. The structure and the properties of the surfactant film is therefore a crucial parameter determining the activity of the enzyme. To compare the influence of the composition of the interfacial surfactant monolayer on the activity of Cal B, microemulsions based on the nonionic surfactant $C_{10}E_5$ were compared with microemulsions containing as well a sugar surfactant $C_{10}E_5/\beta\text{-}C_{10}G_1$ (1:1 mixing ratio). As a model reaction, the hydrolysis of *p*-nitrophenylpalmitate to *p*-nitrophenol and palmitic acid was used and the formation of *p*-nitrophenol was followed photometrically. The reactions were carried out in microemulsions consisting of buffer/NaCl - *n*-octane/substrate - nonionic surfactant(s). Different enzyme and substrate concentrations were measured to obtain the second order rate constants k_2.Results showed that in the presence of the sugar surfactant $\beta\text{-}C_{10}G_1$ a significantly higher enzymatic activity could be observed. The influence of the substrate, the products and the enzyme on the phase behaviour of the microemulsions was measured beforehand, to ensure that the microstructure would be bicontinuous throughout the reaction.

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Foamability and foam stability at low surfactant concentrations

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Surfactants are essential ingredients in laundry, household and personal care products, and in various technological applications. Our work is focused on understanding the basic processes which control the foam formation and stability at low surfactant concentrations, around and below the critical micellization concentration (CMC). The major aims of our study are: (1) To investigate the main factors which control the volume of the produced foam and its stability; and (2) To reveal the mechanisms of foam stabilization/destabilization at low surfactant concentrations. Systematic experiments were performed with anionic and nonionic surfactants. Several experimental methods were combined to obtain complementary information about the studied phenomena: foam tests, dynamic surface tension measurements, equilibrium surface tension measurements, foam film observations in Scheludko-Exerowa cell, and foam film tests with a new experimental method for studying dynamic foam films. The main experimental results could be summarized as follows: (1) In most systems we observed a clear correlation between the stability of the dynamic foam films, generated by the new method and the foamability of the respective surfactant solutions; (2) Correlation between the dynamic surface tension and the foamability was observed only at sufficiently high surfactant concentrations, when the same main surfactant is used and different co-surfactants are added to change the adsorption rate; (3) The observed trends could not be explained by considering only the disjoining pressure or only the kinetics of adsorption of the surfactant molecules. A theoretical model is under development to incorporate all important processes, governing the stability of dynamic foam films.

Solidified Microemulsions

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Microemulsions are well-known nanostructured liquids, made with water, oil and surfactants. These thermodynamically stable mixtures allow to prepare easily nanostructured liquids with high surface to volume ratio, controlled connectivity and characteristic sizes. Quenching these nanostructures into the solid state is a fundamental challenge and would open breakthrough perspectives in many fields like synthesis, catalysis, optics and energy storage.

Here, we address the competition between quenching and crystallization in solidified microemulsions. A nonpolar phase which is solid at room temperature was used to prepare microemulsions above its melting point and then the mixture is cooled down to go towards solidified microemulsions. Ideally, the as prepared material must be a clear solid with the same nanostructure as the starting mixture and containing a large amount of liquid [1]. This type of materials has been to date poorly studied. We are particularly interested in studying the liquid-solid transition as it determines whether the initial structure of the microemulsion may be quenched.

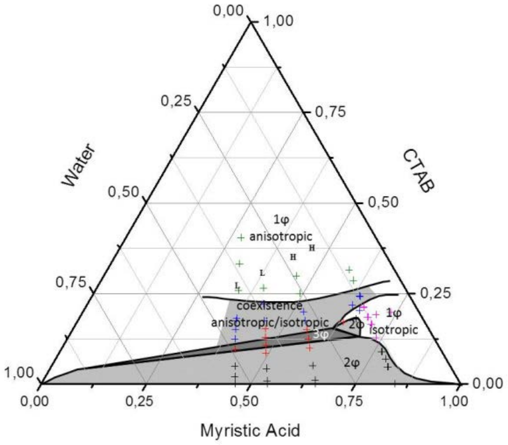

Fig. 1: Phase diagram of the ternary mixture (Myristic Acid/CTAB/H_2O), T = 60°C

As a first system, we have focused on an oil phase with a melting point at 55°C (myristic acid) and strong attractive interactions between oil and surfactant (CTAB). The phase diagram in the liquid state (T > 55°C) was studied (**Fig. 1**). Clear and isotropic mixtures have been identified in the oil-rich part of the diagram. In the liquid state, the mixture has a microemulsion-like structure with unexpected thermotropism. This nanostructure is lost in the solid state because of crystallization of the oil phase, even upon fast cooling.

An original approach to characterize the nanostructure destabilization during crystallization is to replace the crystallizing oil phase by an apolar phase with variable crystallization kinetics. In this talk, I will also present a new system where the crystallization problem is avoided. This study opens a wide range of fundamental studies on how we can keep the microemulsion nanostructure in the solid phase.

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Interfacial Properties Of Mixed Carbon Nanoparticles – Surfactant Suspensions And Application On Carbon Based Foams

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In recent years, an increasing interest has been paid to the study of the effect of solid particles in association with surfactants on the properties and structure of fluid interfaces. This is motivated by the effects that particles segregation may have, under certain conditions, such as the creation of mixed layers stabilizing the interfaces and opposing to the droplet/bubble coalescence.

The work here presented focuses on the interfacial properties of aqueous suspensions containing carbon nanoparticles and different type surfactant species, which can modify the degree of hydrophobicity/philicity of particles favoring their transfer from the suspension bulk to the interfacial layer.

Aim of this work is a deeper understanding of particle/surfactant and particle/fluid interface interactions and their effect on those macroscopic interfacial properties of the mixed systems which are expected to be related to the stabilization of foams and theirs structure.

To this purpose a systematic characterization of dispersions composed by Carbon nanoparticles associated with different ionic surfactants, decane sulfonate (C10), cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS), and polymer, poly(vinyl) alcohol (PVA), have been carried out measuring the dynamic and equilibrium surface tension and surface rheology by using a drop Profile Analysis Tensiometer (PAT). These results have been, moreover, crossed with the characterization of the bulk suspensions by Dynamic Light Scattering (DLS techniques, to check the effects of surfactant on the particle aggregation. The stability of the foams obtained with the same compositions has been also investigated and correlated to the interfacial properties.

The results here obtained contribute to the understanding of the relation between the interfacial properties of nanoparticles (NP) mixed systems and the stability and 3D structure of liquid and solid (green body) foams obtained by carbonaceous NPs. Thus they can be used in the field of tailoring and production of porous materials because provide new insight into the role of the composition of the initial dispersion, used as precursor.

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pH-responsive colloidosomes and their use for controlling release

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Colloidosome microcapsules have been developed which offeroptions for the encapsulation and release of active ingredients.

We use latex particles,stabilised with a responsive polymer, as building blocks for colloidosome microcapsule membranes and demonstrate their use as a pH-responsive delivery system.

Oil-in-water emulsions are prepared and stabilisedwith latex particles produced by emulsion polymerisation. The core-facing polymeron the surface of the latex particles ischemically cross-linked from the oil phase to produce a robust capsule shell.

The pH-responsive polymer on the surface of the constituent particles within the microcapsule membrane can be induced to expand and contract as a function of protonation/deprotanation, thus altering the pore size of the membrane.

We show that fluorescently-labelled dextran molecules can be successfully used to demonstrate successful uptake, retention and release from the core.

Hyaluronan-based porous foams as drug delivery systems

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Hyaluronan (HA) is a biopolymer widely distributed into the human body. Their physicochemical properties and biocompatibility make it a suitable candidate for biomedical and pharmaceutical use.[1] The incorporation of a preformed polymer in the continuous phase of highly concentrated emulsions (HIPREs) allows the preparation of porous materials with very high pore volume.[2] In the present work, O/W highly concentrated emulsions were used as template for the preparation of macroporous materials based on chemically crosslinked hyaluronan. The hyaluronan-based porous foams were prepared from HIPREs formulated using biocompatible components: an ethoxylated castor oil surfactant, and a medium chain triglyceride oil. Surfactant and oil were removed from the porous material by solvent extraction with ethanol and water for 12 hours, and finally, the porous foams were freeze-dried (Fig.1). The porosity of the obtained materials was dependent on the surfactant concentration in the HIPREs. Ketoprofen, a model anti-inflammatory drug, was incorporated to the hyaluronan-based porous materials to study their suitability as controlled drug delivery systems. Drug release from hyaluronan-based porous materials, HIPREs and hydrogels[3] to a receptor solution was studied for comparative purposes. The results obtained showed that controlled drug release can be obtained as a function of formulation parameters.

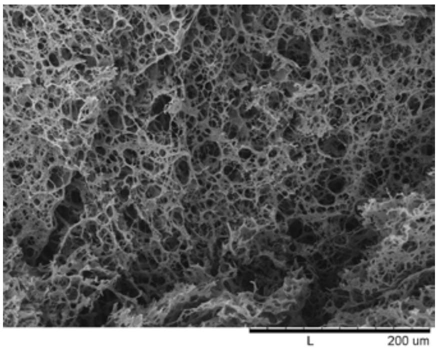

Fig. 1 SEM image of the porous material based on hyaluronan obtained from highly concentrated emulsions.

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Rapid "droppling" devices for the generation of monodisperse emulsions with well-controlled interfacial properties

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Milli/microfluidics is now recognized as a very versatile tool to produce monodisperse droplets which may be polymerized in-situ to generate monodisperse particles. The availability of such systems provides researchers with an unprecedented control over the study of complex physical problems, such as jamming in emulsions, foams or suspensions. For such investigations, large quantities of droplets/particles are required. Classical fluidic geometries such as flow-focusing or T-junction devices yield only small amounts of droplets, making them impractical for high-throughput applications. To produce a lot of objects in a short amount of time, techniques based on parallelized object production have been developed, including terrace emulsification or microfluidic arrays. Studies of these geometries focused on micrometric flows, whilst here we describe the development of these techniques at millimetric scales with low-cost materials. We developed devices to investigate different parameters controlling the formation of droplets, paying particular attention to the static and dynamic properties of the liquid/liquid interfaces covered in interfacially active agents of different kinds. The presence of these agents confers non-negligible visco-elastic properties to the interfaces, which influence the rapid dynamics of the drop generation. It also modifies significantly the interaction of the generated drops, prohibiting, for example, their coalescence.

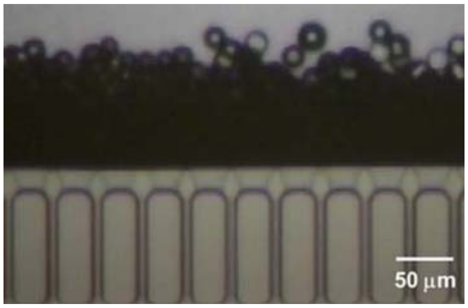

Fig. 1 Optical micrograph of generating fine

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Effect of Phase Transition in the Adsorbed Film on Foam Film Thickness

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A thin foam film held in a porous glass ring is utilized for understanding the stability of foams. The foam film stabilized by the electrical double-layer repulsion is called Common Black Film (CBF) and the one stabilized by the steric repulsion is Newton Black Film (NBF). Thus the CBF – NBF transitions have been well investigated by increasing salt or surfactant concentrations. Recently we found that some alkyltrimethylammonium halides show a first-order transition of the adsorbed film in the presence of alkanes of similar chain length to the surfactant[1], which motivated us to study the influence of surface phase on the foam film thickness. For this purpose, we applied hexadecyltrimethylammonium chloride (HTAC) – tetradecane (C_{14}) mixed adsorbed film in the presence of a small amount of NaCl.

We first measured the ellipticity and surface tension to examine the state of adsorbed film and then the foam film thickness *h* by the microinterferometry around the phase transition temperature. Figure 1 shows the results of the thickness as a function of temperature *T* at fixed HTAC and NaCl concentrations. It was demonstrated that *h* changes discontinuously at the temperature close to the surface phase transition, indicating that the phase transition promotes the binding of chloride ions to the adsorbed films and shields the double-layer repulsion. Our previous study demonstrated that, since the surface density of surfactant is changed only slightly, this phase transition occurs mainly by the penetration of alkane molecules in the adsorbed film.

Figure 1 shows that *h* still remains in the thickness range of CBF even after the thickness transition. It should be noted that the salt concentration of 50 ~ 100 mmol kg $^{-1}$ is required to reduce the foam film thickness to about 15 nm. Therefore, it can be said that the counter ion binding driven by the surface phase transition effectively shields the surface potential compared to the salt addition. In literature, the CBF – NBF transition occurs at salt concentrations at several hundreds mmol kg $^{-1}$. Thus, we are examining whether the CBF – NBF and NBF – NBF transitions are induced by the surface phase transition in the presence of oil at a lower salt concentration.

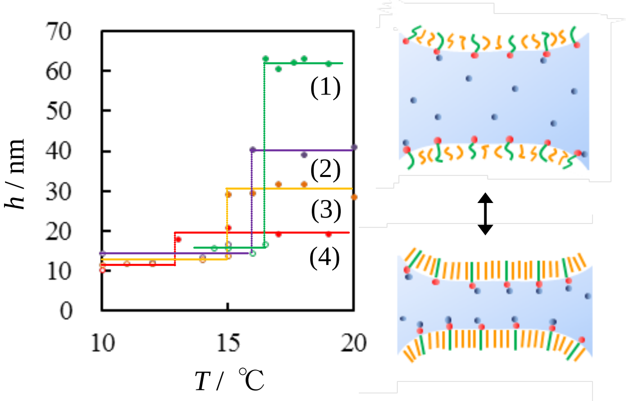

Fig. 1 Foam film thickness vs. temperature curves and schematic illustrations of the foam film at phase transition temperature. The concentration of HTAC was fixed at 0.300 mmol kg $^{-1}$ and that of NaCl was at (1) 2.20, (2) 5.00, (3) 10.0, and (4) 50.0 mmol kg $^{-1}$, respectively.

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Effect on nonionic surfactants on the emulsification and stability of emulsions

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We study the relation between emulsion stability and surfactant structure and concentration. The emulsion stability is determined by both kinetic (as rate and time of stirring, rate of coalescence) and thermodynamic factors related to the processes of adsorption, partitioning and micellization. The ***thermodynamic parameters*** determine the emulsion composition in terms of surfactant distribution between water, oil, micelles and the interface (fig. 1). The calculation of the emulsion composition requires knowledge of: **(i)** adsorption parameters (surfactant adsorption constant and molecular area α), **(ii)** partition coefficient, **(iii)** critical micelle concentration, **(iv)** disjoining pressure as a function of surfactant hydrophobic tail length and hydrophilic head structure.

The knowledge of the emulsion composition allows the analysis of ***criteria for stability*** (resp. instability). Emulsion experiments suggest that the following criteria are significant:

(i) Condition for a critical surface coverage, $\alpha\Gamma_{\mathrm{cr}}$, above which emulsion is stable. The degree of coverage is limited by the depletion effect;

(**ii**) Conditions related to the dynamics of emulsification (e.g., Bancroft instability due to the location of the surfactant);

(iii) Condition for stratification stabilization due to presence of ordered layers of micelles.

The analysis of the suggested stability parameters as a function of surfactant structure shows that there are optimal lengths of the alkyl and the polyethyleneglycol chains, at which the surfactant's performance is maximized.

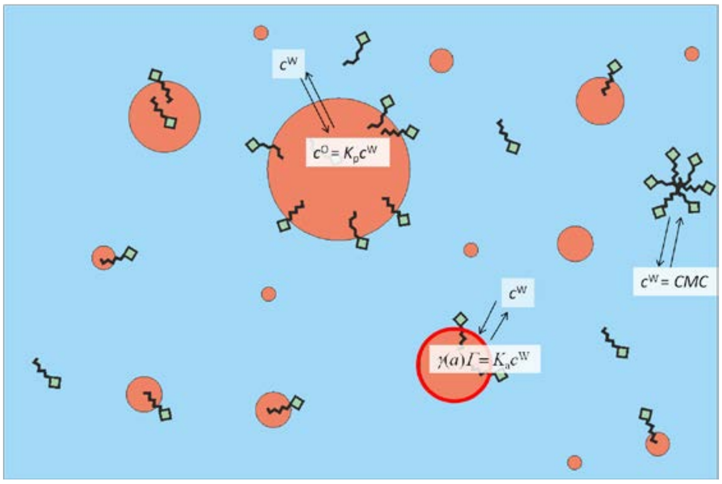

Fig. 1

Acknowledgements: the study is supported by BASF and Project BG 051PO001-3.3.06-0038.

Separation and Concentration of Hydrogen Peroxide Using Microfluidics

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Hydrogen peroxide (H_2O_2) is widely used in industry for bleaching purposes and water treatment. So far the production is made through the Riedl-Pfleiderer (or antraquinone) process, which faces problems with byproducts of antraquinone that are not biodegradable. Another issue which needs to be addressed is that the manufacture of concentrated hydrogen peroxide cannot be made on-site; therefore it requires transporting H_2O_2 to the place where it will be used, which is neither cost-effective nor eco-friendly. In that context, the production of H_2O_2 by direct synthesis using microfluidic technology has become an active research topics[1] as it solves both of the above mentioned issues. One of the crucial steps in this microfluidic process is to obtain after reaction concentrated H_2O_2 by separation from the other liquids present in the synthetic process. In this research, we therefore define and outline the conditions for efficient microdistillation and concentration of hydrogen peroxide.

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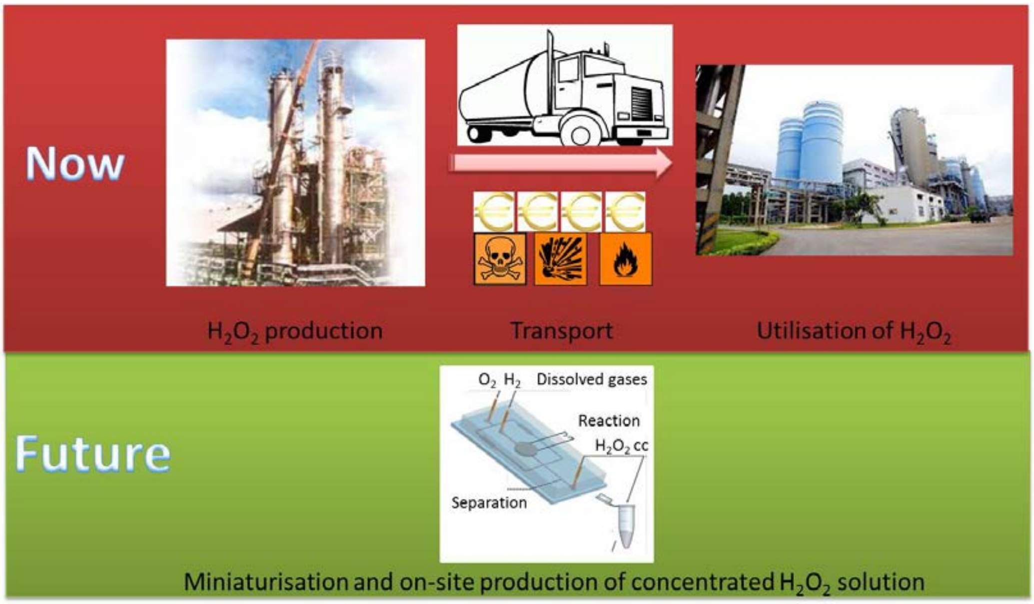

Fig. 1 Illustration of H_2O_2 production

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Stabilization of O/W Emulsion with Nanoclay

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In this study, we investigate whether nanoclay particles can give a stabilization effect on an oil-in-water(O/W) emulsion. From the microscopic and macroscopic point of view, emulsion morphology is observed depending on the composition of oil phase, quantity of nanoclay and wetting property of nanoclay. Based on the microscopic observations, emulsion morphology is stabilized with the addition of nanoclay of the balanced wetting property and the size of droplet is reduced with nanoclay(Fig. 1(a)), while, if nanoclay does not, droplets is coalescing each other(Fig. 1(b)). Nanoclay seems to give an effect to prevent a coalescence between droplets when nanoclay has the balanced wetting behavior. When nanoclay shows the balanced wetting behavior, it is localized at the interface and forms interfacial layer (ref 1,2). The formation of interfacial layer seems to give a stabilization effect. When we increases the amount of nanoclay, it gives the further improved stabilization. However, from macroscopic observations, the addition of nanoclay does not stabilize the emulsion as expected from microscopic observations. Two different nanoclay shows different location depending on the wetting behavior of nanoclay. Different with expectation from microscopic observations, emulsion with nanoclay results in phase separation. Nanoclay of the unbalanced wetting behavior rather enhances the separation of oil and water out of emulsion.

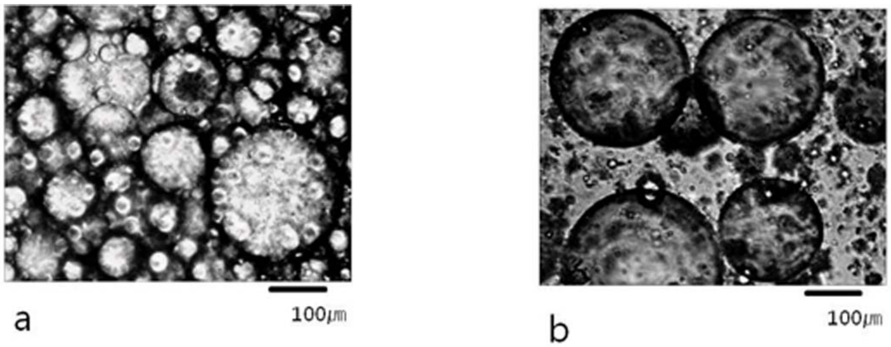

Fig. 1 Morphology of 20 O/W emulsion with nanoclay : a. nanoclay of hydrophilic surface property b. nanoclay of hydrophobic surface property

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Acknowledgements:

This study was supported by Mid-career Researcher Program through NRF grant funded by the Korea government (MEST) (No. 20110016890)

Pickering emulsions stabilized by nanoparticles of bare silica. Adsorption of nanoparticles and emulsion stability

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The stabilization of Pickering emulsions comes from a strong adsorption of solid particles at the oil-water interface that builds a rigid barrier against coalescence. Either particles having a diameter above 100 nm diameter, or aggregates of nanoparticles are usually selected for the stabilization of Pickering emulsions because the adsorption energy of solid particles coming from partial wetting by water and oil, $\Delta_{\mathrm{ads}}F = -\pi R^2 \gamma_{\mathrm{ow}} (1 \pm \cos\theta)^2$, is several *kT*, which means that full adsorption of solid particles takes place.

The adsorption energy reaches the order of magnitude of thermal energy upon decreasing the size of solid particles to ~10 nm, and equilibrium adsorption is therefore expected. The purpose of the present work is investigating the adsorption of individual nanoparticles of 12 nm diameter at the surface of oil droplets of o/w emulsions and looking at the consequences of a weak adsorption on the emulsion stability.

Silica nanoparticles of the Ludox™ series are individual nanoparticles of 12 nm diameter in suspension in water. Most oils do not wet bare hydrophilic silica. However partial wetting conditions are fulfilled with of particular polar oils that could be dispersed as Pickering emulsions stabilized by bare fumed silica [1].

Emulsification of diisopropyladipate oil droplets using Ludox™ AS40 silica stabilizing nanoparticles was successful up to 60% oil content (Fig. 1). An unusual dependence of the oil droplet diameter with respect to silica content occurs. The linear dependence $D = \frac{6}{\rho_{\mathrm{oil}}\, a_{\mathrm{SiO_2}}} \frac{M(\mathrm{oil})}{M(\mathrm{SiO_2})}$ expected for full adsorption of solid particles was not followed, although it is generally followed over a wide silica concentration domain [2],[3].

The adsorption isotherm of silica particles measured by ICP-AES titration of residual silica shows that adsorption equilibrium takes place over the whole silica and oil concentration ranges. A consequence is the possible de-stabilization of emulsions upon shifting the adsorption equilibrium. As example, dilution of emulsions with pure water leads to their progressive coalescence into larger droplets. Several experiments based on optical microscopy, light scattering and adsorption isotherms show this paradoxical behavior. Multilayered adsorption of silica particles is suspected on the basis of adsorption isotherms.

Fig. 1: O/w emulsions of diisopropyladipate oil stabilized by 4% Ludox™ AS40 for increasing amounts of oil from 10% to 70%. Emulsification was successful up to 60% oil and failed at 70%.

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Droplet growth inhibition of concentrated limonene emulsions

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Oil in water emulsions were obtained by using limonene as the disperse phase and Pluronic PE 9400 as the emulsifier. Recent results obtained by our research group have demonstrated that concentrated limonene-in-water emulsions, $\phi = 50$ %, stabilized by Pluronic PE9400, are destabilized by both, Ostwald ripening and creaming. The former is more pronounced in concentrated emulsions (ϕ=50%) and both destabilization processes increase with surfactant concentration in the range 3%-5% (w/w) where monomodal submicron emulsions are obtained (d3,2 ~ 0.8 μm, Uniformity ~ 0.35).

It is well-known that Ostwald ripening can be delayed by adding a second water insoluble compound to the oil phase [1,2]. This study is focused on the development of a stable concentrated (ϕ= 50%) limonene-in-water emulsion formulation by studying the properties as Ostwald ripening inhibitors of different additives (tetradecane, silicone oil and rosin gum). The droplet size growth in the presence of each of these chemicals was monitored by means of laser diffraction (Mastersizer X, Malvern) and creaming destabilization was studied by multiple light scattering technique (Turbiscan Lab-expert, Formulaction).

The influence of additive concentration was also studied. It is shown that a low concentration of tetradecane and silicone oil (ca. 2% (w/w)) drastically reduced the Ostwald ripening rate. Nevertheless, a much higher concentration of rosin gum was needed to prevent droplet growth (>15%(w/w)).

Although emulsions containing tetradecane and silicone oil maintained the same droplet size, they became destabilized by creaming. However, the addition of rosin gum at concentrations higher than 15% (w/w) resulted in stable limonene emulsions avoiding creaming separation. This may be due to the combination of two cooperative effects. Rosin gum acts as a weighting agent increasing the density of the disperse phase and on top of that the droplet size turns out to be lower (d3,2 ~ 0.5 μm, Uniformity~ 0.35), which will also prevent creaming from occurring.

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Acknowledgements:

The financial support received (Project CTQ2011-27371) from the Spanish Ministerio de Economía y Competitividad (MINECO) and from the European Commission (FEDER Programme) is kindly acknowledged. L. M. Pérez-Mosqueda also acknowledges the Universidad de Sevilla for its financial support (Beca PIF IV Plan Propio de Investigación).

Mitigation of Blast-Waves by Aqueous-Foam Barriers - Implementation of the Exploding Wire Technique

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Interactions of blast-waves with foam barriers have been studied mostly for two limiting cases: in the near field of the blast source or in the far field [1]. In the far field, the leading shock wave is weak, and while the foam remains generally intact, the penetrating shock wave loses energy by scattering numerous interfaces and through viscous dissipation of the liquid flowing through the Plateau borders and films [2]. Close to the explosive charge, the processes are far more complicated. The peak overpressures are so high that the foam is shattered into extremely fine droplets immediately behind the leading shock wave. Internally generated blast waves of high intensity are expected to trigger numerous additional mechanisms for energy dissipation, such as high temperature effects at the fireball-foam boundary, heat transfer, bubble shattering, evaporation, rearrangement and pulsation.

In the current work, we implement an exploding wire technique to generate small-scale spherical blast waves. Owing to a high electric current pulse the wire undergoes an extremely fast Joule heating, which causes a rapid expansion of a hot vaporized metal column, accompanied by the creation of a strong blast wave [3]. It was shown by using a similitude analysis that the results obtained from the small-scale experiments can be applied to full-scale problems. Therefore the exploding wire system offers an inexpensive, safe, easy to operate and effective tool for studying blast-wave–foam interaction related phenomena in real explosion scenarios. We consider the transient features of draining aqueous foams and use coal ash particulates to decrease the rate of changing the liquid distribution. Besides serving as effective stabilizers, the particulates also enhance the capacity of particulate foams in blast mitigation [2,4]. We study the mitigation of blast wave as a function of the initial impact intensity, the barrier geometry, the foam structure, the density and the thickness of the barrier, and concentration of the particulates.

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Simulation of a droplet in gravity and non isothermal conditions

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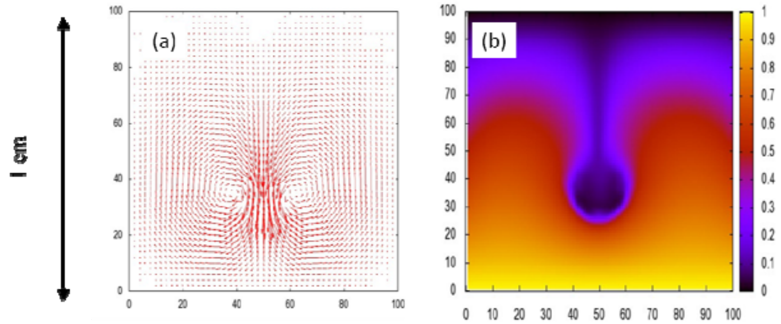
This work presents numerical studies of a water droplet evolving in a paraffin oil continuous phase. This droplet is submitted to gravity and to non-isothermal boundary conditions. The simulation of such a simplified multiphase system is important in both academic and industrial context. This is particularly the case for emulsions, wetting problems and evaporation [1]. But, to achieve the simulation of such complex systems, there are still important algorithmic problems to be solved in particular due to the free moving interfaces and capillarity. Here, a Volume of Fluid (VOF) technique has been implemented with high order temporal and spatial schemes to preserve the sharpness of the interface of the considered droplet. Capillary contributions are fully accounted for using a continuum surface force (CSF) approach [2]. The droplet has one 1 mm radius and is confined in a square two dimensional finite simulation domain (SD) of 1 cm side. Although simplified, this model has the important advantage to allow the study of initially non symmetric configurations and therefore the influence of boundary walls.

The drainage dynamics of the droplet shows the existence of three different regimes with characteristic times that depend on the initial condition [3] and on temperature. The hydrodynamics in the complete SD (figure (a)) and in the frame of the droplet is investigated. When considering an initial condition with a vertical temperature gradient and a symmetric configuration for the droplet position, simulations show an evolution of the temperature field consistent with the literature (figure (b)). But, this situation is strongly changed when the initial droplet becomes closer to one of the side walls of the SD [4].



The role of the droplet initial position and temperature field is described with good numerical stability. But there are still important problems remaining in the simulation of free interface systems. Spurious currents induced by the description of capillarity can in particular come into play. These latter become negligible in this study, once the droplet drainage velocity becomes large enough.

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Effect of adsorbed film composition on foam film thickness in cationic - nonionic surfactant system

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Foam film is a thin aqueous one stabilized by two surfactant adsorbed films facing with each other and its stability depends on interfacial forces determined by the property of the adsorbed film such as surface density, surface potential and so on. Although, it is well known that the mixing of surfactants dramatically changes the property of the adsorbed film, there are only a few studies performed to clarify the effect of surfactant mixing on the foam film stability. Therefore, in this study, we have measured the surface tension γ and foam film thickness h_w of the hexadecyltrimethylammonium bromide (HTAB) - pentaethyleneglycol monododecyl ether ($C_{12}E_5$) system as a function of the total molality of surfactants $\hat{m}$ and the $C_{12}E_5$ composition in the mixture $\hat{X}_2$. All the experiments were done at 298.15 K under atmospheric pressure and in the presence of NaCl of 10 mmol kg^{-1} for the films to be stabilized. The γ and h_w were measured respectively by the pendant drop method and microinterferometry.

The thickness was shown in Figure 1. In the pure HTAB and $C_{12}E_5$ systems, h_w did not change remarkably against $\hat{m}$. The difference in h_w value of these systems can be explained by strong double-layer repulsion in the HTAB system. In the case of $\hat{X}_2 = 0.5005$, however, a rapid increase of h_w is observed around 0.15 mmol kg^{-1}. This is due to that the adsorbed film was enriched with $C_{12}E_5$ at a lower $\hat{m}$ but with HTAB at a higher.

The thermodynamic analysis of surface tension data provides the composition of surfactants at the water/air surface, $\hat{X}_2^{\mathrm{H}}$ and then the phase diagram of absorption is constructed. We will examine the relation between $\hat{X}_2^{\mathrm{H}}$ and h_w and the change in interfacial forces in the foam film of mixed surfactant system.

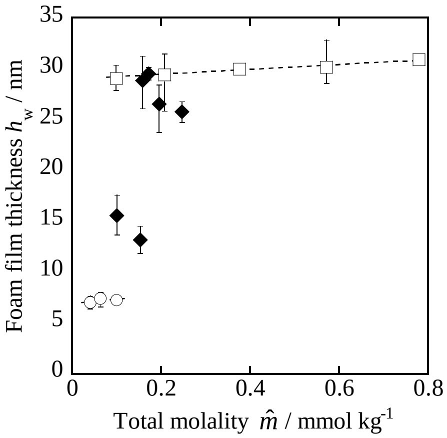

Figure 1. Foam film thickness vs. total molality plots of pure HTAB (□), $\hat{X}_2 = 0.5005$ (◆) and pure $C_{12}E_5$ (○) aqueous solutions.

Dynamics and structure of the lipase *Candida Antarctica B* in bicontinuous microemulsions

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One of the major challenges in biotechnology arises from the fact that interesting substrates for the pharmaceutical industry are insoluble in water whereas enzymes that are supposed to convert them are mainly soluble in water and often require an interface to be active. Recently, bicontinuous microemulsions have been identified as promising reaction media to overcome this enzyme-substrate incompatibility [1]. Bicontinuous microemulsions consist of interpenetrating nanometre-sized domains of water and oil being separated by a connected surfactant monolayer [2] providing a large interfacial area for the enzyme to adsorb and convert the substrate. In contrast to especially droplet microemulsions, enzyme and substrate are confined to the same structural motif. Anticipating similar diffusion we expect a positive influence on the kinetics of the reaction as well. In this contribution we present results on how the conformation of the lipase *Candida Antarctica B* changes if it is incorporated into a bicontinuous microemulsion. In addition, we also investigated to which extent the presence of the lipase changes the properties, *i.e.* the phase behavior and the structure, of the bicontinuous microemulsion. We combined several experimental techniques to obtain a comprehensive picture of the system H_2O/4wt% NaCl/Cal B – *n*-octane – nonionic surfactant $C_{10}E_5$ [3]. The respective phase diagrams of the microemulsion together with UV/Vis, fluorescence and circular dichroism spectroscopy lead to the conclusion that the surfactant monolayer takes up around 80wt.% of the initial amount of lipase whereas the rest is located in the water domains of the microemulsion. Treating the lipase as an interfacially active biopolymer we studied the structure of the microemulsion using PFG-NMR and tensiometry. A comparison between lipase-free and lipase-containing microemulsions completes the picture.

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Formation and stability of foams prepared by concentrated silica suspensions and amphoteric surfactant

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Particle-stabilized foams have attracted considerable research interest, due to their unique properties and potential technological applications. The remarkable stability of these foams (months and years) and the opportunity of using them for production of novel materials have brought a number of researches in the field of "Pickering" stabilization. The major aim of our study is to define the factors controlling the foaming and stabilization processes in the presence of silica particles with high concentration (15-25 wt. % in the foamed suspension) and the amphoteric surfactant cocoamidopropylbetaine (CAPB).

Systematic experiments were made to characterize the foamability of the suspensions with respect to: (a) Concentration of particles, *Cp*; and (b) Concentration of surfactant, *Cs*. In addition, the adsorption of surfactant on particle surface, the behavior of foam films, and the rheological properties of the foamed suspensions were studied to analyse the relation between these properties, on one hand, and the suspension foamability and foam stability, one the other hand. The most important experimental results could be summarized as follows: (1) Three regions with respect to suspension foamability are observed: Region 1 - good foaming, Region 2 - reduced foaming and Region 3 - no foaming. Two sub-regions are seen in Region 1, with respect to foam stability to water drainage: 1S - stable foams and 1U - unstable foams. (2) Some minor component(s) present in CAPB adsorb on the silica surface and modify the interactions between the silica particles. Nevertheless, the silica particles remain predominantly hydrophilic and stabilize the foams to water drainage by blocking the nodes and plateau borders in the foam. No particles are trapped in the foam films and the latter are stabilized by surfactant molecules. (3) Foams stability to water drainage is governed by the suspensions yield stress and bubble size.

Fig. 1 Photo of dried foam, formed from CAPB-silica dispersions at pH=8.5.

Properties of water/sodium dodecyl sulfate/n-propanol/allylbenzene micellar systems

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Water/n-propanol/sodium dodecyl sulfate/allylbenzene micellar systems were formulated. The ratio (w/w) of n-propanol/surfactant equals 2/1. The extent of the micellar region as function of temperature was determined. The micellar systems were characterized by the volumetric parameters, density, excess volume, ultrasonic velocity and isentropic compressibility. The micellar densities increase with the increase in the water volume fraction. Excess volumes of the sodium dodecyl sulfate decrease for water volume fraction below 0.3, stabilize for water volume fractions between 0.2 and 0.5 then increase for water volume fraction above 0.5. Excess volumes of the studied micellar systems increase with temperature. Ultrasonic velocities increase with the increase in water volume fraction up to 0.8 then decrease. Ultrasonic velocities increase with temperature for water volume fractions below 0.8 and increase for water volume fractions above 0.8. Isentropic compressibilities decrease with the water volume fraction up to 0.8 then increase. Isentropic compressibilities increase with temperature for water volume fractions below 0.8 and decrease for water volume fractions above 0.8. Structural transitions from water-in-oil to bicontineous to oil-in-water occur along the micellar phase. The particle hydrodynamic diameter of the oil-in-water micellar systems was found to decrease with temperature. In the diluted region nanoemulsions systems were observed.

Effect of cationic polymers on foam rheological properties

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We study the effect of two cationic polymers, with trade names Jaguar C13s and Merquat 100, on the rheological properties of foams stabilized with mixture of anionic and zwiterionic surfactants (SLES and CAPB) and series of five co-surfactants leading to high or low surface dilatational moduli of the foaming solutions. The experiments revealed that the addition of Jaguar to the foaming solutions leads to: (1) Significant increase of the foam yield stress for all systems studied; (2) Presence of consecutive maximum and minimum in the rheological curve stress *vs.* shear rate, for foams stabilized by co-surfactants with high surface modulus, see Fig. 1. These systems cannot be described by Herschel-Bulkley rheological model anymore; (3) Presence of significant foam-wall yield stress. These effects are explained with the formation of polymer bridges between the neighboring bubbles in slowly sheared foams (for inside foam friction), and between the bubbles and the confining solid wall (for foam-wall friction). In contrast, the addition of Merquat does not affect noticeably any of the foam rheological properties studied. Optical observations of foam films formed from these systems showed a very good correlation between the polymer bridging of the foam film surfaces and the strong polymer effect on foam rheological properties. The obtained results demonstrate that the bubble-bubble attraction can be used for efficient control of the foam yield stress and foam-wall yield stress, without affecting significantly the viscous friction in sheared foams [1].

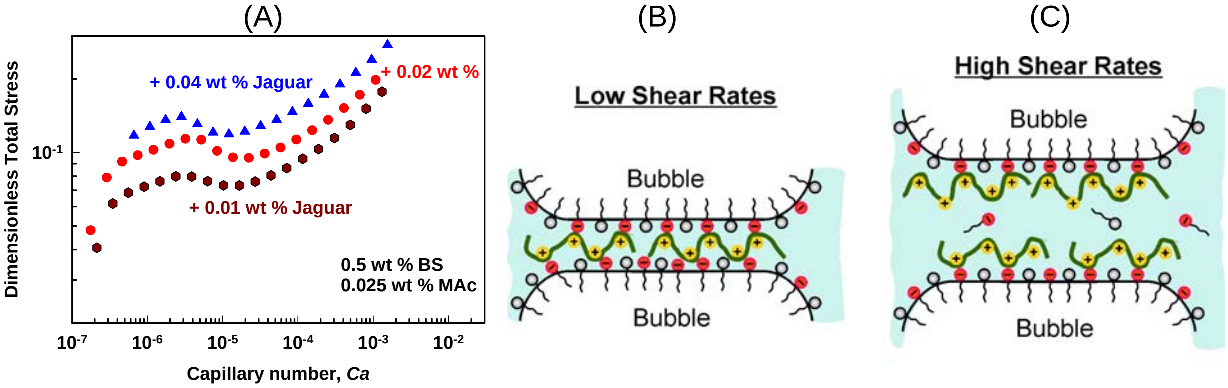

Figure 1. (A) Total stress, as a function of shear rate for foams stabilized by SLES+CAPB+MAc+Jaguar solutions with different concentrations of Jaguar. (B) Schematic presentation of the foam film between two neighboring bubbles at low shear rates - the film surfaces are bridged by cationic polymer chains. (C) At high shear rates, the film thickness is larger than the size of the adsorbed polymer molecules and the polymer bridges are broken.

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Preparation of κ-carrageenan porous particles via multiple O/W/O emulsion templating for the delivery of food actives

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The encapsulation of bioactive compounds to produce healthy and high quality food products is an area of emerging interest. Hence, the design of novel encapsulating structures meeting the increasing demands is a scientific and technological challenge [1]. In this context, the use of multiple emulsions offers, among others, the following advantages: they can entrap agents with a low compatibility with the encapsulating system and release them in a programmed fashion [2]. In addition, multiple emulsions can be used as templates for the production of porous particles [3]. However, the complexity of multiple emulsions implies the interplay of numerous, often competing, interactions among the different components which make their formulation a complex task. Nevertheless, it has been shown that the stability of the primary emulsion play a critical role in achieving a kinetically stable multiple emulsion [4]. The purpose of this work was to prepare and optimize edible κ-carrageenan porous particles suitable for the encapsulation and release of lipophilic bioactive compounds using multiple oil-in-water-in-oil ($O_1/W/O_2$) emulsions as templates. Multiple emulsions were generated by a two-step process, namely, a primary O_1/W emulsion was firstly prepared and further dispersed into the external oil phase O_2. A Box-Behnken experimental design [5] was used to optimize the primary O_1/W emulsion formulation. The studied factors were: the percentage of water, the oil to surfactant ratio, the κ-carrageenan concentration and the concentration of the gel-inducing agent (KCl). The evaluated responses were the emulsion stability, droplet size, melting temperature and elastic modulus. It was found that the optimal formulation was strongly associated with the κ-carrageenan concentration. Such primary emulsion formulation resulted in the formation of stable multiple $O_1/W/O_2$ emulsions. Subsequently, κ-carrageenan porous particles were prepared via a temperature-induced gelation of the intermediate phase. Stable particles with spherical shape, a mean particle size of 11.5 µm and containing multiple inner oil droplets were obtained. Retinyl palmitate was successfully encapsulated in the inner oil phase with a 86% of efficiency. Moreover, particles were found to be thermo-sensitive, undergoing disruption and releasing the inner oil droplets above 35ºC. Such thermal sensitivity could be a promising and attractive mechanism to release the encapsulated retinyl palmitate. Therefore, these particles could be useful to produce multivitamin supplements, functional and fortified food products.

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Molecular Dynamics Study of the Structure and Stability of Toluene Layers in Water

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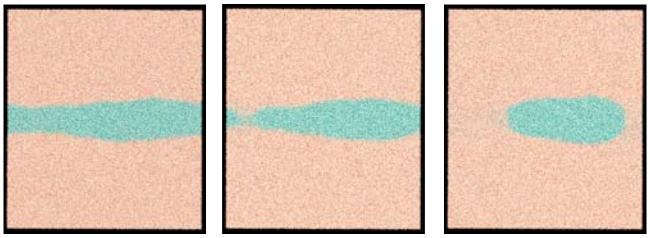
The mechanical properties of thin toluene film and rupture caused by applied external electric field have been studied using molecular dynamic simulation approach. The critical value of external field and thin film capacitance were obtained. The mechanism of thin film rupture driven by the applied local pressure is proposed and comparison with thin film experiment is provided.

We have performed 5ns large-scale molecular dynamics simulations of model of the toluene layer with GROMACS package. The simulations were performed in the NVT ensemble at temperature T=298 K. The simulation parameters were generally maintained at the default values offered in GROMOS force field. The water model is SPC (simple point charge). The size of the simulation box: 25x25x25 nm. Molecular dynamics simulations were run with applied electric fields ranging from 0 to 120 mV/nm.

Film Rupture Mechanism Revealed from Simulations
/Side view/



Physical factors influencing beer overfoaming

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Gushing is a negative phenomenon characterized by spontaneous overfoaming of beer after opening a bottle or can which is not caused by hight temeratures or shaking. Despite long-term research it is still not possible to predict. The aim of this work was to find a gushing-active matrix on which it would be possible to observe the influence of physical factors (pH, pressure, surface tension).The solution of bovine serum albumin of concentration 0.5 g/l was determined as the most convenient matrix. In this solution micelles of albumin are formed which act like nucleation sites for the formation of gushing foam. This solution was used to estimate the influence of pH, surface tension and the suppressing effect of increased pressure over the solution on gushing. All measurements were carried out in for this purpose specially constructed apparatus consisting of a pressure column, a high-speed camera and a pressure probe. The results are the relationships between the phycial factors and beer overfoaming.

Acknowledgements:

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Aqueous foam generation: What determines the foam properties

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Foams are widely used in a large number of technical processes, such as flotation. They are also present in various forms in our daily lives as soft solids or fluids in food and beverage products or in insulating materials as solids. For many practical applications it is very important to control the foam formation parameters, the most important of which are the bubble size and the liquid fraction. However, dependence of these parameters on conditions of foam generation is still unclear despite of the large amount of experimental and theoretical work.

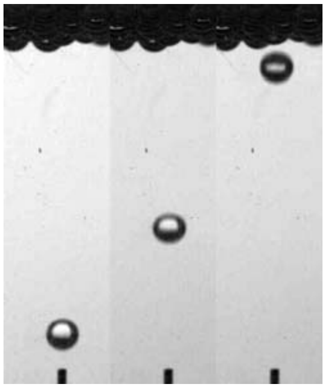

Fig. 1 Sequence of images of a single bubble rising to form foam.

In the present study foam is generated by a number of methods: by blowing gas through nozzles, sieve plates and porous plates at fixed flow rates and by turbulent mixing into a T-junction module at fixed pressures. The radii and the liquid fraction of the foam are measured for different foaming solutions (varying the surfactant type and concentration). The properties of the foam formed depend strongly on the experimental conditions and the method of fabrication. But in all cases a strong and universal correlation between the bubble size and the liquid fraction is observed. This dependence can be fully accounted for by describing the entry of the bubbles into the foam. The impossibility of controlling the bubble size and the liquid fraction independently in any given method of generation is demonstrated.

Our work sheds some light on the complex process of foam generation and highlights the difficulty of controlled foam production, opening up many further questions.

Imaging ellipsometry at the liquid/liquid interface

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Imaging and metrology of thin films at the liquid/liquid interface is of increasing interest for a number of applications like emulsion, crude oil technology, biophysics. Imaging ellipsometry can be used to characterize the behavior of molecules, polymers, nanoparticles or cells at the liquid/liquid interface. Benjamins et al. (2002) presented a light guides based setup using ellipsometry to study the liquid−liquid interfaces. Based on developments at Twente University the setup was adapted to Brewster angle microscopy and Imaging ellipsometry. With this new tool, imaging ellipsometry at variable angles of incident can be performed at liquid/liquid and solid/liquid interfaces.

A number of different amphiphilic molecules were characterized at different interfaces. Examples are DMPE at the water/oil interface (Fig. 1a), cetylpyridiniume chlorid at the toluene/water interface (Fig1b,c).

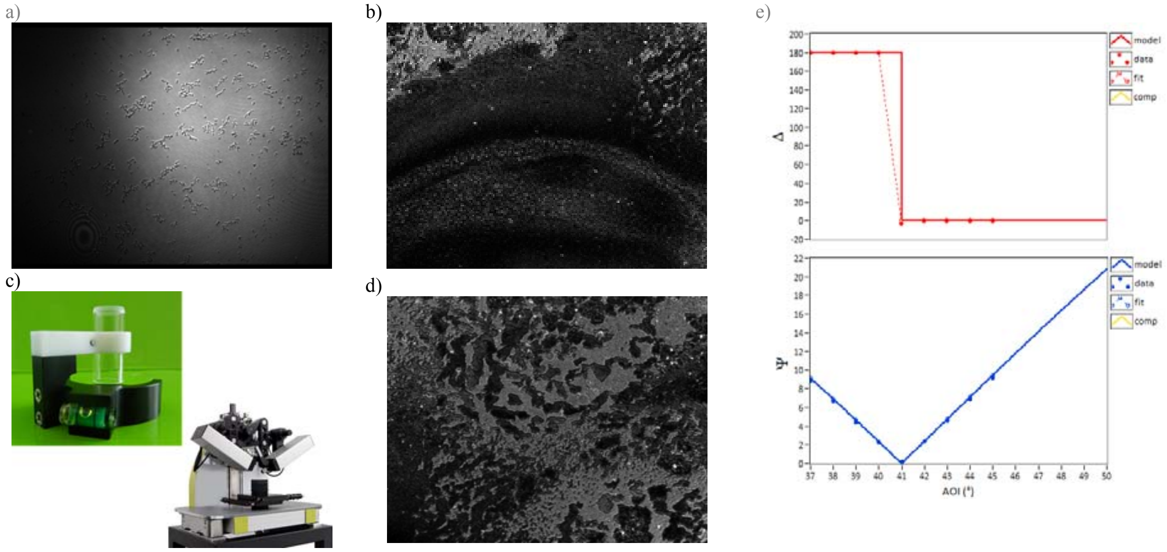

Fig. 1. Imaging ellipsometry (c) at the liquid liquid interface: ellipsometric contrast micrographs of DMPE (a), cetylpyridinium chlorid (b,d) and angle of incident spectra at the toluene/water interface

Based on molecular and particular systems, methods to increase the image quality, effects of four zone nulling and optical modeling will be discussed.

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Acknowledgements:

We thank the working group of Prof. Mugele (Twente University) for their good collaboration.

Carboxylate based surfactant for ion flotation : Salt and pH effects

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The process called *ion flotation* allows to concentrate metal ions or other charged entities from aqueous solution by developping interfaces. This is achieved using a surfactant molecule which complexes ion and entrains it in a foam. Afterwards the drainage of the foam leads to concentrate the metal ions and the surfactant. The skimming of the foam enables ultimately to extract metal ions from the native solution. *Ion flotation* covers two main application fields: recovery of valuable material and water decontamination. Compared to solvent extraction, used for example in the nuclear fuel recycling, *ion flotation* shows the main advantage of using gas instead of an organic solvent.

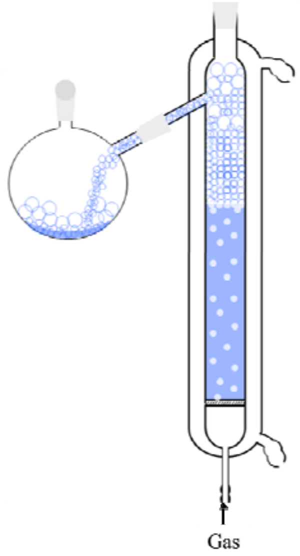

Fig. 1 : Ion flotation column

In the present contribution a commercial carboxylic surfactant (AKYPO® RO 90 VG) is investigated in terms of ion flotation. This surfactant is composed of an alkyl chain, ethoxy groups keeping efficient the foaming property, even after complexation, and a terminal carboxylic acid function which acts as a complexing part when it is under its charged carboxylate form.

The efficency of this process in term of decontamination factor, enrichement ratio and effluent volume is a subtle interplay between the solution chemistry and the physical of the foam. The main part of the study focuses on the influence on pH and the nature of metal ion such as neodymium (Nd^{3+}), europium (Eu^{3+}), copper (Cu^{2+}), calcium (Ca^{2+}), strontium (Sr^{2+}), and lithium (Li^{+}), both on the solution speciation of metals and surfactant than on the hydrodynamics and wetness of the foam. The complexation between the surfactant and neodymium ion in the bulk was studied by pH titration and the complexation constants were estimated by modelisation of the titration curves. The foam structure was characterized by conductometry and small angle neutron scattering.

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Role of polymer-surfactant interactions in foams

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Solutions of surfactant-polymer mixtures often exhibit different foaming properties, compared to the solutions of the individual components, due to the strong tendency for formation of polymer-surfactant complexes in the bulk and on the surface of the mixed solutions. In this study we combine foam tests with model experiments to evaluate and explain the effect of several polymer-surfactant mixtures on the foaminess and foam stability of the respective solutions. Anionic, cationic, and non-ionic surfactants (SDS, $C_{12}TAB$ and $C_{12}EO_{23}$) were studied to clarify the role of surfactant charge. Highly hydrophilic cationic and non-ionic polymers (polyvinylamine and polyvinylformamide respectively) were chosen to eliminate the effect of direct hydrophobic interactions between the surfactant tails and the hydrophobic regions on the polymer chains. Our experiments showed clearly that the presence of opposite charges is not a necessary condition for boosting the foaminess and foam stability in the surfactant-polymer mixtures studied. We showed that the foamability of the cationic polymer polyvinylamine (PVAm) and anionic surfactant dodecyl sulphate (SDS) is strongly reduced, whereas the stability of the formed foams is strongly enhanced, as compared to the solutions of SDS alone [1]. The effect of the surfactant head group is studied [2] by comparing SDS with another anionic surfactant (sodium dodecyl oxyethylene sulphate, SDP1S) which contains an additional ethoxy fragment in the charged head group. For changing the electrostatic polymer-surfactant interactions, we varied pH between 6 and 10, thus crossing the polymer pKa ≈ 8.6. The foam tests showed that the foamability of all mixed solutions is strongly reduced in the entire range of pH values studied. Surprisingly, we found that the stability of SDP1S foams is also strongly reduced by PVAm, at lower pH, when the polymer charge density is high (contrary to SDS and to the common understanding). These results clearly demonstrate that the effect of cationic polymers on the foaming properties of anionic surfactants could depend significantly on the specific head group of the surfactant. Moreover, we showed that excessively strong polymer-surfactant interactions could be a serious problem in the formation and stabilization of foams from mixed polymer-surfactant solutions.

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Study of Polyelectrolyte and Oppositely Charged Surfactant Mixture for Stabilization of Emulsion

B. Mutaliyeva, A. Sharipova, G. Madybekova, S. Aidarova, R. Miller, D.Grigoriev

Emulsion is a very complex but at the same time most interesting object for studies in modern colloid chemistry. Although much work is devoted to this topic, the stabilization of emulsions remains an actual problem. The emulsifying ability of low molecular weight surfactants is sufficiently studied. However, the use of complexes formed by surfactants and oppositely charged polymers is of interest due to their high adsorbability at interfaces, a key property for the formation and stability of emulsions.

In the presented work complexes of the water-soluble polymer Polysterensulphonate (PSS) and cationic surfactant dodecyltrimethylammonium bromide (DOTAB) were prepared and their stabilizing effect on oil-water emulsions investigated. The PSS-DOTAB complexes were prepared by mixing the solutions of the individual compounds at concentration ratio 0,1; 0,2; 0,3; 0,4; 0,5. Solutions of the complexes were used 24 h after mixing. The interfacial tension at the tetradecane-water interface was measured by Drop profile analysis tensiometry (PAT-1, SINTERFACE), and DLS and zeta-potential measurements were performed at 25°C using Nano-ZS90 system (Malvern Instruments). Emulsions were prepared at room temperature by ultrasound at a mixing time of 2 minute. The obtained emulsions were poured into 14 ml calibration tubes and then their emulsifying efficiency was studied by observation of emulsion stability every 30 minute. The principle of observation was based on the determination of the volume of the separated oil phase. The size distribution of emulsion droplets was measured directly after emulsion formation by using a Zetasizer (Malvern), and repeated over 10 days.

It was established that there is an optimum ratio for the surfactant-anion-active polymer mixture at which the emulsion stability reaches a maximum. As it was proposed very recently in [1] this optimum ratio, probably, correspond to the stoichiometric composition of surfactant-polymer complexes. Any further increase in the surfactants concentration above this optimum leads to a decrease in the emulsion stability.

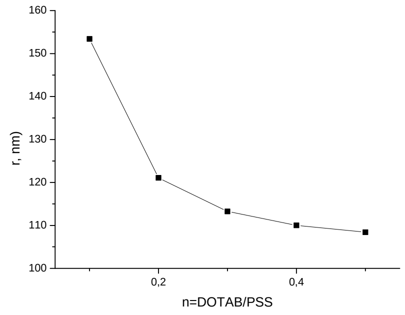

Fig 1. Mean drop size of the dispersed phase of an oil-water emulsion, in dependence on concentration of the stabilizing system DOTAB/PSS

The mean drop size shows that within optimum concentration ratios the emulsion stability is growing. The results after 3 days show that there was no coalescence in the emulsion, i.e. a negligible change of the mean droplet size was observed.

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Protein concentration and protein exposed hydrophobicity as dominant parameters determining flocculation of protein-stabilized oil-in-water emulsions

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The DLVO theory is often considered applicable for the description of flocculation of protein-stabilized oil-in-water emulsions. To test this, emulsions made with different globular proteins (β-lactoglobulin, ovalbumin, patatin and two variants of ovalbumin) were compared under different conditions (pH and electrolyte concentration). As expected, flocculation was observed under conditions in which the zeta potential is decreased (around the iso-electric point and at high ionic strength). However, the extent of flocculation at higher ionic strength (>50 mM NaCl) decreased with increasing protein exposed hydrophobicity. A higher exposed hydrophobicity resulted in a higher zeta potential of the emulsion droplets, and consequently in increased stability against flocculation. Furthermore, the addition of excess protein strongly increased the stability against salt induced flocculation, which is not described by the DLVO theory. In the protein poor regime, emulsions showed flocculation at high ionic strength (>100 mM NaCl), whereas the emulsions were stable against flocculation if excess protein was present (figure 1). This research shows that the exposed hydrophobicity of the proteins, and the presence of excess protein affect the flocculation behavior.

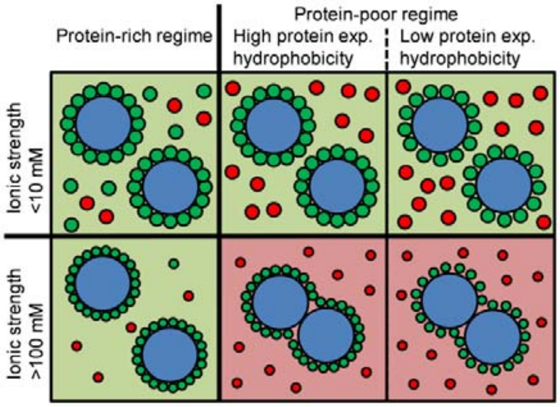

Fig. 1 Graphical overview of the effect of ionic strength, protein hydrophobicity and protein concentration on the flocculation behavior of protein-stabilized emulsions.

Instability of stretched and twisted soap films in a cylinder

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If a single rectangular soap film is confined between parallel walls it can be stretched indefinitely. However, if the rectangular film is confined in a cylinder, oriented parallel to the axis, we find that this cylindrical constraint induces a surface-tension-driven instability in sufficiently long films. Once this instability is triggered, at some critical aspect ratio, the film rapidly deforms (Figure 1) and collapses. If the film is twisted, taking the shape of a helicoid, then this critical aspect ratio is reduced.

We describe soap film experiments and Surface Evolver simulations that were carried out to determine the critical aspect ratio of both stretched and twisted films. A theoretical analysis confirms the values for the critical aspect ratio found in experiment and simulation for the stretched film, and this threshold decreases with increasing twist of the film.

This instability places an upper limit on the aspect ratio of any structure where a soap film, or any flexible membrane without bending and torsional stiffness, is confined in a cylinder.

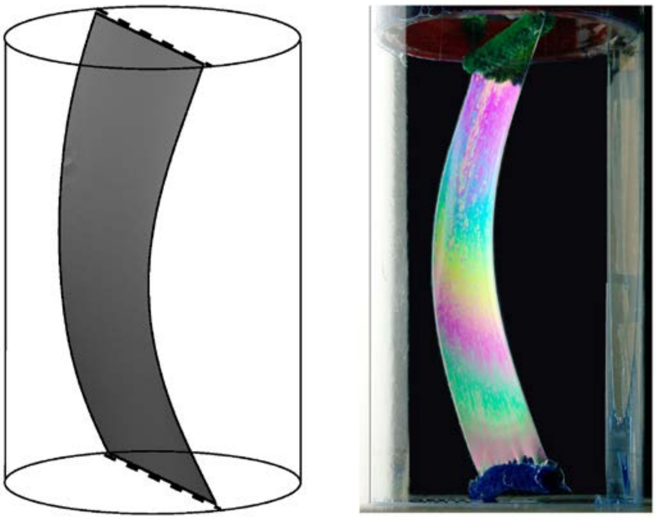

Fig. 1 The shape of a single stretched film just after the instability is triggered, in simulation (left) and experiment (right).

Impact of the surface rheology on the kinetics of Ostwald ripening of foams stabilized with saponins

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Saponins are a class of natural surfactants found in more than 500 plant species, which are known to have very good foaming properties. They consist of flat hydrophobic head group (triterpenoid or steroid) with hydrophilic oligosaccharide chains. In previous articles [1] we studied the surface rheological behavior of saponin adsorption layers, subjected to steady or oscillatory shear deformation, which we have recently extended to include surface dilatation as well. Generally triterpenoids exhibited high modulus both in dilatation (E) and in shear (G) deformation, while steroids had moderate modulus in dilatation, and negligible modulus in shear. In this work we study the kinetics of Ostwald ripening (OR) [2] of foams stabilized by various saponins, with well-characterized surface rheological properties as motioned above. Our experimental results indicate that triterpenoid saponins where able significantly to inhibit the rate of OR, while the steroidal type of saponins have much less pronounced inhibitory effect, which seems to be in line with the findings from surface rheology experiments and in support of some of the OR models proposed in the literature. However when all the surface rheological data are combined and correlated with foam stability, it become clear that that for similar values of given surface rheological parameter (e.g. example surface dilatational or shear viscosity/elasticity) one can have foams with markedly different OR stability and vice versa, foams with same OR stability can be made with systems having markedly different surface rheological parameter. Thus it became clear that no clear correlation can be established between the rate of OR and the surface modulus in particular mode of deformation (shear or dilatational). The impact of other surface properties and phenomena on the rate of OR will be discussed, alongside with analysis of several literature proposed mechanism to control OR in liquid foams.

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Stabilization of W/O Emulsions by Hybrid Amphiphilic Polymers: Exploration of Emulsion Stability and Its Mechanism

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We have developed a hybrid amphiphilic polymer (AIM-FN) consisting of a silicone backbone modified with hydrocarbon chains and hydrolyzed silk peptides. AIM-FN is molecularly soluble neither in water nor in most of organic solvents, but is attractive with these solvents due to its amphiphilic nature. This property enables the polymer to form “an independent third phase” being located at a silicone oil/water interface (Fig 1), and hence, the emulsions are stabilized effectively based on a fundamentally distinguishable mechanism from the approach by conventional surfactants[1].

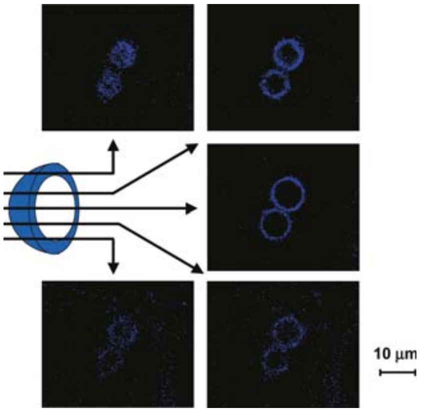

Fig 1 CLSM images of W/O emulsion droplets with fluorescence-labeled AIM-FN.

The size of the emulsion droplets prepared with AIM-FN is ca. 2 to 4 µm, independently on the composition in the stable water-in-oil (W/O) emulsion region[2]. This W/O emulsion has long kinetic stability: coalescence hardly takes place, although creaming and flocculation are operative. Thus, the water droplets in the emulsion can be redispersed by a weak energy input.

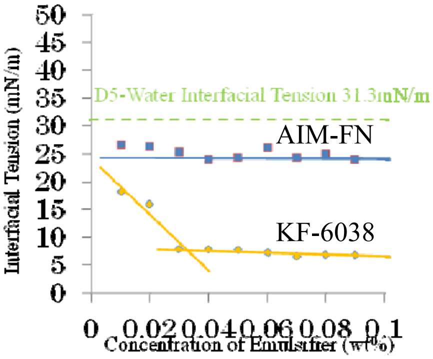

Fig 2. Change in the interfacial tension upon addition of AIM-FN or KF-6038 in the D5/water solution. The interfacial tension of D5/Water system is 31.5mN/m.

Unlike conventional surfactants, AIM-FN does not lower the interfacial tension between water and silicone oil (decametylcyclopentasiloxane, D5) at room temperature (Fig.2). The behavior seems like “pickering emulsion”, in which an interfacial active agent does not need to compensate the interfacial free energy to make the dispersed phase stable. We will bring a key outlook in terms of novel stabilization mechanism using the sustainable material.

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Acknowledgements:

We thank Seiwa Kasei for providing the hybrid amphiphilic material for us. A part of this work was supported by Japan Aerospace Exploration Agency (JAXA).

Effect of monoacylglycerides and polyglycerol esters of fatty acids on physical and sensory properties of aerated water-in-oil emulsions

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Incorporation of air/gas bubbles into (semi-)solid food products is well known. Examples of aerated food products include e.g. bread, cheese, ice cream, mousses, chocolate, protein shakes, whipped cream and cereals. While aeration of water-continuous compositions is quite well understood, aeration of oil-continuous systems received much less attention. Here we discuss fundamental aspects of aeration of w/o emulsions containing elevated (0.2-1.0 wt%) levels of emulsifiers compared to regular usage levels in margarines and spreads. We concentrated our research on w/o-promoting emulsifiers with low HLB values, such as monoacylglycerides (MAG) and polyglycerol esters of fatty acids (PGE). Experimental design included preparation of 40 wt% and 60 wt% w/o emulsions based on a triacylglyceride oil blend and aerated with nitrogen (0-35 vol% of gas phase in final compositions).

Rheology of aerated w/o emulsions was investigated at various temperatures in the interval between 5 and 35°C. Also, inversion of w/o emulsions under simulated oral conditions was quantified. Based on the experimental evidence we conclude that excessive amounts of emulsifiers with low/medium (3-7) HLB values have a profound effect on rheology, but to less extent on emulsion inversion and formation/stability of foam phase. Oral behavior of aerated emulsions was assessed by a small sensory panel (N=5), and results of this trial are summarized in Table 1. While compositions prepared with PGE, cis-unsaturated and saturated MAG exhibit negative sensory qualities (e.g., graininess and lack of consistency), aerated w/o emulsions made with elevated amounts of trans-unsaturated MAG have clearly superior sensory behavior. We attribute our observations to the partitioning of MAG and PGE in aerated w/o emulsions between oil-water and oil-gas interfaces. Excessive amounts of emulsifiers introduced to w/o emulsions prior to aeration lead to the increase of the relative amount of the emulsifier in the fat blend. As a result, properties of aerated emulsions will be influenced by both crystallization behavior of fat blends in the presence of emulsifiers and molecular properties of emulsifiers at gas-oil interfaces.

We conclude that trans-unsaturated MAG have outstanding effect on physical and sensory properties of aerated w/o emulsions compared to fully saturated and cis-unsaturated MAG, as well as PGE. The nature of the observed effect is not fully understood and can be linked to the peculiarities of fat crystallization in the presence of trans-unsaturated MAG, as well as with properties of the latter at gas-oil interfaces. Understanding of the mechanism of this phenomenon will be addressed in our future studies and should enable structural design of aerated spreads with desired consumer properties through the tailored use of selected emulsifiers.

Table 1: Sensory behavior of 60 wt% w/o emulsions aerated to 35 vol% of gas phase, formulated with an elevated dosage (1.0 wt%) of low/medium HLB emulsifiers.

Emulsifier	Sensory behavior
fully saturated MAG	too hard, grainy, sandy (poor)
trans-unsaturated MAG	soft, creamy (good)
cis-unsaturated MAG	very soft, bitter, watery (poor)
PGE	sticky, waxy (poor)

Foamability, foam stability, and foam structure of various types of milk

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Milk foams are colloidal systems formed by air bubbles, water, and surface active proteins. Not only the recent emerging growth in the consumption of cappuccino-style beverages revived the scientific interest in the foaming properties of milk. In the past, various studies have investigated milk-foam properties (Ref.1,2,3, and references therein) and interesting characteristics were reported. For example, whereas, the fomability of UHT skim milk and pasteurized skim milk was found to increase continuously with rising temperature from 5 to 80 °C, the fomability of pasteurized homogenized whole milk exhibits a strong anomaly around 25 °C (Ref. 1). In this work, the foamability and foam stability of different types of milk as determined by a fully automized foam-height measurement will be presented and compared to previous studies. The effect of temperature on fomability and the different kinetics in the foam-decay phase are investigated. As in previous studies, foam is generated by purging air through the liquid. In addition to this, foam is generated by stirring whereby different stirrer geometries are compared. Moreover, the foam-structure characterised by the bubble-size distribution and the total number of bubbles within a well-defined area was determined. In contrast to previous studies on the foam structure of milk, in this work the optical set-up of the foam-structure measuring device is based on the principle of total-light reflection guaranteeing sharp images of highest contrast (Fig.1). This, in combination with a digital image analysis has the great advantage that the foam structure is continuously monitored during the foaming and the foam-decay phase (Fig.1 right panel). As a result, a simultaneous and continuous observation of the total-foam volume and the foam structure during the foam-decay phase is possible. This provides valuable information about decay kinetics depending on temperature and / or type of milk.

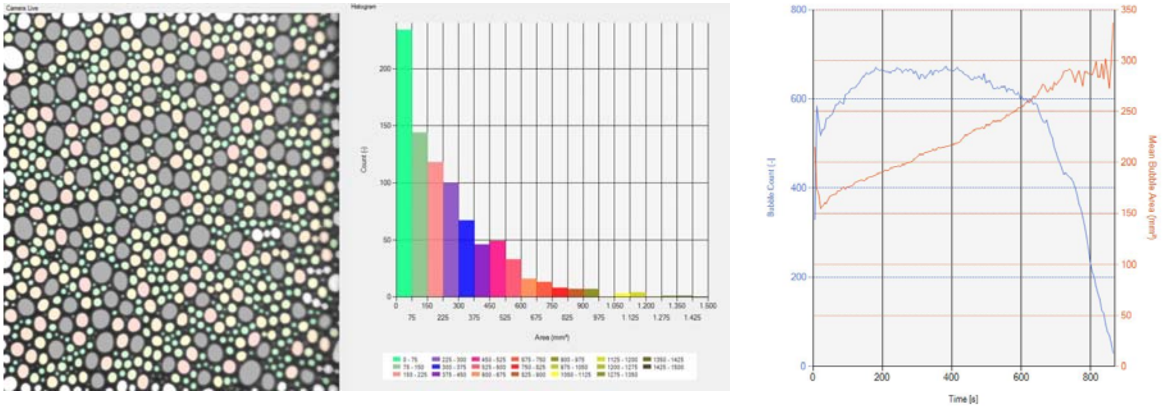

Fig. 1: Foam structure of UHT whole milk: Image (left) and bubble size distribution at 600 seconds after foaming (center). Time dependence of total bubble count and mean-bubble area (right)

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Stabilization of multiple emulsions using hydrocolloids and evaluation of their encapsulation efficiency by rheometry

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Over the last years, the interest of research and industry in food grade multiple emulsions has constantly been growing. This is mainly due to the fact that multiple emulsions offer interesting possibilities to encapsulate sensitive bioactive substances or can be used to reduce the fat content of food products. One of the crucial points in formulating and producing such emulsions is to ensure the stability of the emulsion's microstructure during shelf-life. Release of innermost droplets goes hand in hand with a loss of emulsion functionality. Bioactive substances could be exposed to harsh environmental conditions and fat reduced emulsions might lose their creamy mouthfeel. In order to avoid this, one current research focus is the development of new encapsulation systems for active substances in food and pharmaceutical emulsions. In this context, particularly natural or even organically produced materials are of interest. Citrus pectin is a suitable substance to form and stabilize multiple oil-in-water-in-oil (O/W/O) emulsions. This hydrocolloid exhibits surface active behavior to a satisfying extent and increases the viscosity of aqueous solutions. In emulsions, this can enhance stability by suppressing droplet movement and also coalescence which in turn leaves the microstructure of an emulsion unchanged. In order to evaluate the stability of the microstructure of multiple emulsions integrally, the encapsulation efficiency is mostly used. This term describes how much of a given substance or inner dispersed phase is still encapsulated after a certain amount of time or energy intake into the system during emulsification. However, measuring this quantity is still a challenge. Although there are several measurement methods available for water-in-oil-in-water emulsions, most of these cannot be applied to O/W/O emulsions. Rheometry is a promising tool to quantify the encapsulation efficiency of multiple O/W/O emulsions. A loss of encapsulated oil phase reduces the volume of encapsulating water phase and dilutes the continuous phase which leads to changes in the viscosity of the overall emulsion. In this presentation, we want to outline how hydrocolloids can be used to form and stabilize O/W/O emulsions. It will be demonstrated how the application of hydrocolloids can reduce the amount of conventional synthetic emulsifier employed. Rheological measurements regarding the encapsulation efficiency will be introduced and limits of this measurement technique will be discussed. Furthermore, measurements will underline the extraordinary encapsulation efficiency of the investigated formulations.

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Acknowledgements:

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Characteristics of spontaneously formed biocompatible nanoemulsions stabilized by ionic dicephalic-type surfactants

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In the recent years much effort has been made in the nanomedicine research to develop new effective and biocompatible nanocarriers for hydrophobic molecules having a colloidal phase as a key prerequisite for their effectiveness. Among these systems an important role is played by nanoemulsions which constitute transparent or translucent isotropic dispersions comprising water and/or oil nano-domains and coexisting in high kinetic equilibrium due to the presence of a surfactant layer at the oil/water interface. Those formulations can be fabricated using either high-energy or low-energy methods, but the latter offer advantages in terms of low cost, higher energy efficiency, and simplicity of implementation. Therefore, it can be seen that the influence of an appropriate surfactant on the long-term stability of designed nanosystems is very important [1-2].

The present work has been carried out to explore the potential to form spontaneously stable and nearly monodisperse oil-in-water (o/w) nanoemulsions of two recently synthesized ionic dicephalic-type surfactants, i.e., positively charged N,N-bis[3,3′-(trimethylammonio)propyl] dodecanamide dimethylsulphate, $C_{12}(TAPAMS)_2$ and anionic, disodium N-dodecyl iminodiacetate, $C_{12}(COONa)_2$ [2-3]. Initially, we examined by titration method the ternary phase diagrams of surfactant-oil-water (SOW) systems containing different ratios of $C_{12}(TAPAMS)_2$ or $C_{12}(COONa)_2$ as the surfactant (S), oleic acid or isopropyl myristate as the oil phase (O) and the water phase (W). Then, the obtained nanoemulsions were characterized by visual and microscopic observations (Cryo-TEM), the particle size and distribution (DLS) as well as ζ-potential measurements (Doppler electrophoresis), showing that the nanoemulsions' droplets have a nearly monodisperse size distribution (D_H <100nm, PDI<0.2) and spherical morphology. as well as a long-term stability. Oil composition, surfactant type, and surfactant-to-oil ratio were all found to influence the droplet size, charge and stability of the systems produced. Our results give new insights of the o/w nanoemulsions containing didephalic-type surfactants and may serve as guidelines for design and preparation of new nanoemulsion-based delivery systems for practical applications such as personal and household care products, drug delivery, particle synthesis, detergency and nanoparticle phase-transfer.

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Acknowledgements:

The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Technology (research related to $C_{12}(TAPAMS)_2$) and by the Wroclaw Research Center EIT+ under the project'Biotechnologies and advanced medical technologies'-BioMed (POIG 01.01.02-02-003/08-00) financed from the European Regional Development Fund Operational Programme Innovative Economy, 1.1.2 (research related to $C_{12}(COONa)_2$).

Double emulsion for encapsulating B12 vitamin

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Water-in-oil-in-water double emulsions are dispersions of an inverse emulsion in an aqueous continuous phase. These emulsions are interesting systems to encapsulate hydrophilic substances in the inner aqueous phase. Double emulsions enable a good protection of encapsulated agents against external environment, and a controlled release thereof. Despite their interest, they are still not widespread in industrial applications because of the difficulty to formulate stable systems. Indeed they require the presence of two antagonistic types of stabilizers: a more lipophilic surfactant to stabilize the inverse emulsion, and a more hydrophilic one to disperse the oil droplets in the aqueous phase.

Herein, we propose to study double emulsions stabilized by a polysaccharide or a protein. We determine the influence of both formulation and process parameters on the encapsulation rate just after emulsification as well as during storage. We build up a "stability map" evidencing the formulation regions where the capsules are stable or not. For non-stable systems, we identify the destabilization mechanisms and determine the kinetics of release combining several techniques (confocal microscopy, tensiometry, rheology, and UV-visible spectrometry).

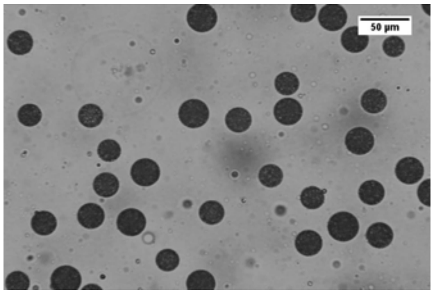

Fig. 1 Example of a water-in-oil-in water emulsion. The scale bar corresponds to 10µm

Generation of crystalline polyurethane foams using Lab-on-a-Chip techniques

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We show here how polyurethane (PU) foams with well-controlled polymer and structural properties can be generated using millifluidic Lab-on-a-Chip techniques. In this approach, the foam is created by injecting a gas and the liquid solutions at constant flow rate into a purpose-designed channel network of millimetric dimensions. This network is designed such that physical bubble blowing and homogeneous mixing of the chemicals form an integrated, continuous process. Chemistry and foam stability are adapted in a way which ensures that an initially liquid foam with equal-volume bubbles leaves the Lab-on-a-Chip. Within this foam, the bubbles have enough time to self-order into crystalline foam structures under gravity or confinement before solidifying in-situ. This approach provides explicit and simultaneous control over the chemistry, the foam density, the bubble size and the pore connectivity of the final foam via the flow rates of the different reactants. This currently unequalled control over the properties of the final PU foam is hoped to provide new experimental insight into their structure/property relationships and to open up new avenues for PU foam applications.

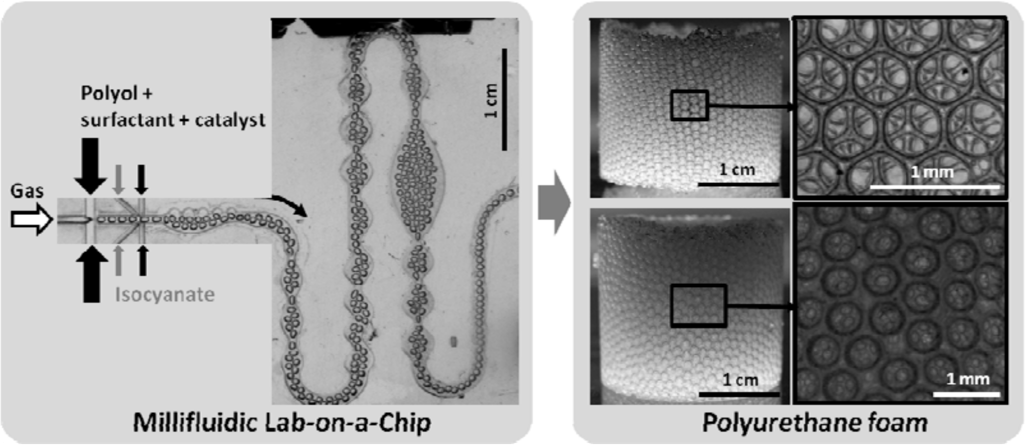

Fig. 1 Left: Example of a Lab-on-a-Chip used to generate equal-volume bubbles and to perform the flow-chemistry for on-chip generation of PU foams. Right: Examples of obtained fully polymerized PU foams.

Literature:

A. Testouri, M. Ranft, C. Honorez, N. Kaabeche, J. Ferbitz, D. Freidank, W. Drenckhan, "Generation of crystalline polyurethane foams using millifluidic Lab-on-a-Chip technologies", to appear in *Advanced Engineering Materials*

Double stimuli responsive O/W emulsions act as magnetic fluid and heat-induced gelator

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Magnetic fluids are colloidal liquids made of ferromagnetic nanoparticles (NPs), which become strongly magnetized in a magnetic field, and the fluids are of considerable interest because of their potential novel applications in several technological fields of nanoscience. To make high performance magnetic fluids, control of the magnetic NPs dispersibility is a vital issue. In this work, we synthesized highly dispersive magnetite nanoparticles (Fe_3O_4 NPs) using a long-chain amidoamine derivative (**Fig.1** : C18AA), and demonstrated that the aqueous dispersion has a magnetic fluid property. Further, we showed that the combination of Fe_3O_4 NPs and C18AA enable to prepare double stimuli responsive O/W emulsions which act as heat induced gelator and magnetic fluid.[1]

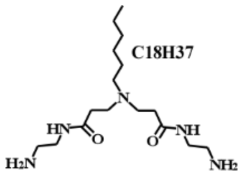

Fig.1 Molecular structure of long-chain amidoamine derivative (C18AA).

Synthesis of Fe_3O_4 NPs is as follows. 1 M aqueous solution of $FeCl_2$ was added into C18AA aqueous solution, and the mixture was stood for 24 h at room temperature without stirring. Double stimuli responsive O/W emulsions were prepared by adding Fe_3O_4 NPs obtained at [C18AA]=200 mM into O/W emulsions consisting of C18AA, toluene and aqueous LiCl. The resultant Fe_3O_4 NPs were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and zeta potential analyzer.

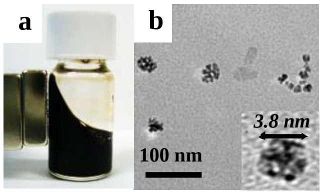

Fig.2 (a)Fe_3O_4 nanoparticles are well dispersed and attracted to a neodymium magnet as magnetic fluid. (b)TEM images of Fe_3O_4 nanoparticles obtained at [C18AA]=200 mM .

Fe_3O_4 NPs obtained at [C18AA]>200 mM were dispersed in water for a long time and the dispersion showed magnetic fluid property (**Fig.2a**), whereas Fe_3O_4 NPs prepared at a low concentration of C18AA rapidly precipitated, because the former and latter diameters were ~10 nm (**Fig.2b**) and ~60 nm, respectively. Obviously, this result indicated that the size control of Fe_3O_4 NPs is essential for preparing magnetic fluid. Further, the presence of C18AA brought about a shift of zero-point of charge (ZPC) of Fe_3O_4 NPs from pH7 to pH11, as shown in **Fig.3**, which is probably caused by the adsorption of C18AA onto Fe_3O_4 NPs. Consequently, the dispersion of Fe_3O_4 NPs capped with C18AA had a high resistance against pH.

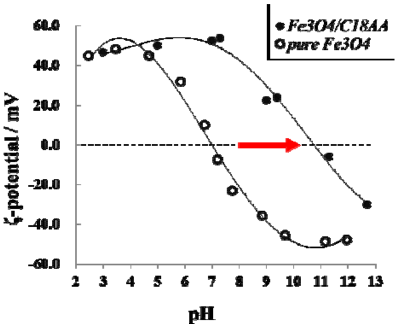

Fig.3 Zeta potential of Fe_3O_4 NPs as a function of pH.

Interestingly, we can easily prepare magnetic fluids of Fe_3O_4 NPs dispersed in toluene, instead of water. Apparently, this fact leads to the result that Fe_3O_4 NPs can be easily dispersed in O/W emulsions of C18AA/toluene/aqueous LiCl. The O/W emulsions containing Fe_3O_4 NPs were acted as both magnetic fluid and heat-induced gelator. This enable us to give an opportunity to hold the shape of the dispersion by heating, after we made a desirable shape by magnetic field.

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Demulsification Behavior ofO/WEmulsions Using aPhotoresponsive Cationic Surfactant

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Stimuli-responsive surfactantshaveinterfacial properties that can be controlledby external stimulisuch as pH, temperature, electricity,and light. In particular, the useof light as the external stimuli isveryattractive because of its lowcost, lowenergy consumption, andease of use.Photoinduced demulsification of O/W emulsions, using a photoresponsive gemini surfactant,havebeen successfully accomplished. The phenomenon results fromcoalescence of the emulsion dropletswith photoisomerization of the surfactant molecules at the O/W interface because of UV lightirradiation.In this study, a photoresponsive cationic surfactant, (**AZTMA, Figure 1**)containing an azobenzene group,was applied to abinary mixture of *n*-octane and water, and the influence of UV light irradiation on the resultant stable emulsionswas examined.

When mixtures of the*trans*-AZTMA aqueous solution and *n*-octane were homogenized for 5 min at 10,000 rpm, stable emulsions were obtained in a region of specific weight fractions.The emulsions were stable for over a week and found,by dilution method,to be of the oilinwater (O/W)-type.UV light irradiation of the stable O/W emulsions promoted *cis* isomerization of *trans*-AZTMA; however, nophase-separation of the emulsions was observed.

Next, the influence of UV light irradiation on stable emulsions consisting of *n*-octane and aqueous AZTMA/SDS solutionswas investigated. Aqueous *trans*-AZTMA/SDS solutions and *n*-octane were homogenized tothe same condition to obtain the corresponding emulsions. UV light irradiation of the stable O/W emulsions led to the coalescence of oildroplets in the emulsions, i.e. demulsification, and then the oil and water phases were separated (**Figure 2**). These results suggest that*cis* isomerization of the *trans*-AZTMA molecules with UV light irradiationbrought about the exposure of the*n*-octane/water interface in the emulsions. Consequently, the stability of the obtained emulsions was drastically decreasedby UV light irradiation in this novel system.

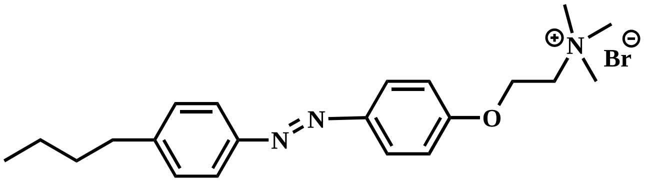

Figure 1: Chemical structure of AZTMA.

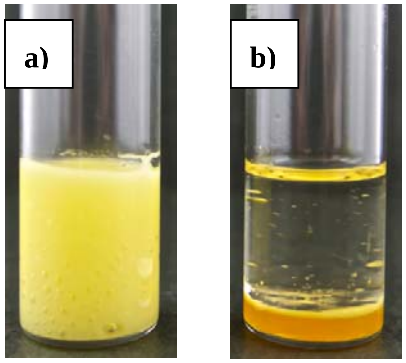

Figure 2: *n*-octane/(*trans*-AZTMA/SDS)aqueoussolution system: a)stable emulsion before UV irradiation; b) phase separation after UV irradiation.

In situ monitoring of the droplet size distribution of o/w emulsion during the emulsification process

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The aim of the study was to investigate the evolution of the droplet size distribution *in situ* inside the stirred emulsification vessel. An *in situ* video probe has been designed in order to record images of the droplet in line during the emulsification process. The expected outcome is a better understanding of the emulsion droplets fragmentation and re-coalescence as a function of time, and to disclose the influence of the main parameters that control the emulsification such as the type of stirrer, the stirring speed and the emulsifier concentration.

The size distribution of droplets oil (molten ethylene glycol di-stearate at 70°C) stabilized by the (tricosaethylene glycol dodecyl ether) surfactant was measured using an optical probe EZ Probe D25 L220® designed for *in situ* monitoring inside stirred vessels [1] (Fig. 1). Mechanical stirring was ensured by either a four blades propeller or Rushton propeller. Recorded frames were treated off line after the recording in order to extract the droplet size distributions (DSD). The Hough circular transform appeared a suitable method for the automatic treatment of pictures since it allows considering several thousands of droplets for building a statistically relevant DSD (Fig. 2). The droplet sizes could be measured in the range 10 µm - 100 µm; the relative accuracy on the droplet number average diameter was 10 %. The DSD was finally obtained as a function of time, showing the different transient stages before a stationary regime was reached where the fragmentation and re-coalescence rates are the same (Fig. 3). The measured sizes were in agreement with the characteristic size of the smallest eddies of the turbulent flow calculated according to Kolmogoroff.

The specific power input of stirring was the main parameter acting on the reduction of the mean droplet diameter and of the width of the DSD owing to its action on the droplet break up mechanism. The surfactant concentration was a parameter of secondary relevance on the DSD probably due to the reduction of the coalescence rate and to a faster stabilization of the o/w interface. The use of a flat blade propeller instead of a Rushton turbine was preferred for the production of a narrower DSD. Finally the time required to reach the stationary regime was found higher by a factor of 3 to 4 than predicted in the literature.

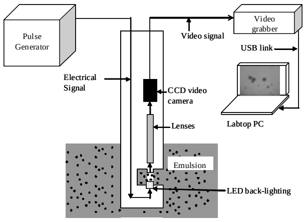

Fig 1: Scheme of the EZ Probe D25 L220®

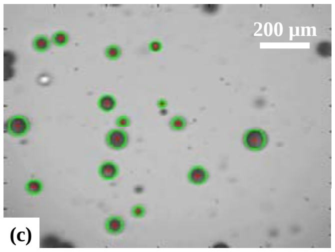

Fig 2: Picture of an emulsion analyzed using the Hough circular transform

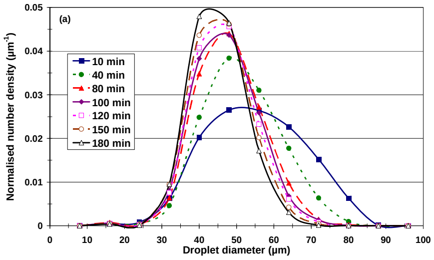

Fig 3: Droplet size distribution asa function of emulsification time

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Crystallization-in-emulsion process: in situ video monitoring of the evolution of droplet and particle size distributions

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Crystallization of an emulsified melt is a common process taking place in the manufacture of several fat emulsions for food and cosmetic applications [1]. Several fundamental phenomena are still open issues such as the mechanism of nucleation in confined media, the competition between nucleation and growth with respect to supercooling conditions, the role of the interfacial species (surfactants) on crystallization events. The aim of this study was to get more insight into the mechanisms occurring upon cooling molten droplets dispersed in stirred vessel.

A molten organic model material (ethylene glycol distearate) was emulsified in water in the presence of an emulsifier (tricosaethylene glycol dodecyl ether) leading to an o/w emulsion. The stirring conditions and amount of emulsifier allowed the control of the droplet size distribution [2]. The emulsion was progressively converted into a suspension of solid particles upon cooling. The hydrophilic emulsifier avoided the inversion of the emulsion in the whole temperature range. An optical probe EZ Probe D25 L220® was designed for *in situ* monitoring of the transition from droplets to particles under stirring into the vessel [3]. Since crystallization in a droplet took less than one tenth of a second, the visualized items appeared either totally liquid or wholly crystallized. Droplet and particle diameters were measured on captured frames (Fig. 1).

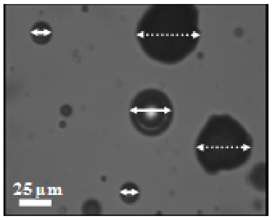

Fig 1: Frames captured at 50°C - droplet diameter (solid arrow); particle diameter (dotted arrow)

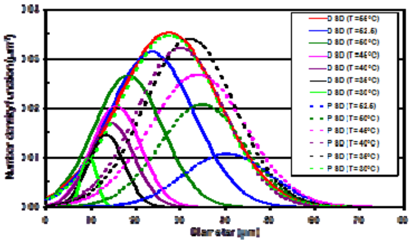

Fig 2: DSD and PSD evolution with the temperature

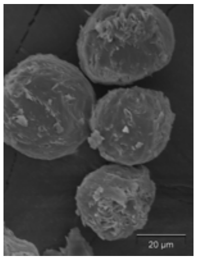

Fig 3: SEM images of final particles

Fig 2 displays an example of the evolution of the droplet size distribution (DSD) and particle size distribution (PSD) during a cooling profile of 1°C.h^{-1}. The DSD slowly shifted to smaller sizes and the distribution width progressively became narrower. In the same time the PSD progressively moved to smaller sizes and the distribution became broader. Indeed the induction time of primary nucleation depends on the droplet size: the larger droplets first nucleated with a reduced induction time at low supercooling, and a higher supercooling was necessary to crystallize the smaller ones. There was also a close match between the initial DSD (at 55°C) and the final PSD (at 30°C) when almost all the droplets had been solidified (Fig. 2). A qualitative examination of the particles under SEM showed rounded dense particles which size corresponded to the initial droplets (Fig. 3) showing that each droplet was converted into one solid particle.

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Efficient control of the rheological and surface properties by using C8-C18 fatty acids as cosurfactants

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Systematic experimental study is performed about the effects of chain length (varied between C8 and C18) and concentration of fatty acids (FAc), used as cosurfactants to the mixture of the anionic surfactant SLES and the zwiterionic surfactant CAPB. The following properties are studied: bulk viscosity of the concentrated solutions (10 wt % surfactants), and dynamic and equilibrium surface tensions, surface modulus, and foam rheological properties for the diluted foaming solutions (0.5 wt % surfactants). The obtained results show that C8-C10 FAc induce formation of worm-like micelles in the concentrated surfactant solutions, which leads to transformation of these solutions into visco-elastic fluids with very high apparent viscosity, see Fig. 1. The same FAc shorten the characteristic adsorption time of the diluted solutions by more than 10 times. In contrast, C14-C18 FAc have small effect on the viscosity of the concentrated solutions, but increase the surface modulus above 350 mN/m which leads to higher friction inside sheared foams and to much smaller bubbles in the formed foams. The intermediate chain C12 FAc combines some of the properties seen with C10 FAc and other properties seen with C14 FAc. These results clearly demonstrate how appropriate cosurfactants can be used for efficient control of the rheological properties of concentrated surfactant solutions and some of the foam attributes.

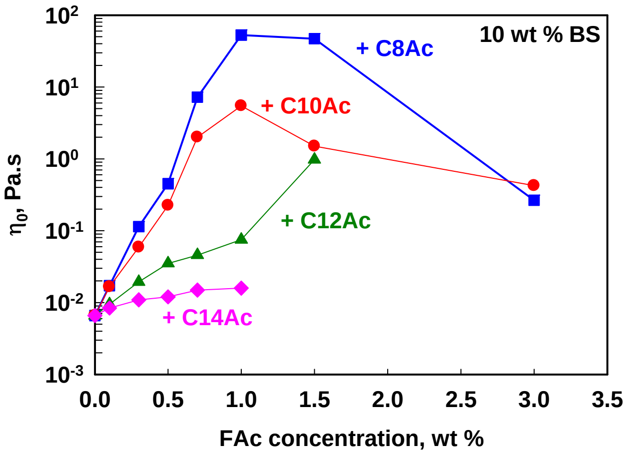

Figure 1. Apparent shear viscosity as a function of fatty acid concentration, in 10 wt % BS solution for C8Ac (blue squares), C10Ac (red circles), C12Ac (green triangles), and C14Ac (pink diamonds).

Acknowledgements: The authors are grateful to Dr. Konstantin Golemanov from Sofia University for the useful discussions. This study is supported by the Unilever R&D Center in Trumbull, USA. The study is under the umbrella of the FP7 European project “Beyond Everest” and the COST action MP1106 “Smart and green interfaces”.

Surface and foam properties of SLES + CAPB + fatty acid mixtures: Effect of pH for C12-C16 acids

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Recently we showed that triple surfactant mixtures, comprising the anionic surfactant SLES, zwitterionic surfactant CAPB and long-chain fatty acid (FAc), possess very high surface modulus which can be used to modify the dynamic properties of foams.[1] In the current study[2] we investigate the effects of several factors on the surface and foam properties, for such triple surfactant mixtures. The factors studied are: (1) chain length of fatty acid; (2) fatty acid concentration; (3) pH; (4) presence of glycerol in the aqueous solution. We observed that increasing FAc concentration above threshold value, leads to significant decrease of surface tension, increase of surface modulus, decrease of mean bubble size in sheared foams, and strong increase of the inside-foam friction and foam-wall friction. The main role of FAc is to induce a surface phase transition, leading to formation of surface condensed phase in the mixed adsorption layer. For all systems studied, the increase of pH above a certain transitional value leads to a sharp increase of surface tension and decrease of surface dilatational modulus, which is accompanied with a decrease in the inside-foam and foam-wall viscous friction (see Fig.1). The transitional pH value varies between 8 and 11, and increases with the FAc chain length. The increase of pH causes ionization of the FAc molecules – the latter start to behave as usual anionic surfactant without forming surface condensed phase. These results clarify the compositional domain, in which the FAc can be used for control of surface and foam properties in such surfactant mixtures.

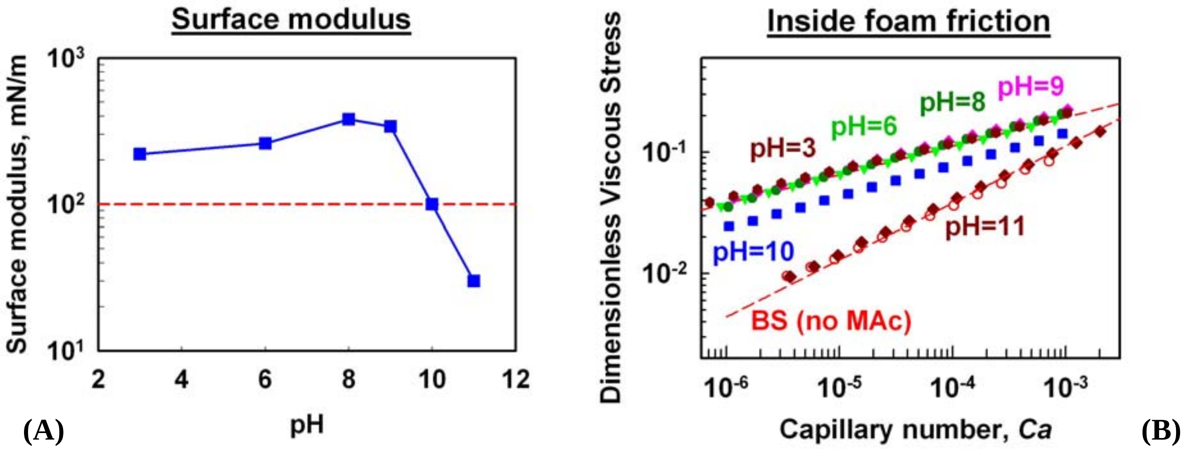

Fig.1 (A) Surface dilatational modulus as a function of solutions pH, (B) Dimensionless viscous stress vs. Capillary number for BS+FAc system at different pH.

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Construction of Janus Structure by Janus Emulsion

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Janus Particles (JPs), with different composition or morphology as its hemispheres, have special properties of isotropic and asymmetry. They have been used as colloidal surfactants, chemical and biological sensors, display materials of the electronic paper, and self-motile colloidal particles.[1] The Janus emulsions received an intense attention after the introduction of the microfluidics method[2] and the number of applications multiplied rapidly[3,4]. However, in spite of this remarkable progress, the method suffers from the inevitable volume limitations, preventing a general commercial application. This limitation was removed by the introduction of the bulk process [5,6] to prepare well defined Janus emulsions. In the present report, the structure of the emulsion droplets including the size distribution and the ratio of the two hemispheres were controlled by the composition of emulsion, the energy of emulsification, and the methods of phase inversion temperature (PIT) and phase inversion concentration (PIC). Based on the fundamental investigations on the Janus emulsion, the Janus materials will be synthesized by replacing the oil phases with polymerizable monomers.

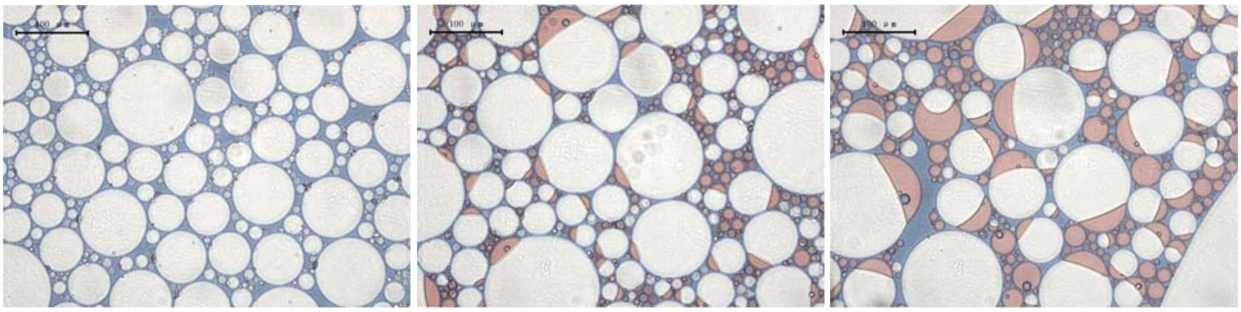

Fig. 1 The microscope images of janus emulsion in the system of methacrylate/silicon oil/Tween $80_{(aq)}$ with increasing molar ratio of methacrylate to silicon oil.

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How Long Does a Soap Film Last During Generation?

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Soap films are well-known for being unstable entities, with lifetimes ranging from less than a second to several hours. However, the mechanism leading to the rupture of a vertical thin film during its generation from a surfactant solution is still poorly understood.

We have built an experiment, in which we measure the life time of a film during its generation. We showed that the faster the film is pulled, the longer the film and the shorter its lifetime. It turns out that to understand this feature, it is necessary to determine first the entire shape of the liquid film [1].

We founded that the film is made of two parts: the bottom part is of uniform and stationary thickness, well described by the Frankel's law [2]; whereas in the top part, the film thins until a black film appears near the frame upper boundary. We showed that the lifetime is controled by the drainage of the upper zone due to film deformation.

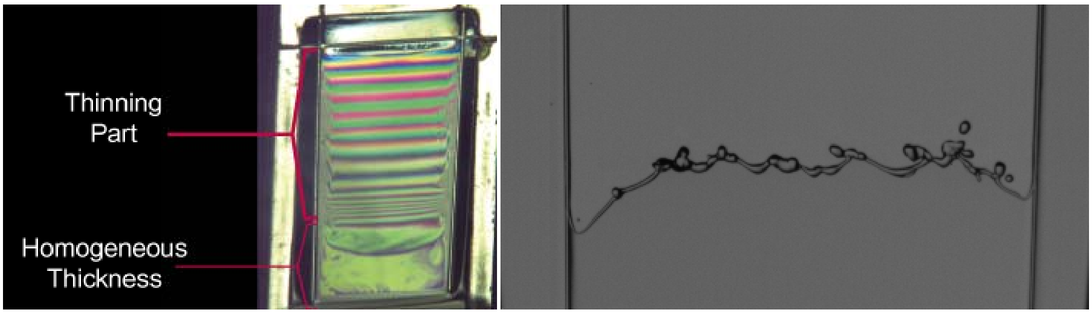

Fig. 1 (a) Photography of a film during vertical entrainment and just before spontaneous rupture. It is made of a bottom part of uniform and stationary thickness and a thinning part where a black film appears.(b) Photography of the film bursting during its generation.

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Does Poloxamer 188 Improve the Surface Characteristics of Inhibited by Albumin Exogenous Surfactant Preparations?

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In patients with proven alveolar dysfunction the concentration of albumin in the alveolar fluid is significantly increased leading to inability of the lung surfactant (LS) to spread effectively at the air/water interface. LS inactivation can be prevented by amphiphilic polymers like Poloxamer 188 (P188) due to incorporation into lipid bilayers, either strengthening the plasma membrane against wounding or "patching" injured cells.

Poloxamers are amphiphilic copolymers capable of interacting with biological membranes. Poloxamer P188 ($PEO_{75}PPO_{31}PEO_{75}$ - hydrophilic polyethylene oxide PEO, hydrophobic polypropylene oxide PPO and hydrophilic polyethylene oxide PEO) is shown to have membrane sealing and repairing properties on skeletal muscle cells, cardiac myocytes, neurons, fibroblasts, etc. [1-4]. Moreover, it was found that P188 facilitates plasma membrane repair in alveolus resident cells, which are identified in human and experimental acute respiratory distress syndrome models [5].

Based on the literature data regarding the sealing effect of the poloxamer in the present work the effects of P188 on inhibited with serum albumin exogenous surfactant preparations (ESPs) were studied. By the pending drop method, which uses the Axisymmetric Drop Shape Analysis the equilibrium surface tension (γ_{eq}, mN/m), and the dynamic surface characteristics, maximal (γ_{max}, mN/m) and minimal (γ_{min}, mN/m) surface tension and the hysteresis curves shape of pure ESPs, mixed ESPs+albumin before, and after the addition of P188 were observed. In addition, by Dynamic light scattering analysis the particle size distribution into dispersions of ESPs, ESPs+albumin before, and after the addition of the Poloxamer was measured. Our preliminary results showed that the addition of P188 to ESPs+albumin resulted in increasing the inhibitory effect of albumin most probably due to its ability to "squeeze out" from the monolayer dragging out surface active components from ESPs at low surface tension values. These results should be considered in clinical practice in treatment of respiratory dysfunctions with unknown etiology.

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Different Time Scales in Relaxation of Spherical and Cylindrical Micelles According to the Becker-Döring Kinetic Equation

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Formation of micelles is a striking example of self-assembly in solutions with surfactant molecules. At smaller surfactant concentration, the master kinetic equation for micellization is the Becker-Döring kinetic equation [1-4] assuming that all transitions between micelles are realized through a chain of captures and emissions of single surfactant molecules. There are two forms of the Becker-Döring kinetic equation, discrete and continuous. The continuous form is justified for relatively large micelles and can be reduced to the Fokker–Planck differential equation in partial derivatives. For relaxation of spherical and cylindrical micelles, the analytical solution of this equation showed [1-3] an existence of hierarchical set of the specific times of fast and slow relaxation corresponding to different relaxation modes. In the case of coexisting spherical and cylindrical micelles, the spectrum of times and family of the modes appeared to be considerably richer. The theory predicted [3] here four different time scales, where two scales characterize fast relaxation and other two refer to slow relaxation. However the analytical theory has internal approximations, requires some additional model simplifications and is restricted in application to surfactant concentrations close and above the critical micelle concentration. The goal of this report is to bring the results of direct numerical analysis of micellization and relaxation in solution with spherical and cylindrical micelles developed on the basis of a discrete form of the Becker-Döring kinetic equation with using the droplet model for spherical aggregates [2-4] and the linear model for the cylindrical micelles [5]. These results are free of many shortcomings of the continuous form of the kinetic equation, but nevertheless confirm many predictions of the analytical theory. The discrete form of the Becker-Döring kinetic equation allowed us to follow the very initial stages of micellization and relaxation, where only the aggregates with smallest aggregation numbers play a role, and to study the micellization in vicinity of the first and second critical micelle concentrations. All time scales and modes of micellar relaxation in their dependence on equilibrium monomer concentration have been analyzed.

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Self-assembly of three-antennary oligoglycines in aqueous media and at the solution/air interface

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The self-assembly of three-antennary oligoglycines in the bulk of aqueous media and their adsorption at the solution/air interface are investigated.

These oligomers are able to form intra- and inter-molecular hydrogen bonds which leads to the formation of nanoplatforms – the so-called tectomers. The research of Bolvin et al. [1,2] shows that the three-antennary oligoglycines can form a monolayer, as well as a bilayer on mica surface. The methods of Profile Analysis Tensiometry, Microinterferometric technique of Scheludko-Exerowa are used in our research.

Being non-toxic, these oligoglycines may have a significant potential for applications in the medicine, for water purification, etc.

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Polyelectrolytes adsorbed onto oppositely charged lipid monolayers – influence of electrostatic forces

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Polyelectrolytes in dilute solutions (10^{-5} mMol/L) adsorb in a two-dimensional lamellar phase to oppositely charged lipid monolayers at the air/water interface.[1] To investigate the influence the electrostatic interaction, either the line charge density of the polymer (a statistic copolymer with 90% and 50% charged monomers) or the surface charge of the monolayer (mixtures between charged and uncharged lipids) is reduced.

Using Grazing Incidence X-ray diffraction, we observed the two-dimensional lamellar phase of negatively charged polyelectrolytes adsorbed to positively charged surfaces [1]. As Fig. 1 shows, the chain separation can be either increased (by decreasing the surface charge) or decreased (by decreasing the line charge density). However, non-electrostatic forces influence both the exact separation of the polyelectrolyte chains and the isotherms. If the surface charge or the linear charge density is to low, then the polyelectrolytes adsorb in a flatly disordered state as evidenced with X-ray reflectivity. We suggest that a strong electrostatic force is a necessary condition for the two-dimensional lamellar phase.

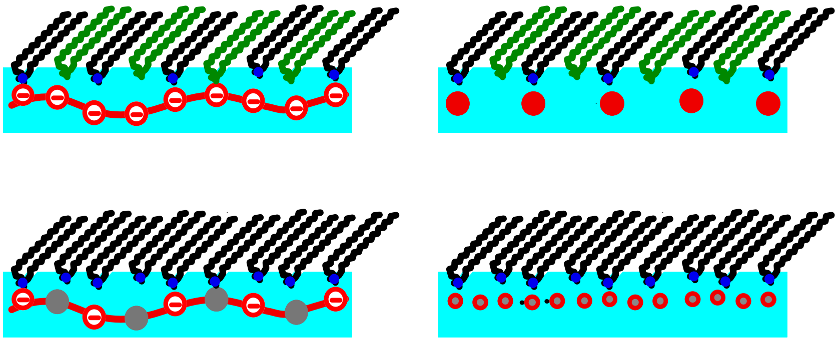

Fig. 1 Scheme of adsorbed polyelectrolytes in the two-dimensional lamellar phase below a lipid monolayer. Top: The surface charge is reduced by mixing charged and neutral lipids. Left is shown the view along an adsorbed chain and right the view perpendicular to the adsorbed polyelectrolyte chains.. Bottom: The line charge density is reduced by a statistical copolymer.

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Acknowledgements:

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Bending elasticity of lipid bilayers at low pH values of the surrounding aqueous solutions

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The extensive research on the pH influence on the elastic properties of lipid membranes [1-3] is contributing to the understanding of its impact on processes in biological cells, which are intimately related to the membrane bending elasticity [4,5]. The stability, morphology and mechanical properties of charged lipid membranes were studied using phase-contrast and fluorescence microscopy of giant lipid vesicles in aqueous solutions of sucrose with controlled ionic strength (0.01 M NaCl) and high acidity (pH < 5). A coexistence of two structural phases was observed in stearoyl oleoyl phosphatidylcholine (SOPC) membranes containing more than 10 mol% of dioleoyl phosphatidylserine (DOPS) at temperatures below 29˚C. Flicker spectroscopy of quasispherical vesicles with homogeneous liquid membranes was applied for the measurement of their bending modulus. Experimental results are reported and discussed about the bending rigidity of SOPC bilayers containing various concentrations of DOPS.

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Preparation and characterization of liposomal-pegilated calix[4]arenes nanoparticles as drug delivery systems for curcumin

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Curcumin, the constituent of Curcuma longa, is considered a very promising anticancer agent due to its potent and pleiotropic antineoplastic activity and low nonspecific toxicity to normal cells (1). However the clinical realization of its potential has been limited due to its poor aqueous solubility (11ng/ml) and very low systemic bioavailability. A possible aproach to overcome these limitations is the design of nanosized vechicles of curcumin.

The present work reports the preparation, characterization and in vitro evaluation of antineoplastic activity of curcumin loaded calixarenes-in liposomes nanoparticles. The hydrophobic properties of curcumin allow it to be incorporated into the liposomal bilayer, but the amount of the incorporated drug is limited in terms of drug to phospholipid ratio. In order to increase the entrapment capacity of curcumin into the liposomes we encapsulate calixarene-solubilized curcumin within the liposomes' aqueous cavity.

The pegilated tert-butylcalix[4]arenes (PEG-CX-4s) have been synthesized by anionic polymerization of ethylene oxide and proved to be practically non-hemolytic and devoid of intrinsic cytotoxic and immune modulating activity (2). By forming water soluble complexes the PEG-CX-4 proved to drastically increase the water solubility of curcumin from 11 ng/ml up to 100μg/ml. This ca. 10^4 fold increase in aqueous solubility of curcumin results 1,5 fold increase of entrapment capacity of curcumin into liposomal-PEG-CX-NPs as compared with conventional (PEG-CX-4s free) liposomes. Both formulations-conventional and PEG-CX-4s-loaded curcumin liposomes are characterized with high citotocix activity against Kg-1 and RPMI-8226 human tumor cell lines with IC_{50} values 2,19 and 1,59 μmol/L respectively. Thus on the grounds of the excellent *in vitro* biocompatibility profile and the favorable physicochemical and drug loading characteristics of the tested liposomal nanoparticles, and their ability to retain the instirsnic pharmacological properties of encapsulated drug they could be considered promising drug delivery platforms for lipophilic curcumin.

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Surface rheology of adsorption layers and foam film drainage kinetics of aqueous solutions of hexadecyltrimethylammonium chloride

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The properties of adsorption layers and foam film drainage for aqueous solutions of hexadecyltrimethylammonium chloride are studied at two different salt concentrations 0.1 mol/l NaCl and 0.5 mol/l NaCl. Dynamic surface tension and viscoelastic properties in frequency range 0.005- 0.2 Hz are conducted using PAT-1 (profile analyser tensiometry). Foam film drainage kinetics is studied using microinterferometric technique of Sheludko-Exerowa. We found a good correlation between plateau portions of the surface tension isotherms, the maxima in dilatational elasticity vs. surfactant concentration and the initial slowdown in film drainage. Peculiarities in adsorption layer properties are related also to the probability for the formation of black spots in foam films. These results help to understand better the important role that adsorption layer properties play in foam film drainage and stability.

Nanoparticle Agglomeration in a Flow Processing System

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Having arisen from basic research, nanoparticles today are found in many research and industrial applications. Their synthesis and processing can take place in liquid dispersion. During their lifetime, the particles often form agglomerates.This may be unwanted agglomeration due to ageing, or a consequence of deliberately removing the solvent in processing. For particle based functional materials, agglomerate morphologies affect their interactions and influence material properties. We are interested in tuning material properties by controlling agglomerate morphologies. Despite the ubiquity of agglomeration, the basic morphology-determining mechanisms are only understood for special cases. Recent results show that for sterically stabilized gold nanoparticles (An NPs), agglomeration is governed by the interactions of the stabilizing ligand layers (1.). These interactions depend on the solubility and the process temperature. By adjusting these parameters, we were able to switch the structure of the grown agglomerates from disordered, non-crystalline structures to close-packed supercrystals.

In a typical agglomeration experiment, the NP dispersion and an agglomeration agent are prepared in separate vessels and then mixed. This results in reproducibility problems due to mixing and sedimentation issues, and allows only transient measurement of agglomeration states. Here we show how equivalent experiments can be performed in a flow processing system, but with improved reproducibility and steady state observation of agglomerates. The system and UV/Vis absorbance spectra of aqueous Au NPs precipitated with dilute HCl averaged over one to several minutes are shown in Fig. 1. It is shown that we can measure reliable data with tightly controlled parameters. By adjusting flow ratios of gold dispersion and acid, we can observe the influence of concentration on the agglomerating sample, all in a single experiment (Fig. 1). It is intuitively clear that higher acid concentrations accelerate the agglomeration process. By varying total flow speed it is possible to observe different sample ages in a single experiment. The spectra show a nonlinear time dependence. A simple model allows comparisons to batch measurements. This reveals a surprising match between spectra measured in flow and in a cuvette.

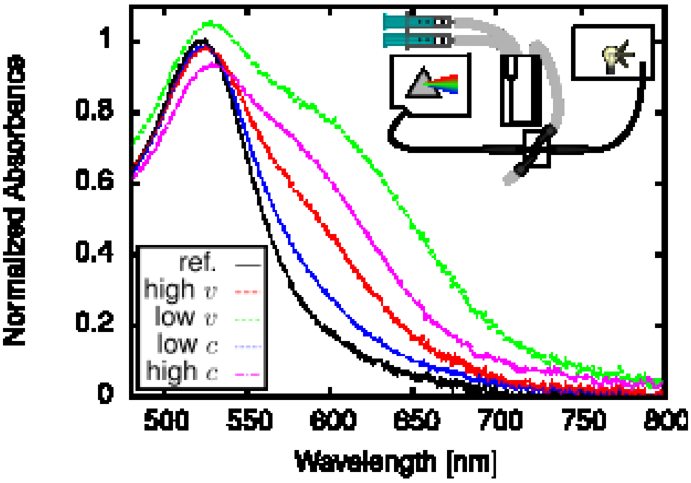

Fig. 1 UV/Vis absorbance spectra for agglomerating aqueous Au NPs. Black: pure particles; colored: agglomerates measured at higher and lower flow speeds and concentrations respectively. Inset shows schematic of the setup.

Premicellar concept: Foam films drainage properties and adsorption layers

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Premicellar concept arised to explain the remarkable concentration coincidence of the foam film drainage peculiarities and the kink and plateau portions of the surface tension isotherms in the case of the anionic surfactants. Its assumption is that amphiphilic structures (premicelles) exist in the initial surfactant solutions and influence the drainage properties of the mickroskopic foam films and the properties of the adsorption layers. The purpose of this study is to answer the question if the premicellar concept is valid only for the anionic surfactants or it is universal and can be used for cathionactive and non-ionic surfactants. These results are importent beceause they make posiible by using the two types experimental technic (microinterferometric and adsorption) to indicate the presence of amphiphilic nanostructures in the aqueous solution of surfactants.

Acknowledgements:

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Supercritical CO_2 extract from strawberry seeds as a valuable component for mild washing composition

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Fragaria ananassa L. commonly known as strawberry is widely cultivated and valued plant providing the sensory-rich fruits [1]. Strawberry fruit seeds, waste material from vegetables & fruits processing industry, are the source of rich in essential fatty acids oil [2]. The oil is usually obtained by cold pressing process and is used in the food industry. Because of rich chemical composition [2,3] (triglycerides of linoleic and linolenic acid, tocopherols, phytosterols, antioxidants) the strawberry oil could be a valuable raw material for cosmetic products.

The aim of the work was an elaboration of mild washing compositions, containing strawberry oil as a moisturizing and skin softening ingredient. Series of the products containing mild surfactants (sulfosuccinates, sarcosinates, betaines, glucoside alkyl ethers) and different amount of the oil (0,5 up to 5,0%) were obtained. The strawberry seeds oil obtained by supercritical CO_2 extraction was purchased from Fertilizer Research Institute in Puławy, Poland.

The physicochemical and rheological properties of the cosmetics were studied. The foam ability, foam durability index, surface tension, wettability, pH and reological properties were determined. Additionally, for the selected products, the skin conditioning properties were investigated.

The result obtained showed that the strawberry oil could successfully be used in formulation of washing composition. The prepared formulations exhibit the high stability and good user properties.

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Acknowledgements:

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Molecular dynamics simulations reproduce and explain the high affinity of triflate ion to the dodecyltrimethylammonium micellar interface

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Dodecyltrimethylammonium (DTA) micelles with trifluoromethanesulfonate (triflate, Tf) as counterion (DTATf) are rigid and ordered disk-like aggregates. These properties are different from those observed in other DTA-based micelles, such as DTA-bromide (DTAB) and are related with the small degree of counterion dissociation [1]. We performed molecular dynamics (MD) simulations of DTATf and DTAB aggregates to investigate the dynamics of the counterions at the micellar interface. We have found that Tf is highly associated to the micellar interface with a preferential orientation. The tight interfacial binding of Tf was related to a favourable electrostatic interaction between the DTA headgroup and the $–SO_3^-$ group. Also, a non-electrostatic interaction between the tail of the monomers and the $–CF_3$ group of the triflate induced the preferential orientation of the counterion at the interface.

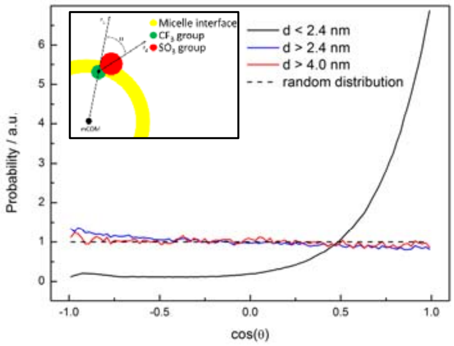

Figure 1. Probability distribution of cos(θ) of r_1 and r_2 (see text).

The probability distribution (PD) of the cosine of the angle θ formed between the vector pointing from $–CF_3$ to $-SO_3^-$ (r_1) and the vector pointing from the micellar center of mass (mCOM) to $–CF_3$ in Tf (r_2) is shown in Figure 1.The PD were calculated for different distances from the mCOM. For Tf at the micellar interface (d < 2.4 nm) the value of PD increased as the angle between the two vectors approached zero ($\cos(\theta) = 1$). These results were consistent with a preferential orientation of Tf at the interface. The orientation of Tf vanished as the distance from mCOM increased (d > 2.4 nm) and the distribution was random for Tf located at the *bulk* (d > 4.0 nm).

Comparing the DTATf and the DTAB systems, one readily notes that the electrostatic interaction between Tf and DTA is almost four times the corresponding energy in DTAB (Fig 2). Also, a significant Lennard-Jones interaction between DTA and the counterion was observed in DTATf, which was absent in DTAB.

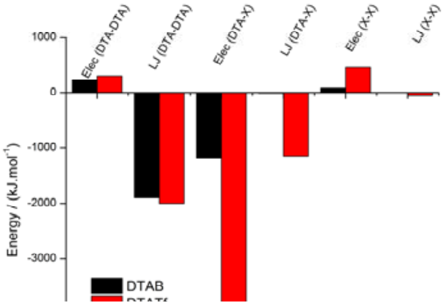

Figure 2. Energies of interaction between counterions and DTA in DTATf and DTAB.

Specific ion interactions are responsible for the DTATf properties, which are distinct from the well-studied DTAB system. The preferential orientation of Tf at the micellar interface arises from the energies of interaction between the counterion and the micellized monomers. Our data clearly indicate the need of explicitly including specific ion interactions to adequately model specific ion effects in micellar systems.

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Acknowledgements: FAPESP, CAPES and INCT-FCx

Raft-like domains in phospholipid monolayers promote lysozyme aggregation and misfolding

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A vast number of severe neurodegenerative disorders including Parkinson's and Alzheimer's diseases are currently associated with the deposits of insoluble protein aggregates (amyloid fibrils), increasing scientific reports also evidence the implication of raft-like domains in the above pathologically relevant phenomena. The role of lateral phase separation that produce these transient microdomains has been extensively investigated in models of cell membrane with different radii of curvature and composition to ascertain whether externally induced curvature changes may drive the lateral organization of the membrane components [1]. The results suggest that all investigated biomimetic systems give comparable information although they can be studied by complementary techniques. In this work, we report the results collected for planar membrane models, i.e. Langmuir monolayers, where direct visualization of the phase domains, flanked by the thermodynamic and spectroscopic characterization, is easily accomplished. We reproduced and characterized lipid rafts for mixed phospholipid monolayers of DSPC/DOPC/Cholesterol at the water-air interface by means of surface-pressure area isotherms and Brewster Angle Microscopy as a function of monolayer composition and temperature. The same techniques were adopted to investigate the interaction of a water-soluble protein at the monolayer interface: lysozyme was selected as model protein since lysozyme misfolding and pre-amyloid fibril-like aggregation was recently shown to occur at phospholipid liposome interface [2]. Native as well as preliminary fibrillated lysozyme was injected in the subphase under the phospholipid monolayer at selected lipid composition, temperature and surface pressure. Lysozyme insertion was studied for homogeneous expanded phases of the monolayer as well as in the presence of raft-like domains. For both native and fibrillated lysozyme, we observed that the protein is adsorbed at the monolayer/water interface but with different kinetics. In both cases, the adsorbed lysozyme segregates along the border of the condensed domains eventually forcing a transition from a circular to a polygonal structure of the domains. Transfer of the monolayer/lysozyme system onto solid support allowed to characterize the resulting protein structure by means of circular dichroism and FT-IR/ATR spectroscopy. The results evidenced the presence of the characteristic features of β-sheet units not only for the pre-fibrillated protein but, more importantly, for the globular form after interaction with the raft-domains in the monolayer. Spatially-resolved fluorescent spectra were collected by means of Confocal Laser Scanning Microscopy after staining of the monolayer/lysozyme film with Congo Red (CR): the measurements evidenced the typical emission spectra of CR intercalated in β-sheet structures for all systems thus indicating the presence of aggregates enriched in fibril-like structure and confirming the direct the involvement of lipid rafts in amyloidogenic processes.

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Acknowledgements:

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Surface Shear Rheology of Adsorption Layers from the Protein HFBII Hydrophobin; Effect of Added β-Casein

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The surface shear rheology of hydrophobin HFBII adsorption layers is studied in angle-ramp/relaxation regime by means of a rotational rheometer. The behavior of the system is investigated at different shear rates and concentrations of added β-casein. In angle-ramp regime, the experimental data comply with the Maxwell model of viscoelastic behavior. From the fits of the rheological curves with this model, the surface shear elasticity and viscosity, E_{sh} and η_{sh}, are determined at various fixed shear rates. The dependence of η_{sh} on the rate of strain obeys the Herschel-Bulkley law. The data indicate an increasing fluidization (softening) of the layers with the rise of the shear rate. The addition of β-casein leads to more rigid adsorption layers, which exhibit a tendency of faster fluidization at increasing shear rates. In relaxation regime, the system obeys a modified Andrade's (cubic root) law, with two characteristic relaxation times. The fact that the data comply with the Maxwell model in angle-ramp regime, but follow the modified Andrade's low in relaxation regime can be explained with the different processes occurring in the viscoelastic protein adsorption layer in these two regimes: breakage and restoration of intermolecular bonds at angle-ramp, vs. solidification of the layer at relaxation [1].

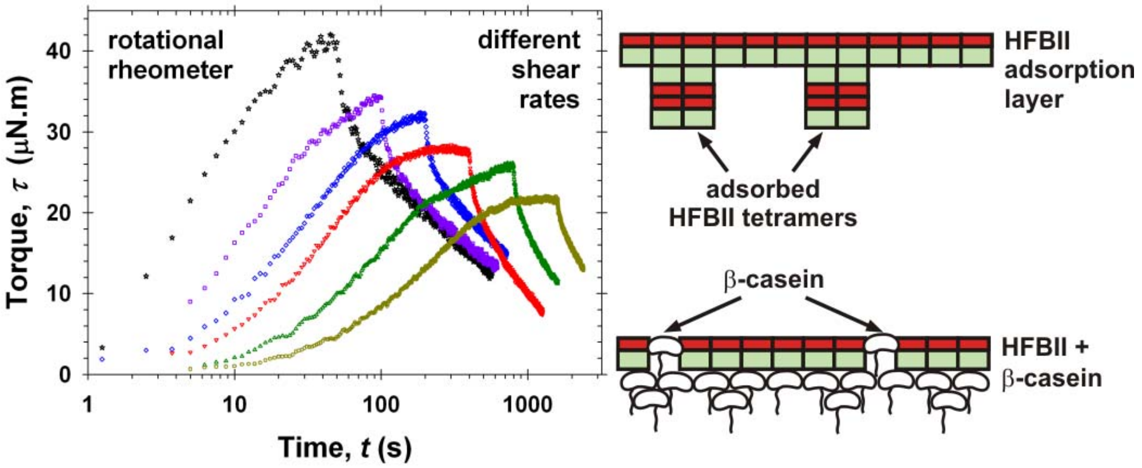

Fig. 1 Experimental torque vs. time curves at different shear rates, and interfacial layer structure.

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Computer Simulation of Self-assembly of Rigid Surfactant Molecules in Aqueous Solution

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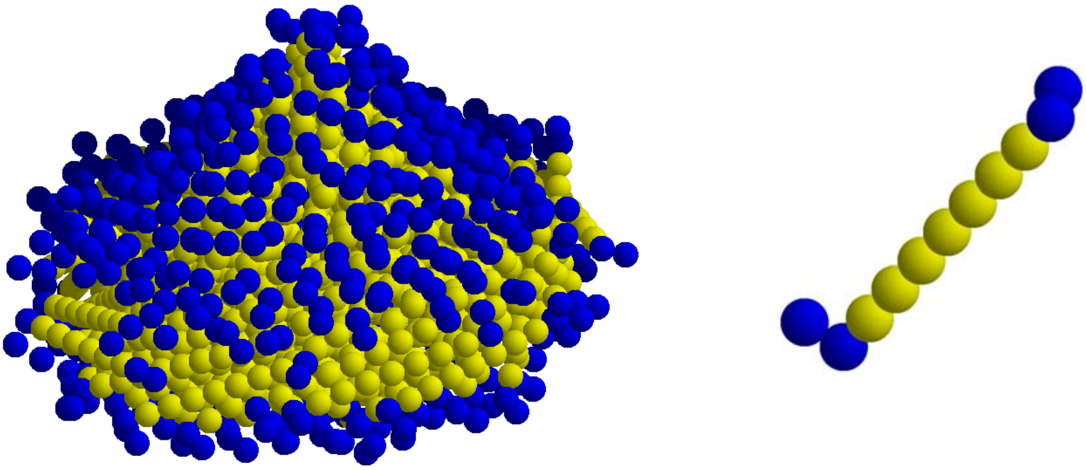
Linear and facial surfactant molecules with rigid hydrophobic cores and variously distributed hydrophilic groups of various sizes are investigated for their aggregation properties. Typical linear molecules used in this study are bolaform amphiphiles, which contain two hydrophilic groups terminating a rigid hydrophobic chain. As models for facial amphiphiles, the biologically important bile salts, consisting of a rigid hydrophobic steroid skeleton and attached hydrophilic groups, have been studied. Using Molecular Dynamics and Monte-Carlo Simulation techniques for studying simple off-lattice coarse-grained models of rigid surfactants, we found a large variety of structures ranging from micelles of varying shape and size to cubic structures and highly ordered linear aggregates. Depending on the temperature and concentration conditions of the surfactant solutions, we observed the occurrence of a diversity of phase structures and the growth of ordered nanostructures. The specific geometrical constraints introduced by the shape and the distribution of hydrophobic and hydrophilic groups within the architecture of the single molecules in combination with the rigidity of the backbone allows for the formation of diverse aggregates which even can be chiral. In this study, we have shown that very simple models built from hydrophobic and hydrophilic segments interacting with short range potentials including non-bonded mutually neighboured segments are adequate to study the molecular aggregation of surfactants by self-assembly. A particular interesting case of structure formation in solutions of rigid amphiphilic molecules is the self-limited self-assembly. We have found two types of molecules which form roughly monodisperse anisometric associates with a non-periodic internal order (Fig. 1). The orientation of the molecular axes changes regularly into radial direction up to a certain angle at the rim of the aggregate. For geometric and energetic reasons this change is not allowed to be continued and, in this way, the size of the anisometric aggregate is limited.



(a) (b)

Fig. 1 Equilibrium structure of associate (a) of rigid molecules(b) from self-limited self-assembly: hydrophobic segments- yellow, hydrophilic segments – blue.

Morphological Transformations in Solid Domains of Alkanes on Surfactant Solutions

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Alkanes on surfactant solutions can form three distinct phases at the air-solution interface: a liquid phase (L), solid monolayer phase (S_1) and a hybrid bilayer phase (S_2). Phase coexistence between any two, or all three, of these phases has been observed by Brewster angle microscopy (BAM) of tetradecane (C_{14}), hexadecane (C_{16}) and their mixtures on solutions of tetradecyltrimethylammonium bromide (TTAB). The morphologies of the domains depend on the competition between line tension and electrostatic interactions, which are essentially different depending on the pair of phases in contact. Domains of S_1 in the L phase are long and thin; however, long, thin domains of L in an S_1 phase are not stable, but break up into a string of small circular domains. The bilayer S_2 domains are always circular owing to the dominance of line tension on the morphology.

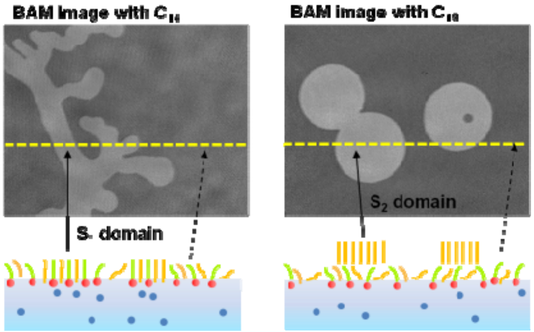

Fig. 1 BAM image of S_1 (left) and S_2 (right) domains on TTAB aqueous solution. Schematic illustrations indicate cross section of these domains and surrounding L phase.

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Formation of a Multiscale Aggregate Structure through Spontaneous Blebbing of an Interface

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Spontaneous formation of spatio-temporal orders in nonequilibrium systems has attracted interest of scientists. However, almost all of these studies focused only macroscopic orders but not microscopic structures. It would be more interesting if we can discuss the macroscopic spatio-temporal order formation based on microscopic structure formation. We have studied blebbing at a periphery of an oil droplet including anionic surfactant (palmitic acid; PA) which floats on cationic surfactant (trimethyl-stearylammonium chloride; STAC) aqueous solution [1]. The blebbing is induced by repetitive formation and removal of aggregates made of PA and STAC at an oil/water interface. By small angle X-ray scattering (SAXS) measurements, it was suggested that the aggregates have lamellar structures with an interval of around 40 nm [2]. Recently, we designed a Hele-show-like system, in which millimeter-scale pillar structures composed of the aggregates were formed through the interfacial motion. The pillars grew downward in the aqueous phase, and the separations between pillars were roughly equal. Small-angle X-ray scattering using a microbeam X-ray revealed that these aggregates had nanometer-scale lamellar structures whose orientation correlated well with their location in the pillar structure [3]. It is suggested that these hierarchical spatial structures are originated from the spontaneous interfacial motion.

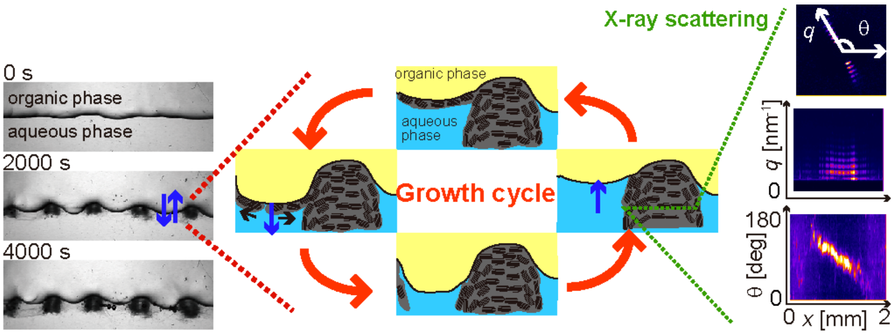

Fig. 1 Schematic illustration on the spontaneous surface motion and aggregate structure.

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Liquid expanded adsorbed layers of soluble surfactants

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The ability of soluble surfactants to form liquid expanded (LE) phase is studied. The applicability to the LE phase of various statistic mechanical models of monolayers is investigated. It is shown that the classical models based on Langmuir and Volmer models fail to describe unambiguously all properties of the adsorbed layer in terms of molecular characteristics. A better approach is to use theoretically better justified models such as the adsorption models derived by Helfand-Frisch-Lebowitz, by Smith and by Ivanov et al. [1-2]. Procedures, both theoretical and experimental, for determination for all adsorption parameters involved (adsorption constant Ka, area per molecule, parameter of lateral attraction β and Langmuir's spreading pressure of the LE phase [2-4]) are discussed. Along with the adsorption isotherm and the surface equation of state, this forms a complete theory of the adsorption at water|gas surface, which describes well the experimental data for several homologous series of soluble surfactants (including tensiometric and Gibbs elasticity data). The possibility for phase transition gaseous to LE phase is investigated and the critical temperature of all surfactants is calculated. Several implications of the models developed are investigated, e.g., the effect of temperature on the adsorption of alcohols at water|gas is predicted, in good agreement with experimental data [4].

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Acknowledgements:

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Self-Organization in Mixed Casein Solutions

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The milk protein kappa-casein is known to form three modes of self organization, namely, micelles, oligomers via formation of intermolecular disulfide bonds, and fibrils similar to the pathological amyloid structures. Reduced kappa-casein forms a simpler system where oligomers of kappa-casein are absent, due to absence of intermolecular disulfide bonds.

The major milk protein, beta-casein, known for its chaperone-like activity [1], has been claimed in a number of recent studies to prevent the fibrillation process of kappa-casein. However, the mode of this beta-casein action is still unresolved.

In the present work we studied the mode of interaction between these two milk proteins, using isothermal titration calorimetry (ITC), cryogenic-transmission electron microscopy (cryo-TEM) and circular dichroism spectroscopy (CD).

Microcalorimetry analysis clearly demonstrates that beta-casein interacts with both reduced and native kappa-casein, resulting in mixed micellization. ITC- thermograms point to the involvement of different mixed micellization modes, depending on the concentration of kappa-casein species available for micellization. Combined with the cryo-TEM and CD analysis we conclude that only under certain conditions the presence of beta-casein can inhibit kappa-casein fibrillation, and that the effect on native kappa-casein is more pronounced than on the reduced form of the protein. Quantitative analysis of the microscopy data confirm that the fibrils formed by kappa-casein as well as by the mixed proteins are amyloid fibrils.

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In Situ and Green Synthesis of Hexagonal Silver Nanoparticle Using Prepared Capping Agent

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The paper reported one-step in situ, facile and green synthesis of silver nano particle using sunlight as reducing agent as well as new prepared surfactant as capping, sizing and shaping agent. The chemical structure of new prepared surfactant was confirmed using FT-IR and ^{1}HNMR spectroscopy. The silver nanoparticle formation was investigated using UV-vis spectrophotometer and transition electron microscope. The result showed formation uniform, well arrangement and hexagonal shape of silver nanoparticle. Both prepared surfactant and surfactant capping silver nanoparticle showed high antimicrobial activity against gram positive (*Bacilluspumilus & Micrococcusluteus*) and gram negative bacteria (*Pseudomonas erogenous & Sarcina lutea*).

Adsorbed Films of Conditioner Components on Damaged Hair-Surface Model

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In hair care products, the conditioner and treatment are essential items to make the hair smooth and soft, and reduce the static electricity. The hair cuticle surface is originally coated by the hydrophobic F-layer and thus water-repellent. However, the F-layer is chemically removed by the hair coloring, and then hydrophilic groups such as anionic $-SO_3^-$ and nonionic $-CONH_2$ originating from an underlying protein layer become exposed on the hair surface, leading to dry feeling of hair [1]. On the other hand, main components of conditioning ingredients are cationic aggregates formed by long-chain alcohols (A) and cationic surfactants (C). Since these aggregates are cationic, it is difficult to expect that they adsorbed on the nonionic sites of the hair surface. In order to improve the adsorptive property of the cationic aggregates, we developed an anionic polymer as a binder between the aggregates and the nonionic hydrophilic surface sites. In the present work, the structure and property of adsorbed film prepared from a hair conditioner solution including the anionic polymer were investigated using a hair-surface model substrate.

A silicon wafer of which surface was chemically modified by an amide-terminated organosilane was used as the hair-surface model substrate. The anionic polymer (P) was designed to give an affinity for the cationic aggregates through an electrostatic interaction and also for the hydrophilic nonionic sites by hydrogen bond. To clarify the effect of the polymer as a binder, X-ray reflectivity and water contact angle measurements were performed on surfactant adsorbed films in water and in air after drying, respectively.

XR data and fits for films adsorbed from AC and ACP solutions at the hair-surface model substrate/water interface are shown in Fig. 1. Good agreement between the measured reflectivites and the calculated curves was achieved by assuming the film structure composed of a uniform bilayer of AC on the amide monolayer, bilayer islands distributed on the top of the uniform bilayer, and thin water layers (for the AC solution) or polymer layers with high electron density (for the ACP solution) between the bilayers and the amide surface. Water contact angles for films adsorbed from the AC solution and dried in air were changed with the increased number of water rinse, whereas the angles for films from the ACP solution were unchanged, indicating that the anionic polymer stabilizes adsorbed state of the cationic aggregates to the nonionic polar sites and improves the wash-resistance of the adsorbed film.

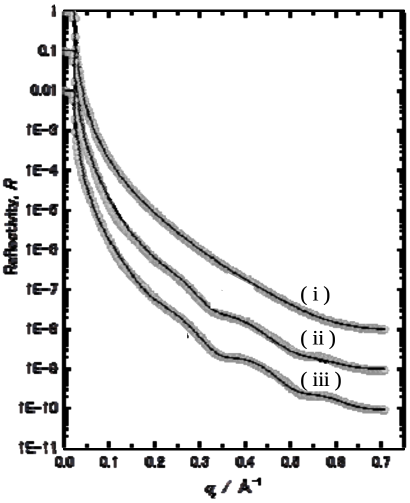

Fig. 1 XR profiles (symbols) and fitted curves (solid lines) for the solid/water interfaces: (i) amide-modified Si-wafer/water, and adsorbed films of (ii) AC and (iii) ACP at the interface. The reflectivity scale of (ii) and (iii) are shifted for clarity.

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Rheological investigation on crystallization of an unhydrogenated vegetable fat dissolved in sunflower oil

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Vegetable fats, with relatively high melting temperature, are often used as ‘oil adsorbers’ and rheology modifiers for vegetable oils. They are e.g. used for margarine flow properties control. The flow control is achieved by creating a space–spanning network of fine fat crystals throughout the oil phase. The objective of this work was to investigate crystallisation of an unhydrogenated vegetable fat (UVF) dissolved in sunflower oil by performing rheological measurements. Influence of UVF concentration and temperature was investigated. Also, effect of polyglycerol polyricinoleate (PGPR) and PGPR/distilled monoglycreides (DMG) mixtures addition on UVF crystallisation were investigated. Concentration of UVF was varied from 2 to 15 % wt., while the temperature range was from 10 to 70^{o}C. At higher temperatures, UVF is dissolved in sunflower oil, and solutions are of low viscosity with typical Newtonian flow profile. On decreasing temperature, in a particular temperature range, crystallization of UVF takes place and dispersion of UVF in the oil are formed. Formation of the dispersions is accompanied with an increase in viscosity, and change in flow profile from Newtonian to shear–thinning. The higher concentration of UVF, the lower temperature range where the onset of the viscosity increase is observed. PGPR and PGPR/DMG mixtures influence crystallisation process and network formation of UVF crystals, as evidenced by change in rheological properties of the dispersions. Rheological measurements were found highly suitable for studying UVF crystallisation process.

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Solid Lipid Nanoparticles as novel template for hierarchical porous silica and hybrid drug loaded materials

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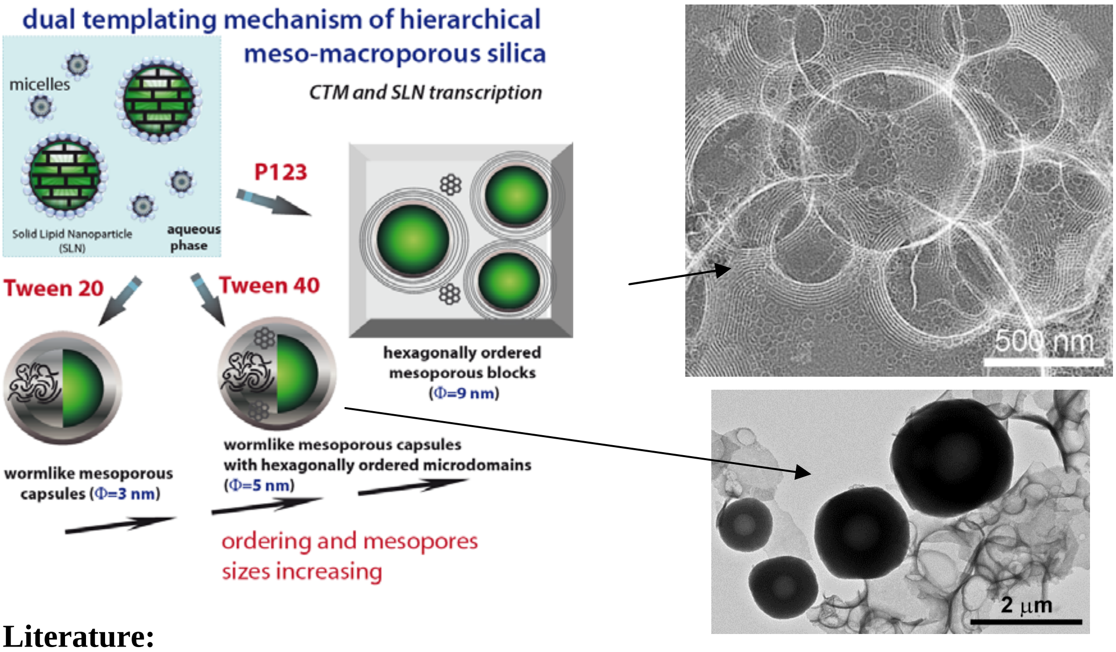
Colloidal templating has been widely used to design porous materials with different shapes and sizes ranging from several nm to several microns. Hierarchical macro–mesostructured silica has been successfully synthesized by the use of self-assembled templates of colloidal spheres. Silica is also known to be safe, not only for the environment, but also for the human body within a certain range of administrated dose. Therefore, its application field was extended to biocompatible materials and, recently, for oral drug delivery. In the soft matter field, Solid Lipid Nanoparticles (SLN) appeared very recently as promising drug carriers especially for their potential applications in pharmaceutics. Therefore, combining mesoporous silica with solid lipid nanoparticles is a straightforward approach for the design of advanced formulations in drug delivery or food chemistry. Herein, we present the first examples of SLN templating silica reported in the literature [1,2]. SLN stabilized by nonionic polysorbate or block copolymer surfactants were used for the preparation of hierarchical silica through a co-templated approach combining a self-assembling mechanism with micelles and spherical soft matter particles imprinting. Depending on the reaction conditions, the morphology of the final material can be tuned to capsules or to block matter. The size of the mesopores is strongly dependent on the nature of the surfactant in excess whereas the size of the macropores depends only on the size of SLN. The organization degree of the silica wall depends on the surfactant: only wormlike mesoporous capsules were obtained with Tween 20, and hexagonally ordered microdomains embedded in wormlike mesoporous silica capsules were obtained with Tween 40. Hexagonally ordered silica with circularly ordered mesoporosity could be achieved with P123.



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Stimuli-Responsive Lyotropic Liquid Crystal-Nanoparticle Hybrids

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We demonstrate the dual magnetic and light responsive nature of hybrid mesophases constituted by Fe_3O_4 nanoparticles dispersed in lipid-based lyotropic liquid crystals. When subjected to an external magnetic field above the order-disorder transition of the mesophase (i.e. in the isotropic state), the nanoparticles aggregate and orient along the magnetic field direction, and upon cooling the system through the disorder-order transition, the nanoparticle aggregates drive the orientation of the mesophase via heterogeneous nucleation [1]. The system is also shown to respond to the exposure of visible light, with order-disorder transitions in the lipidic mesophase triggered by Fe_3O_4–induced photothermal effect [2]. Both the orientational order and the photothermal effect of the hybrid mesophase can be tuned by the nanoparticle concentration, offering a general route for controlled assembly of complex fluids with combined magnetic and light responsiveness. We finally show how this unique system can be used to design stimuli-responsive anisotropic physical properties and we demonstrate this feature by illustrating the effect on the anisotropic diffusion of drugs within a columnar hexagonal mesophase embedded with Fe_3O_4 nanoparticles [3].

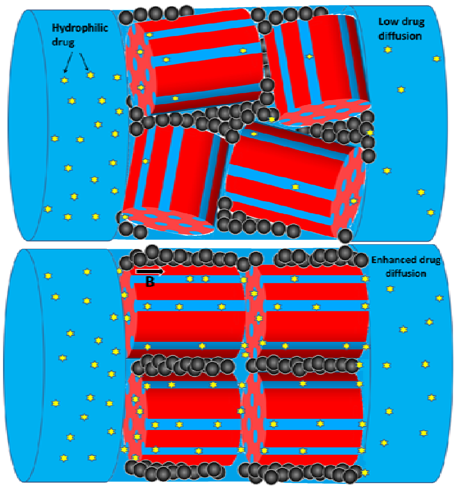

Fig. 1 Illustration of enhanced drug diffusion using magnetic responsive lyotropic liquid crystals

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Effect of Adsorption Behavior of Anionic Surfactants on the Wetting Property of $CaCO_3$ Substrate

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The adsorption behavior of various types of anionic surfactants such as linear alkyl benzene sulfonate (LAS), dodecyl benzene sulfonate (DBSA), sodium alcohol ethyoxysulfonate (SLES) on the $CaCO_3$ substrate was investigated by a quartz crystal microbalance with dissipation monitoring (QCM-D), contact angle measurement, and zeta potential analyzer technique. Additional tests such as fourier transform infrared spectrometry (FT-IR) analysis, floating test have been conducted to evaluate the adsorption behavior of anionic surfactants on the $CaCO_3$. Under acidic conditions, the adsorption of anionic surfactant on the substrate was mainly due to an electrostatic interaction between the positively charged $CaCO_3$ surface and the negatively charged head group of surfactant molecules. Contact angle measurements have shown a different wetting behavior depending on surfactant concentration. In a low surfactant concentration region, $CaCO_3$ surface becomes more hydrophobic with an increase in concentration. However, further increase in surfactant concentration caused a reverse change in a wetting property from hydrophobic to hydrophilic. QCM-D measurements have been performed using quartz crystals coated with $CaCO_3$ to observe mass of adsorbed surfactant molecules and structural properties of molecular layers. The results revealed that monolayer adsorption of surfactant molecules at the particle-water interface occurs in a low surfactant concentration region and the thickness of forming molecular layers was found to be almost the same as the length of a single surfactant molecule. On the other hand, both the mass of adsorbed surfactant molecules and the thickness of forming molecular layers indicated multilayer adsorption of surfactant molecules in a high surfactant concentration region, which evidently resulted in an increase in hydrophilicity of $CaCO_3$ surface. Also, the thickness of forming molecular layers corresponds to twice the length of a single surfactant molecule. Visual floating test results have shown a good agreement with measurements of contact angle and QCM-D.

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Effect of Fatty Acid Structure on the Vesicle Membrane Fluidity of Liposomes

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Fatty acids are widely distributed in living bodies as a constituent of various complex lipids such as triglycerides, phospholipids, glycolipids, and so on. Although the level of free acids is generally low in body tissue and fluids, they affect a variety of physiological functions of biomembranes [1,2]. The partitioning of free fatty acids between the aqueous phase and the lipid bilayer phase is of importance not only from a pure physicochemical point of view, but also in relation to a large number of biological and biotechnological processes where the amphiphilic fatty acids act as regulatory lipids for the functioning of several lipid membrane associated processes [3]. The incorporation of fatty acids into the membrane leads to a change in the property of lipid membrane stability and bending rigidity as well as for the functioning of membrane-associated enzymes, peptides, and proteins. Furthermore, important drug and drug delivery aspects are closely related to the way free fatty acids incorporate into lipid membranes and distribute themselves laterally in the heterogeneous membrane structure [3]. From the viewpoint of performance and applicability, it is important to understand how fatty acids have an influence on changing packing property of lipid membranes. Even though many studies have been carried out to investigate the effect of amphiphilic solutes such as lysolipids and fatty acids on liposome systems, no systematic work has been performed on the structure of fatty acids with an 18 carbon chain on the membrane fluidity of liposomes. In the present work, the interaction of fatty acid with the vesicle membrane of phospholipids was investigated by using 4 different kinds of soybean lecithin and 3 different types of fatty acid of different molecular structure. It has been found that the addition of fatty acid produced close packing of liposomes mainly due to the penetration of fatty acid molecules into liposome vesicles, which resulted in a decrease in liposome size. The closest picking of liposomes with stearic acid, oleic acid and linoleic acid was found at the molar ratios of fatty acid to lecithin of 0.70, 0.50, and 0.25 respectively. Further increase in fatty acid contents in liposomes produced aggregates of lipid particles. The membrane fluidity of liposomes was characterized by measuring membrane deformability, fluorescence anisotropy, and transmission electron microscopy (TEM) and compared with measurements of particle size and zeta potential of liposomes.

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Molecular interactions of cationic gemini surfactants (m-*s*-m) with an environmental friendly nonionic sugar-based surfactant (β-C_{12}G): Interfacial, micellar and aggregation behavior

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Mixtures of different types of surfactants are practically important. In the present study, mixtures of cationic gemini surfactants; alkanediyl-α,ω-bis(alkyldimethylammonium bromide) with non-ionic sugar-based surfactant n-dodecyl-β-D-glocopyranoside (β-C_{12}G) in aqueous solutions containing electrolyte NaBr have been studied using tensiometry, fluorimetry and viscometry. The experimental results for surface parameters and interaction parameters in mixed micelles were evaluated using regular solution theory. Since all the surfactants have different alkyl groups and spacers, the strength of interaction is attributed to the sterical and electrical factors on mixed monolayer and mixed micelle formation and of surfactant-surfactant interactions. Presence of electrolyte reduced synergism between the above mentioned cationic and non-ionic surfactants. The results show strong interaction at the air/water interface and greater preference for adsorbing at the air/water interface relative to mixed micelle formation in the solution phase. The alkyl chain length and spacer of gemini governs the aggregation behaviour of the mixed micelles. The short spacer and the higher alkyl chain geminis have ability to strongly affect the morphology of the present system.

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Self-spreading behavior of lipid bilayer at the interface between solid and aqueous ionic liquid

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Self-spreading is a lipid wetting process whereby lipid molecules are self-organized to form a lipid bilayer at a solid-liquid interface. We have proposed and demonstrated several new devices that employ the self-spreading phenomenon including a microchannel device [1], a molecule-gate device using nanogap electrodes [2] and a supported lipid bilayer microarray [3]. Self-spreading has been observed in electrolyte solutions such as saline and phosphate buffer. A thin water layer is known to exist between the bilayer and the solid, and so the electrolyte ions in the layer are assumed to play an important role. We are interested in the effect of the ions and investigate the self-spreading behavior using an ionic liquid as an electrolyte.

A Ti (~10 nm thick) micropattern was fabricated on a SiO_2 wafer with a conventional photolithography technique. L-α-Phosphatidylcholine (egg-PC) and DOPC, mixed with 1-5% of Texas Red-labeled DHPE, were examined for self-spreading in a 1-100 mM aqueous solution of choline-dihydrophosphate.

We observed that self-spreading occurs in an aqueous ionic liquid with a confocal laser scanning microscope. The lipid bilayer spreads only on the SiO_2 surface, and thus its position can be controlled with the Ti pattern (**Fig. 1a**). The lipid bilayer retains its lateral diffusion characteristics (**Fig. 1b**). The thickness of the spreading bilayer was confirmed by using an atomic force microscope. The topography shows that both the egg-PC and DOPC were about 4 nm high, which is consistent with the thickness of the single lipid bilayer (**Fig. 1c**). The results are compared with those of self-spreading behavior in commonly used buffer solutions.

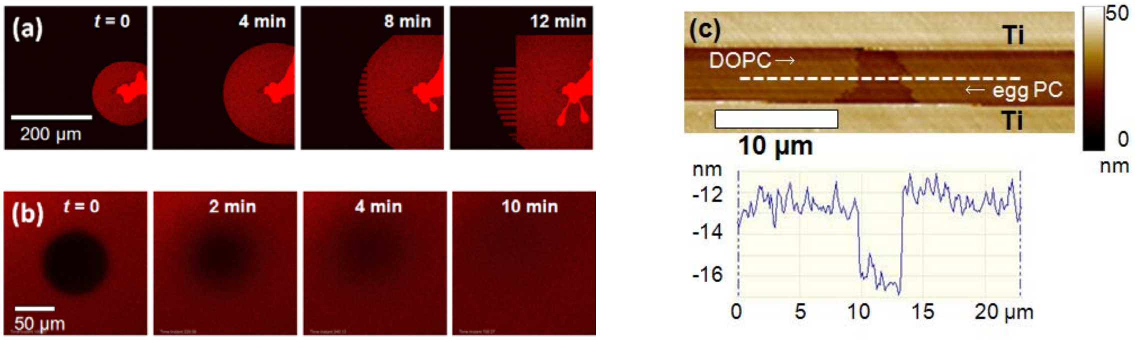

Fig. 1. Self-spreading behavior in 100 mM aqueous solution of choline-dihydrophosphate. (a) Egg-PC on an SiO_2 surface with a Ti pattern. (b) Fluorescence recovery after photobleaching. (c) Topography of self-spreading egg-PC and DOPC within 5 μm wide line pattern and its sectional view.

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Structure Characterization and Photocurrent Response of Adsorbed Films of Photosynthetic Proteins from Thermophilic Purple Sulfur Bacterium *Tch. tepidum*.

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Fabrication of artificial organized films with protein-pigment complexes, extracted from photosynthesis bacteria, is of great interest because of its potential for development of photoelectric conversion elements as well as for understanding photosynthesis systems. In the present study, light-harvesting antenna - reaction center (LH1-RC) complexes from *Tch. tepidum* [1] were immobilized on solid substrates, and the film structures and photoelectrochemical characteristics were evaluated.

Details of preparation and purification of LH1-RCs were described elsewhere [1]. FTO-coated glass slides were used as electrode substrate. The FTO electrode surface was beforehand modified with (3-aminopropyl)triethoxysilane (APTES) or vertically aligned ZnO nanorod (ZnO NR) array. Adsorption of the LH1-RCs was conducted by immersing the electrodes into an aqueous LH1-RC dispersion. Photocurrent response was measured with a conventional three-electrode system with Pt and Ag/AgCl as a counter and a reference electrode, respectively, upon illumination of light from Xe lamp. The adsorbed film structures were investigated by ultraviolet-visible (UV-vis) spectroscopy and atomic force microscopy (AFM).

A UV-vis spectrum for the LH1-RCs adsorbed on the APTES-coated FTO substrate was consistent with that measured for the aqueous dispersion, indicating the LH1-RCs were not denatured by adsorption on the substrate surface. AFM observation in water exhibited that the LH1-RCs were uniformly distributed to form planar single-layered patches in the adsorbed film (Fig. 1). Photocurrent generation was confirmed for the adsorbed film although the photocurrent observed was as small as around a few nA/cm^2. Highly enhanced photocurrent generation was achieved by using the ZnO nanorod array electrode. Since ZnO is a photo-responsive semiconductor, the ZnO nanorods themselves generated the photocurrent. However, adsorption of LH1-RCs on the ZnO nanorods further increased the photocurrent up to several times larger than that for the bare nanorod electrode.

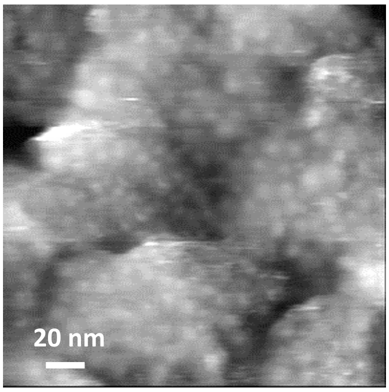

Fig. 1 An AFM image for an adsorbed film of LH1-RCs (*Tch. Tepidum*.). The LH1-RCs are observed as white dots.

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Investigation of Cholesterol Transfer between Unseparable Vesicles

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Cholesterol (Chol) transfer between lipid membranes is an important biological process related to activities and diseases of living bodies. Former investigations on the Chol transfer were made by measuring Chol content in donor and acceptor vesicles after their separation. Thus, the donor and the acceptor vesicles had to be separable, which gave a great limitation on the experimental systems. In this paper, cholesterol transfer between unseparable donor/acceptor vesicles was investigated using fluorescent measurements, thermal analysis, and Langmuir monolayer study. NBD-Chol was incorporated to the vesicles as a fluorescent probe and change in the florescence spectra after mixing vesicles with different Chol concentrations were observed. The intensity ratio at 495 and 520 nm was used as an indicator reflecting Chol concentration in the vesicles. L_α/L_β transition temperatures were also an effective parameter for investigating the Chol transfer. In the Langmuir monolayer study, DPPC monolayer is known to cause structural transition during the compression. Thus, the Chol transfer to the DPPC membrane was qualitatively detected from the existence of the structural transition.

Fig. 1 shows examples of the fluorescence measurement. Initially, NBD-Chol was included in the vesicles that contained 20% Chol. Upon mixing with Chol-free vesicles, shape of the spectra was altered due to the Chol transfer, and the behavior depended on characteristics of the constituent lipids. Comparison of DMPC and DPPC vesicles revealed that the cholesterol transfer from cholesterol-rich to cholesterol-poor vesicles proceeded promptly if the constituent lipids were in the L_α state. Introduction of charged component, SA, suppressed the cholesterol transfer slightly, presumably due to electrostatic repulsion between the vesicles. Thus, the transfer was enhanced in the presence of NaCl due to the shielding effect. The same conclusion was obtained from the thermal analysis. Also investigated was effect of albumin on the cholesterol transfer. Combination of multiple investigation techniques presented here is expected to prove various biological phenomena related to Chol transfer.

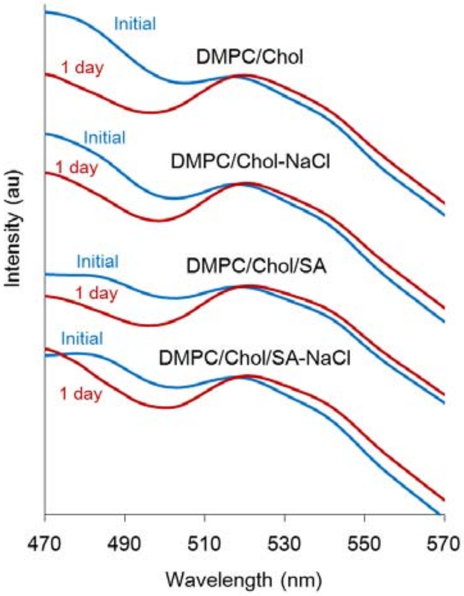

Fig. 1 Change in the fluorescence spectra after incubation at room temperature for 1 day. DMPC vesicles and DMPC/Chol=8/2 vesicles, or DMPC/SA=9/1 vesicles and DMPC/Chol/SA=7/2/1 vesicles were mixed in the presence/absence of 100 mM NaCl. NBD-Chol was added only to Chol-containing vesicles.

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Comparison of the surface rheology of saponins on air-water and oil-water interfaces

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Saponins are a class of natural surfactants found in more than 500 plant species. They consist of flat hydrophobic head group (triterpenoid or steroid) with hydrophilic oligosaccharide chains. Depending on the number of the chains they are classified as monodesmosidic or bidesmosidic – having one or two chains, respectively. Saponins have strong surface activity and find commercial application as foam and emulsion stabilizers. Knowledge about the surface rheology of saponins on the air-water (A-W) or oil-water (O-W) interface is essential in order to understand and control the bulk properties of the respective system (foam or emulsion). In a previous article [1] we studied the rheology of various saponins in shear deformation on the A-W interface. 4 saponins, which had the same aglycone (triterpenoid, oleanane type), exhibited very high surface modulus, *G*. 3 of them were monodesmoosidic, and one bidesmosidic. In all systems the elastic component, *G*\`, was much higher than the viscous, *G*\`\` (*G*\`>>*G*\`\`). Here we study the behavior in shear deformation of the same saponins on the O-W interface. The oil used was hexadecane. We employed the cohesive energy density, E_{CH}, to characterize the mechanical strength of the adsorption layers. On the O-W interface the monodesmosides had significantly lower *G* and ratio *G*\`/*G*\`\`. For one of the saponins the behavior switched from predominantly elastic (*G*\`>*G*\`\`) to predominantly viscous (*G*\`\`>*G*\`) on introduction of hexadecane. The layers were much more fragile (lower $E_{CH}$) as compared to A-W interface. The effect of the oil phase on the adsorption layer of bidesmosides was different. The ratio *G*\`/*G*\`\` was similar for O-W and A-W interfaces, and *G*\` was only moderately lower. The mechanical strength of the layer was the same at both types of interfaces. The observed difference between the properties of the mono- and bi-desmosides was explained with specifics of the packing of the molecules. The arrangement of the molecules would depend both on their structure (one or two sugar chains), and on the nature of the non-aqueous phase (see Fig. 1). More efficient packing leads to stronger interaction between the molecules and consequently to higher surface modulus.

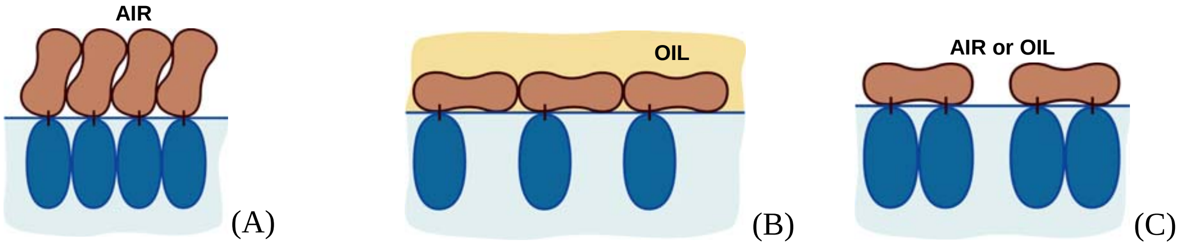

Fig. 1 Suggested orientation of saponin molecules on the non-aqueous phase-water interface. Lower phase is water, upper phase is air or oil. (A)Monodesomosidic molecules on air-water interface; (B)Monodesmosidic molecules on oil-water interface; (C)Bidesmosidic molecules on air-water or oil-water interface.

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Surface shear rheometry of saponins: measurement and modeling

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It has been known for over a century that certain surface active agents form absorption layers which exhibit substantial surface modulus, *G*, in shear deformation. The spectrum of such systems includes proteins, polysaccharides, phospholipids, saponins, solid particles etc. The surface shear modulus can be measured via tools with a particular geometry, which are used with a rotational rheometer. Such instruments are the bicone tool (BT), and the double wall ring (DWR), see Fig 1. The rheometer measures the torque *M* at a given angle of rotation, Ω. From *M* and Ω the surface stress, τ, and the shear deformation, γ, can be calculated. Although there are a lot of articles dedicated to the surface rheology of various systems, relatively few of them aim to determine correctly the rheological parameters of the layers. Sometimes the authors present the results in terms of "effective viscosity", instead of describing them with a particular rheological model (viscous, visco-elastic etc.). Probable artifacts like non-homogenous shear deformation or wall slip are often overlooked. In this study we aim to obtain a self-consistent set of parameters, and rheological model which describe the adsorption layer. We compare results obtained with different methods (BT, DWR) or bicones with different radii. Such comparison is necessary because certain tools can generate non-uniform shear field, which compromises the measurement. We also compare results obtained with the same method but different rheological tests (steady or oscillatory deformation). As model systems we used adsorption layers of different saponins on the air-water interface. The measurements with BT and DWR compared well, when the gap, *h*, between the bicone and the inner wall of the vessel was small enough (2 mm) to provide a well-defined shear field. For some of the studied saponins we determined the same value of *G* from an amplitude sweep on one hand, and form the "creep ringing" during steady creep deformation on the other. The behavior of the adsorption layers in creep deformation was described well by the compound Voigt rheological model. Using the rheological parameters obtained from the creep test we calculated the dependence of *G* on the frequency of oscillation. Although the calculation predicted the right trends, it differed quantitatively form the experimental data. Possible explanations for the observed discrepancies are suggested.

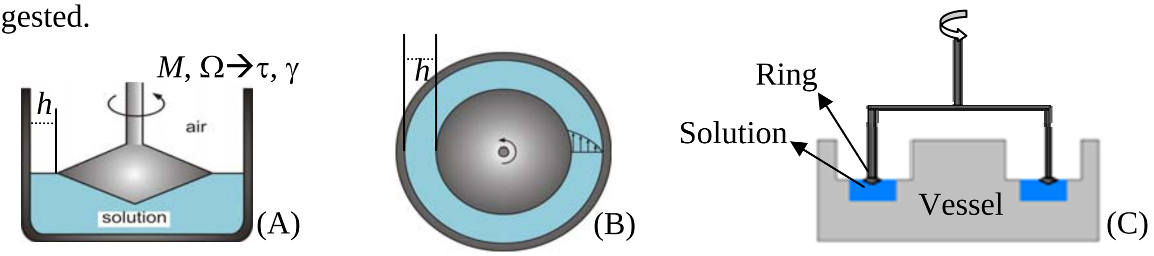

Fig. 1 (A) Bicone tool, side view; (B) Bicone tool, top view; (C) Double wall ring, side view.

Investigation of properties of Langmuir monolayers at the air/water two-component systems of silsesquioxanes (POSS) and low molecular weight polyethylene glycol (PEG)

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In recent years there has been increasing interest in surface properties of binary mixtures due to their potential application in biology, biochemistry, polymer science, detergents, solar panels, electronics and pharmaceuticals. Mixture of cage silsesquioxane (POSS) and polyethylene glycol (PEG) is an interesting one because of properties connection of POSS with the polymer. POSS are a large group of the organosilicon compounds, constructed of resistant and rigid silicon-oxygen core and variety of functional groups attached to the vertices.

The aim of this study is to investigate the surface properties of mixed Langumir monolayers at the water/air interface, characterization of morphology and stability of the monolayers formed, evaluation of thin surface films formed by functionalized POSS 1,3,5,7,9,11,14-hepta-isooctyltricycol [7.3.3.15,11] and binary system of the POSS with an addition of the amphiphilic polymer PEG 2000.

For the compound and the mixture mentioned above basic researches on behavior of POSS & PEG mixtures at the water/air interface were made. The measurements were carried out by means of a Langmuir balance (KSV Nima) integrated with the Brewster Angle Microscope BAM and SPOT potential meter.

The research carried out so far shows that POSS considered forms a stable monolayer. The amount of the polymer addition affects the structure of the monolayer, which is visible at the water/air interface and confirmed by the course of π-A isotherms and BAM micrographs.

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Acknowledgements:

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Time-Resolved Fluorescence Quenching Studies of Sodium Lauryl Ether Sulfate Micelles

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The present work examines the [detergent]- and [salt]-induced growth of the important commercial surfactant sodium dodecyl ether sulfate (SLES), which has an average of two ethylene oxide subunits in the ether bridge ionic micelles. Micelles of simple ionic detergents are typically spherical or roughly spherical in aqueous solution at low to moderate detergent concentrations in the absence of added salt [1-4]. At higher detergent and/or added salt concentrations, many ionic detergents, including SLES [5], undergo a relatively abrupt change from a spherical to a rod-like shape, with a marked increase in the micellar aggregation number.

Aggregation numbers (N_{Ag}) of the micelles of the commercial anionic detergent sodium lauryl ether sulfate (SLES), with an average of two ethylene oxide subunits, were determined at 30 ºC and 40 ºC by the time-resolved fluorescence quenching method with pyrene as the fluorescent probe and the N-hexadecylpyridinium ion as the quencher. The SLES micelles grow with detergent and/or added NaCl concentration according to the relationship:

$$\log N_{Ag} = \log N_{Ag} + \gamma \log [Y_{aq}]$$

where $[Y_{aq}]$ is the sodium counterion concentration free in the intermicellar aqueous phase. The γ values for the growth of SLES (0.11-0.15) are significantly smaller that found for SDS (ca. 0.25). Fluorescence data for pyrene, including the I_1/I_3 vibronic intensity ratio and the rate constant for intramicellar quenching, show that micellar properties such as the effective polarity of the solubilization microenvironment and the intramicellar microviscosity are insensitive to micelle size or the presence of added salt.

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Acknowledgements:

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Mixtures of biopolyelectrolytes and oppositely charged surfactants: How micelle curvature and charge density determine the structure of the complexes.

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Mixtures of polyelectrolytes and surfactants are widely used in a large number of fields, such as detergency, pharmaceutical formulations, food industry, etc. In the past decades the interactions of synthetic polyelectrolytes and oppositely charged surfactants have been widely studied and the fundamental rules are rather well understood[1].

However, more recently there is an increasing need for systems based on bioderived and biodegradable materials. These systems are of particular interest for medical and food industry. The most common biopolymers are polysaccharides: chitosan, alginate or cellullose are three examples for natural polycations, polyanions and neutral polymers, respectively. In general, biopolymers show different properties when compared to typical synthetic polyelectrolytes. Two of the reasons are the relatively large distance between the charges and the stiff backbone. The general behaviour of mixtures of biopolyelectrolytes and oppositely charged surfactants has been reviewed recently [2].

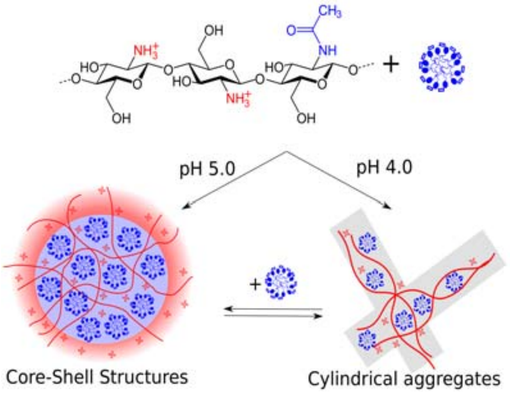

Fig 1. Schematic representation of the structures formed by chitosan and alkyl ether carboxylates at pH 4.0 and 5.0

We performed a structural investigation by using light and neutron scattering of mixtures of the biopolycation chitosan and an oleyl oligoethylenoxide carboxylate, whose degree of ionization can be finely tuned by pH. A surprisingly broad structural variety is found when pH and mixing ratio are changed: i) a micelle decorated network at low pH, ii) a one-dimensional complex with the presence of aligned ellipsoidal micelles at medium pH and iii) a compact core of micellar aggregates surrounded by a chitosan shell at high pH. The formation of such different structures is the result of the delicate balance of different energetic contributions arising from: a) the release of counterions and specific interactions between surfactant and polymer; b) the bending of the polymer chains and c) a change in the optimal curvature of the surfactant aggregate.

Concluding, the delicate balance of forces, the complex headgroup of the surfactant and its partial ionic nature, the characteristic stiffness and length of the chitosan chains, result in an amazing structural variety, which can be exploited to the formulation of biobased, highly tunable and low-cost systems.

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An improved method for analyzing isothermal titration calorimetry data from surfactant polyelectrolyte mixtures

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A correct thermodynamic description of mixtures of polyelectrolytes and oppositely charged surfactants is of fundamental importance for understanding the forces governing this highly complex mixtures. In the past decades several models have been developed for the description of the thermodynamics of surfactants binding to polymers, in particular if they are oppositely charged. A successful description of this process is provided by the Satake-Yange model[1], which foresees three states for the surfactant: free, non-cooperatively bound or cooperatively bound. According to this model an approximated description of isothermal titration calorimetric experiments was derived[2].

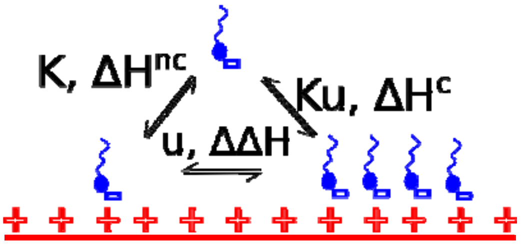

Fig 1. Schematic representation of the three equilibria in surfactant polyelectrolyte mixtures.

In our work we present a fully consistent thermodynamic description of the binding of surfactants to oppositely charged polyelectrolytes within the Satake-Yang model[3]. In the newly developed model three processes are considered for the derivation of the ITC formalism: the non-cooperative and cooperative binding and, as the newly introduced contribution, the transition of non-cooperatively bound surfactants to cooperatively bound state (see schematic representation in Fig 1).

The newly developed formalism is tested on experimental data of binding of sodium dodecyl sulphate (SDS) to a cationically modified cellulose (JR-400) where we could show that a correct description of the binding process is needed in order to obtain accurate and reliable heats of binding.

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Stimuli Responsive Derivative of Cholic Acid

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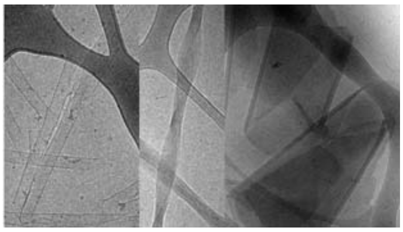
The design of new molecules that are capable to reversibly modulate their aggregation in response to external stimuli has been of considerable interest in the recent years in the light of their applicative potentiality in complex nanotechnological processes which require an accurate control of the system response. In particular the possibility to switch among more than two different morphologies by tuning several external parameters is a desirable condition to enhance the applicative versatility. In this context this study finds its relevance, analyzing the multi-stimuli responsiveness of a cholic acid derivative, obtained by substituting the OH group in position 3 with a naphtoylamine residue. In addition to the pH–induced evolution of supramolecular aggregation previously reported[1], temperature and ionic strength effects were now investigated, identifying other reversible transitions that involve tubular, twisted ribbon and cone structures (Figure). Because of the aggregate chirality, circular dichroism was used to follow the molecular packing changes of the structures and test the reversibility. Moreover transmission electron microscopy and small angle X ray measurements were performed to determine the aggregate morphologies. The results confirm the peculiarity of the self-assembly behavior of bile salt derivatives that constitute a novel class of rigid surfactants with potential biocompatibility.



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Ordered multilamellar vesicle phase under shear flow

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In a narrow shear rate-temperature range 2D-hexagonal symmetry of small-angle neutron scattering (SANS) patterns were observed in triethylene glycol dodecyl ether ($C_{12}E_3$)/D_2O system, indicating disorder-to-order transition: from multilamellar vesicles (MLVs) to hexagonal close packed arrays of MLVs. The formation of disorder MLV in $C_{12}E_3$/D_2O system was reported at 50 wt% [1]. The disorder-order transition was studied by rheology and time-resolved rheo-SANS. The results were compared tetraethylene glycol dodecyl ether ($C_{12}E_4$)/D_2O system [2]. The hexagonal symmetry of the SANS pattern is due to MLVs hexagonally packed into layers that slide relative to each other under shear flow. This transition can explain rheological behaviors under shear flow of other systems that in different experimental condition can reach the hexagonal close packed array. Ordered MLV phases are rarely observed. They are presumably a signature of a narrow MLV size distribution.

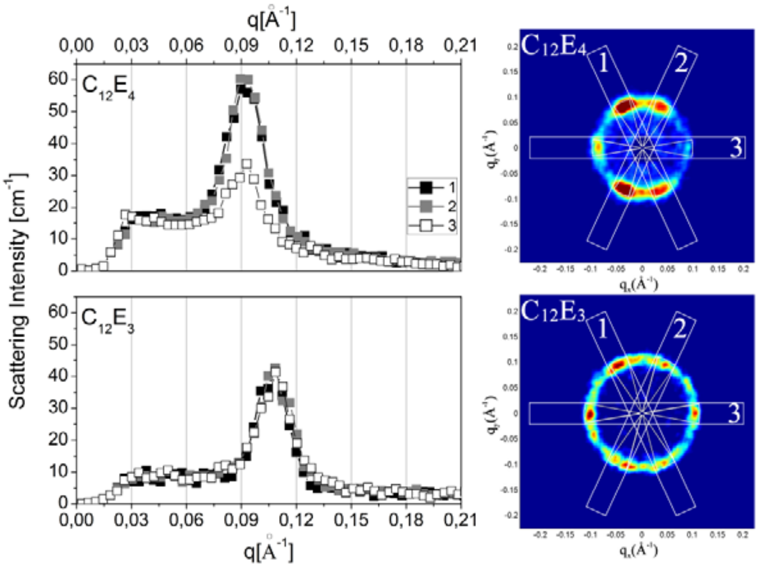

Fig. 1 2D-SANS patterns with radial beam configuration (on the right) and relative q profiles (on the left) in the selected directions where the averaged profiles cover 10 pixel (corresponding to 0.014 Å^{-1}).

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Interfacial Characterization of Pluronic F68 at the Limonene-Water Interface

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Pluronics are non-ionic triblock copolymers, also known as polaxamers, which presents the structure (PEOx-PPOy-PEOx). They have many applications in fields such as cosmetics, pharmaceutical industry, emulsification and foaming. Limonene may be an alternative to benzene-based solvents and others which are being progressively withdrawn from the market due to the increasing concern on SHE (safety, health & environment) hazards.

In this work we provide a characterization of the non-ionic triblock copolymer Pluronic F68 (PEO_{76}-PPO_{30}-PEO_{76}) at the limonene-water interface comprising a systematic analysis of the dynamic and equilibrium surface tension data obtained by means of the drop profile analysis tensiometer PAT-1 (Sinterface, Germany). Surface dilatational rheology results are obtained from the surface tension response to sinusoidal surface area oscillations of Limonene drops emerging in the respective polymer solution.

It is shown that the surface pressure isotherm Π-c displays two different slopes suggesting the existence of different adsorption regimes for F-68 at this interface. The presence of more than one maximum in the surface dilatational modulus vs. interfacial pressure importantly corroborates the idea of the presence of different conformations. Such conformational transitions have been previously reported for various Pluronics at the air-water and hexane-water interfaces (1,2). The adsorption dynamics for different concentration show the presence of an induction time which decreases with increasing polymer concentration. For concentrations above 1.2×10^{-6} M the induction time is lower than the experimental time window and, therefore, it cannot be determined accurately.

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pH of Solutions of Long-Chain (C16, C18) Carboxylates and Their Interpretation in Terms of Precipitation and Micellization

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The experimental concentration dependencies of the pH of carboxylate solutions and the titration curves of fatty acids exhibit kinks and/or inflexion points that are often interpreted as critical micellization concentrations (CMC) or apparent pK_a of the respective carboxylic acid. However, in reality these kinks are due to transitions between different phases (pseudo-phases) formed by the carboxylate in aqueous solutions: micelles, acid-soap crystallites and liquid-crystalline phases. The type of the precipitate present in a given concentration range can be revealed by the method of the precipitate characteristic functions [1]. Our analysis of data for sodium palmitate solutions indicate that with the rise of its concentration they contain precipitates of (i) palmitic acid, (ii) 2:1 acid soap and (iii) coexistent neutral soap + 2:1 acid soap crystallites. Analogous analysis of data for sodium stearate reveals that with the rise of its concentration the solutions contain, respectively, (i) stearic acid and (ii) coexistent neutral soap + stearic acid precipitates. Note that the experimental data have been interpreted by solving the full system of equations, including the corresponding mass-action laws, mass balance and electroneutrality equations. In particular, this system includes the mass-action law for the protonation of the fatty acid, with the true constant value of its p$K_a \approx 4.70$ at 25 °C. At low concentrations, the deviations between theory and experiment are due to uncontrollable dissolution of small amounts of CO_2 (Fig. 1).

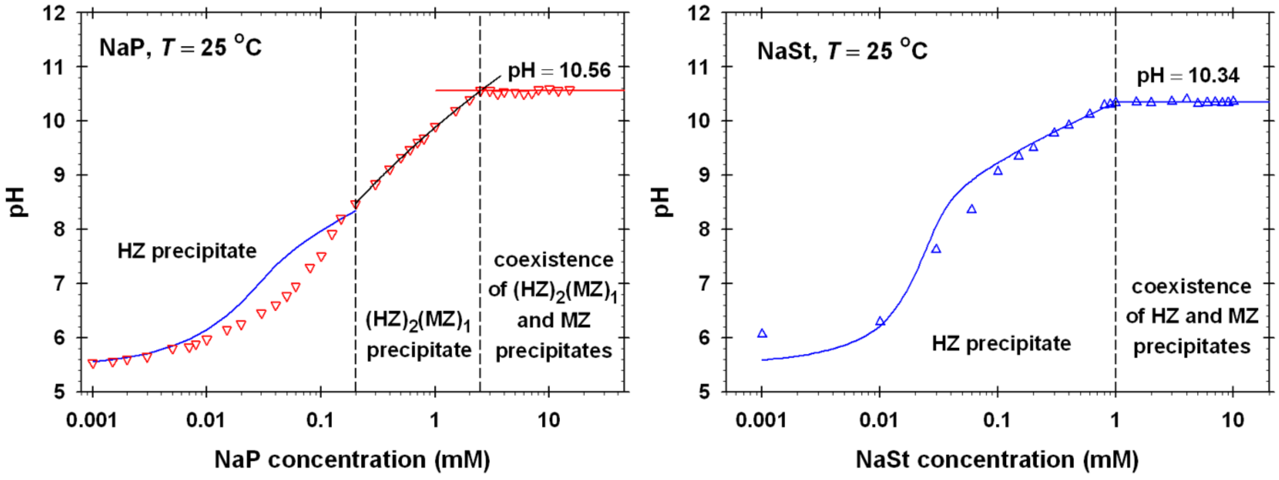

Fig. 1 pH vs. carboxylate concentration for sodium palmitate (NaP) and sodium stearate (NaSt).

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Micellization Behavior of Green Cationic Gemini surfactant with Monomeric Cationic Surfactants

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Mixed micellization properties of the cationic monomeric surfactants of different hydrocarbon chain lengths, cetyltrimethylammonium chloride (CTAC), tetradecyltrimethylammonium chloride (TTAC), dodecyltrimethylammonium chloride (DTAC), and cetylpyridinium chloride (CPC) with an easily cleavable cationic gemini surfactant having ester linked spacer, $C_{12}H_{25}(CH_3)_2N^+(CH_2COOCH_2)_2N^+(CH_3)_2C_{12}H_{25}.2Cl^-$, have been investigated by performing conductivity measurements in aqueous solution [1]. The conductance data were used to obtain the values of the critical micelle concentration (*cmc*) of mixed surfactant systems having different compositions. The *cmc* values show non ideality [2]. These values were used to calculate the interaction parameter (β^m) using Regular solution theory for the mixed surfactant system. The effect of hydrophobic chain length and the negative values of (β^m) indicate an overall attractive force in the mixed state. Also, the measured excess free energy of mixing has negative values for all of the systems.

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Acknowledgements:

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Grazing Incidence X-Ray Diffraction Studies of Langmuir Monolayers of Lupane-type Pentacyclic Terpenes

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Lupane-type pentacyclic triterpenes (lupeol, betulin and betulinic acid) are potent natural pharmaceuticals isolated from various plant sources. They are applied as drugs or chemosupressive agents in therapies for different diseases including numerous types of cancer, AIDS, hypercholesterolemia and different viral, bacterial or parasitic infections [1]. All of them possess amphiphilic structure and it is believed that their interaction with mitochondrial and bacterial membranes is responsible for their biological activity. These terpenes form Langmuir monolayers at the water/air interface; thus, Langmuir monolayer technique can be applied for the investigation of their interaction with membrane lipids. In the first step; however, we intended to thoroughly characterize one component monolayers of these compounds. It turned out that the π-A isotherms as well as Brewster angle microscopy images differ significantly depending on the film-forming terpene. To elucidate these findings and investigate the organization of the terpenes' monolayers we applied the diffraction of synchrotron radiation (GIXD method). In all three cases we observed diffraction signals even at low surface pressure, which proves that the investigated terpenes form crystalline phases in their monolayers. For lupeol we observed only one crystalline phase with upright molecules. In the case of betulinic acid two phases are present: crystalline with upright molecules and amorphous formed by tilted molecules. The most complicated situation was observed for betulin – in its film two crystalline phases coexist, even at low surface pressures, a crystalline monolayer with upright molecules and a crystalline bilayer composed of tilted betulin molecules [2].

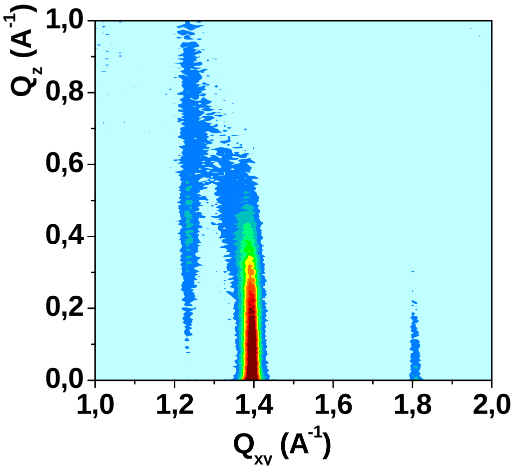

Fig. 1 GIXD intensity map registered for the betulin monolayer.

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Interaction of pentacyclic lupane-type triterpenes with membrane sterols and lipid rafts

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Lupeol and betulinic acid are pentacyclic triterpenes (LT) belonging to lupane family. These terpenes exhibit a wide spectrum of pharmaceutical activity, of which the anticancer properties are intensively investigated. LT are structurally similar to membrane sterols; thus, it is supposed that their incorporation into biomembranes and their further interactions with membrane lipids can be crucial for their pharmaceutical activity. In the present studies we focused on the following problem: can LT incorporate into the lipid rafts and alter their function? To answer this question we applied Langmuir monolayer as a model system in which the interactions of the surfactants of interest can be investigated without the interference of other membrane components. In the first step we studied the interaction between lupeol or betulinic acid with cholesterol or β-sitosterol characterizing the four binary systems within the full range of molar proportions. It turned out that in all cases the systems are non ideal. However, significant differences were observed between betulinic acid and lupeol. The first compound forms miscible films with both animal and plant sterols; whereas lupeol tends to phase separate at higher molar ratios. In the next step we investigated the incorporation of LT into the model rafts composed of sphingomyelin (66 mole %) and one of the sterols (34 mole %). In the subsequent experiments we substituted an increasing amount a sterol with a terpene. The trends observed in the binary systems were also corroborated in the model lipid rafts. The incorporation of betulinic acid into the raft is thermodynamically beneficial (negative values of the excess energy of mixing, ΔG^{exc}); whereas the substitution of a membrane sterol by lupeol has opposite effect ($\Delta G^{exc} > 0$). These results can be correlated with the structure of both terpenes. Lupeol has only one polar group located at the terminus of its hydrophobic moiety; whereas betulinic acid has a bolaamphiphile character possessing two polar groups at two opposite termini of the hydrophobic moiety. The presence of two polar groups allows multiple orientations of betulinic acid at interfaces which gives more options of molecular packing in a multicomponent Langmuir monolayer.

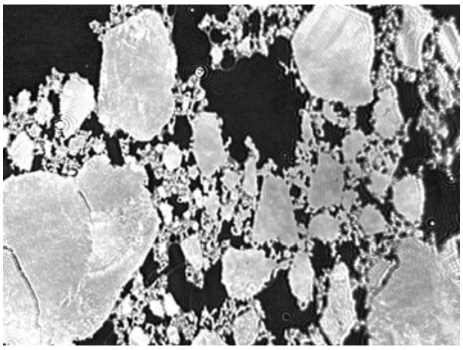

Fig. 1 BAM image of betulinic acid monolayer at 5 mN/m

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Characteristics of lyso-phosphatidylcholines differing in chain length in monolayers at the air/water interface

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Lyso-phospholipids (lyso-PLs) are natural compounds found in cellular membrane in relatively low concentration (0.5 - 6% of total lipid mass); however, their content may increase in some diseases like atherosclerosis, hyperlipidemia, arrhythmia or inflammatory processes.[1] Moreover, it was found that abnormally high concentration of lyso-PLs in lipid bilayers may cause dysfunction of some membrane proteins, e.g. ion channels [2] and in extreme situation may lead to cell lysis. Lyso-PLs are also implicated in a broad range of important cellular processes including signal transduction, gene transcription, mitogenesis and vascular smooth muscle relaxation. Lyso-phosphatidylcholines were also found to be responsible for modulation of the intracellular calcium concentration and are recognized to be a chemotactic factor for monocytes.[3] Despite the vast spectrum of lyso-PLs biological activity, the mechanisms of their action at the level of cellular membrane still remain uncertain and there is an obvious lack of studies devoted to the properties of lyso-PLs in model systems. These facts motivated our studies focused on the physicochemical properties of lyso-PCs. Three representatives of lyso-PLs: C_{18}lyso-PC, C_{22}lyso-PC and C_{24}lyso-PC (Fig. 1) were characterized in Langmuir monolayers by means of surface pressure (π) - area (A) isotherms and with application of modern techniques: X-ray reflectivity (XR) and Grazing Incidence X-ray Diffraction (GIXD).

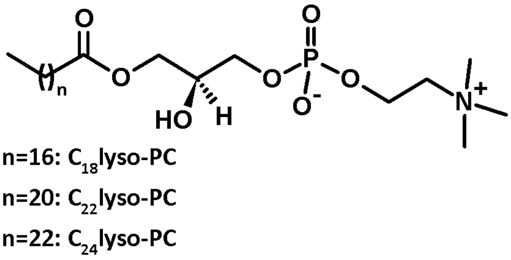

Fig. 1. Structural formulas of the investigated lyso-PCs.

Our studies revealed that the investigated compounds form at the air/water interface stable monolayers of low degree of condensation. It was found that the characteristics of these surface films is strongly affected by temperature modulating phase behavior of the investigated phospholipids. XR experiments proved that the observed phase transitions are connected with the alteration of the immersion of the hydrophobic tail in aqueous subphase during monolayer compression as well as with the changes in hydration of the head-groups. Moreover, GIXD measurements confirmed that in monolayers of C_{22}lyso-PC and C_{24}lyso-PC compressed to high surface pressure (>20mN/m) formation of periodically ordered phases is possible.

Literature:

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Aqueous Phase Behavior of Sodium *N*-Acylglutamates

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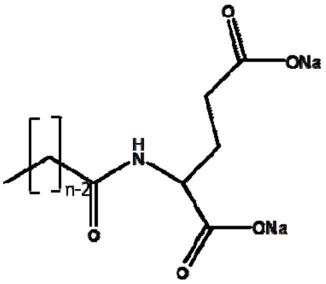
Amino acid-based surfactants have received much attention as an environmentally and human friendly material in the field of personal care applications. Sodium *N*-acylglutamates are typical examples of such amino acid-based surfactants. Their aqueous solution properties have been widely studied in the past$^{1)}$. However, such studies mainly focus on the solution properties in their low concentration region. To the best of our knowledge, no systematic study concerning their aqueous temperature-concentration phase diagram has been reported. In this work, we have studied the aqueous phase behavior of sodium *N*-acylglutamates abbreviated as *n*-Glu (*n* is the hydrocarbon chain length, 8, 10, and 12). The chemical structure of *n*-Glu is shown in **Fig. 1**.

Fig. 2 shows the aqueous phase diagrams of *n*-Glu at 25 °C as a function of surfactant concentration. The solution pH was fixed at 7, where the two carboxylic acid headgroups are expected to be fully neutralized by Na^+. These phases were determined through the combination of visual appearance observations, optical and polarized microscope observations, and small angle X-ray scattering measurements. For all of the samples used in this study, we observed the following phase change with increasing surfactant concentration; isotropic micellar phase (W_m) – discontinuous cubic phase (I_1) – hexagonal liquid crystal phase (H_1). In the case of 12-Glu, we also observed lamellar liquid crystal phase (L_α) at high concentrations. The concentrations we observed these phase transitions shift to lower direction when the hydrocarbon chain length is increased. These results are rationalized by the concept of critical packing parameter (CPP). That is, the longer hydrocarbon analogues exhibit larger CPP and hence tend to form lesser positive curved molecular aggregates. We will also demonstrate the phase behavior of these surfactants as functions of temperature and pH.



(*n* = 8, 10, 12)

Fig. 1 Chemical structure of *n*-Glu

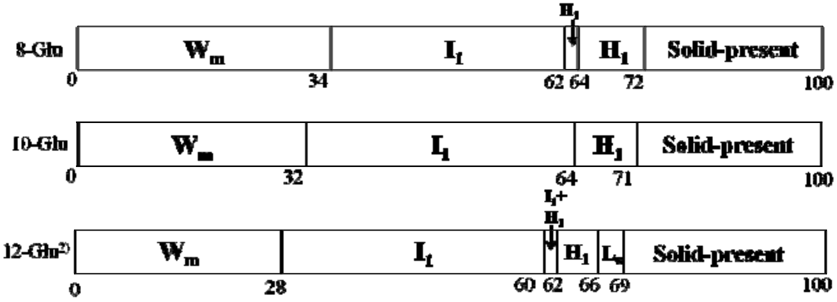


Fig. 2 Aqueous phase diagrams of *n*-Glu as a function of concentration in wt% (at 25 °C, pH 7).

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Acknowledgment:

12-Glu was kindly supplied from Asahi Kasei Chemicals.

Syntheses and Aqueous Properties of Some Anionic Gemini: Surfactants Derived from Oleic Acid

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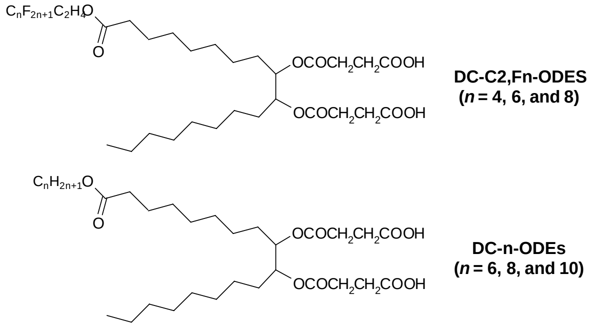
We have developed oleic acid-based gemini surfactants in the last several years in order to provide cost-effective gemini surfactants in the market1). In this work, we have developed oleic acid-based anionic gemini surfactants. The *cis* double bond of oleic acid was modified with carboxylic acid headgroups via disuccinyl units, and either a hydrogenated or partially fluorinated chain is bound to the terminal carbonyl group via an ester unit. Chemical structures of these surfactants are shown in **Fig. 1**. The aim of this study is to understand the physicochemical properties of these surfactants in aqueous media.

In the first step of this study, we measured the aqueous surface tension of these surfactants as a function of concentration. These measurements were performed at pH 9 (adjusted by NaOH) in the presence of 10 mmol dm^{-3} NaCl as a background electrolyte (at 25°C). We summarize the resulting surface tension data in **Table 1**, where one can see the cmc and γ_{cmc} (surface tension measured at the cmc) data of each surfactant. For both of the series of the surfactants, an increased chain length results in lower cmc. This indicates that the increased chain length induces more effective micellization even in the region of low surfactant concentrations as a result of an increased hydrophobic character. In addition, we found that partially fluorinated surfactants tend to lower the cmc and γ_{cmc} values when compared with the corresponding hydrogenated surfactants at a given chain length. We will also demonstrate the temperature-concentration phase diagrams of these surfactants in this conference.



	cmc	γ_{cmc}
	μmol dm^{-3}	mN m^{-1}
DC-C2,F4-ODEs	25	27.8
DC-C2,F6-ODEs	3.4	23.8
DC-C2,F8-ODEs	0.73	22.7
DC-6-ODEs	410	30.1
DC-8-ODEs	40	30.5
DC-10-ODEs	3.7	30.6

Table 1. Summary of surface tension data

Fig. 1 Chemical structures of the surfactants used in this study.

Literature:

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Synchrotron X-ray Scattering techniques for soft matter industrial R&D

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Consumer products based on soft matter technology often exhibit macroscopic properties which are strongly dependent on their micro- and nano-structures extending over multiple length scales. Synchrotron scattering techniques are ideally suited for probing these structures and deliver complementary and in some cases unique information as compared to real space methods like confocal microscopy, cryo-TEM or AFM. The European Synchrotron Radiation Facility (ESRF) is a world-leading synchrotron light source which operates several state-of-the-art instruments for the investigation of soft materials and offers expertise to academic and industrial users. The ESRF supports industrially relevant research both via collaborations/partnerships with industry, as well as through proprietary experiments. For the investigation of complex multi component systems, techniques available at several beamlines can be combined. Fast and flexible access with a modular, fine-tuned service is guaranteed. Certain dedicated sample environments which mimic industrial processing conditions are also available.

This contribution will illustrate the state-of-the-art performance of the following synchrotron scattering techniques by recent examples of industrial relevance.

Simultaneous small and wide angle X-ray scattering (SAXS/WAXS) is a powerful method to determine the microstructure and phase behavior of multi-component systems like detergents, food products, pharmaceutical components, etc. The high photon flux translates to high throughput measurements, while the high degree of collimation and resolution permit to elucidate a wide range of length scales from a few Angstroms up to micron scale.

Scanning microbeam SAXS/WAXS and single micro-crystal/fiber diffraction (µXRD) allows testing the local nanostructure of very small objects like micro-specimens of composite organic/inorganic materials, teeth, bones, micromechanical parts, polymer fibers, micro fluidics, etc. with micro- or nanometric real space resolution.

X-ray reflectivity (XR) and grazing incidence diffraction/scattering (GID /GISAXS) can reveal the nanoscale structure and complexity of nano-structured complex fluids at interfaces, organic films, biological membranes, etc.

The ongoing ESRF Upgrade program will further enhance the user support in the field of applied soft materials and new infrastructure such as the Technology Platform will provide complementary sample characterization capabilities and allow optimal preparation for cutting-edge synchrotron X-ray experiments.

Swelling of Polyelectrolyte Multilayers with Ionic Liquid

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Due to controlled thickness as well as high chemical and mechanical stability Polyelectrolyte Multilayers (PEM) are promising material as ion conducting membrane [1]. Incorporation of suitable electrolyte solvents could possibly enhance the ionic conductivity in PEM for application in Li batteries. The best known electrolyte solvent is Ionic Liquid (IL) due to high conductivity, wide electrochemical window, and non-volatility. Hence, the combination of PEM with IL will be a novel electrolyte solvent system to study.

To study the proposed system, we opt a simple condition where we investigate the swelling of PEM with aqueous solution of IL. Quartz Crystal Microbalance (QCM-D) has been used for the multilayers preparation and in-situ swelling of PEM with IL solutions, Fig 1. PEM are prepared with different combinations of polyelectrolyte, employing PEI(PSS/PAH)$_4$PSS and PEI(PSS/PDADMAC)$_4$PSS. Two water-soluble ILs, i.e. 1-Hexyl-3-methylimidazolium chloride (HMIM) and 1-Methyl-3-methylimidazolium chloride (EMIM), are used for the swelling study. An enhancement of mass coverage and dissipation is found for films in contact with each solution of IL, suggesting incorporation of IL into the films, accompanied by film swelling. Swelling increases with increasing concentration of IL solution. We always find reversible swelling up to a stability limit concentration of IL solution and then irreversible layer decomposition starts. Generally, the overall swelling can be divided into a fast and a slow process of IL uptake and chain reorganization or layer decomposition, respectively. Though for each system absolute swelling and swelling limits are quite different, there is a general qualitative swelling behavior. The swelling can be attributed rather to hydrophobic than to ionic interactions, since we find a correlation of the degree of swelling with the hydrophobicity of the ILs, which can furthermore be compared to swelling of PEM with inorganic salt (NaCl), see Fig 2. Further ATR-IR spectroscopy data support such an incorporation of IL into PEM, accompanying the reversible swelling behavior.

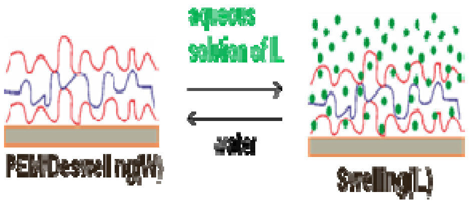

Fig.1 Swelling of PEM with IL

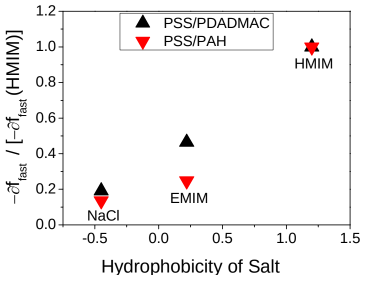

Fig.2 Swelling dependence on hydrophobicity of salt/IL.

Literature:

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Liposomes for Complexing DNA in Gene Delivery

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Amphiphilic surface-active-agents have the ability of self-organization in solvents, forming self-assemblies with a large variety of morphologically different structures. One type of these structures is liposomes. They are formed from phospholipid molecules and are called lipid vesicles. Their structure is defined as a lipid bilayer with the hydrophobic chains of the lipids forming the bilayer and the polar head groups of the lipids oriented towards the extravesicular solution and inner cavity. Liposomes can be prepared by thin film method. In order to control their size and lamellarity, traditional methods, extrusion and sonication, are used. Surface charge of the system can be adjusted by changing the amount of different types of phospholipids used.

Liposomes are similar to cell membranes thus, they are very promising systems for gene-delivery. They can easily fuse with the cell membranes to release their encapsulated materials into the cell. In addition to their high transfecting efficiency, they can have low toxicity depending on their phospholipid types in liposomal structure.

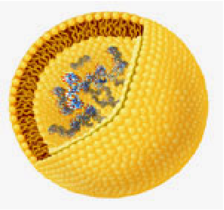

Figure1. Genetic material encapsulated into the liposome

In recent years, anionic lipids have been widely under investigation as a potential gene delivery vector. Since they are the naturally occurring components of eukaryotic cell membranes, they are expected to be non-toxic in vivo and in vitro. Due to the electrostatic repulsion between them, liposomes formed by the anionic lipids cannot directly form charge complexes with naked DNA efficiently. This problem has necessitated the development of a new class of formulations to achieve the complexation between the anionic lipid and DNA. Some researchers aim to have sufficient transfection efficiency with low cytotoxicity in the presence of complexing mediators like divalent and/or monovalent cations and cationic polyelectrolytes, polymers, and dendrimers.

This work involves the study of anionic liposomes that are composed of DMPC (zwitterionic phospholipid), DMPG (anionic phospholipid) and cholesterol as a co-lipid, complexing with DNA in the presence of divalent cations and Ca^{+2}. By the help of cationic mediators, the transfection efficiency and toxicity will be analyzed on the targeted cell populations.

The Equations of the Adsorption Activity and Differential Isosteric Heat of Adsorption

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The adsorption activity ($G_a=da/dc$) adsorbents as surface activity of surfactants ($G=d\gamma/dc$) by the Gibbs equation is the important thermodynamic characteristic (a is value adsorption, γ is surface tension, c is concentration). For nonporous and porous adsorbents the equations of isotherms of the adsorption activity (Ga) and differential isosteric (by θ=constant) heat of adsorption (q_{st}) in various model approximations (Henry, Langmur, BET etc.) are received (the table).

Table. The equations of isotherms of the adsorptions, the adsorption activity G_a pure the differential isosteric heat of adsorption q_{st}.

Authors of the adsorption isotherms	Adsorption isotherms	* Isotherms of the adsorption activity	* Isotherms of the differential isosteric heat of adsorption
Henry	$\theta=K_HP$	$G_a=K_H$	$q_{st}=q_0$
Frandlih	$\theta=KP^n$	$G_a=nKP^{n-1}$	$q_{st}=q_0/n$
Langmur	$\theta=KP/(1+KP)$	$G_a=K/(1+KP)^2$	$q_{st}=q_0$
BET	$\theta=Cx/[(1-Cx)(1+(C-1)x)]$	$G_a=C/[1+(C-1)(1-x)^2$	$q_{st}=q_0(1-x)^2/(1-x^2+Cx^2)$
Huttig	$\theta=Cx(1+x)/(1+Cx)$	$G_a=C/[1+(C-1)(1-x)^2$	$q_{st}=q_0(1+x)/(1+2x+Cx^2)$
Aranovich	$\theta=Cx/[(1-Cx)(1+x)^{1/2}]$	$G_a=(1-2P+KP^2)/[2(1+KP)(1-P)^{1,5}$	$q_{st}=q_0[2(1-x)]/(2-x+Cx^2)$
Kisarov	$\theta'=Bx^n/(1+Bx^n)$	$G_a=nBP^n/P(1+BP^n)^2$	$q_{st}=q_0/n$
Makarevich	$\theta=Kx^{1/g}/(1+Kx^{1/g})$	$G_a=KP^{1/g}/g\,P(1+KP^{1/g})^2$	$q_{st}=gq_0$
Dubinin–Astakhov	$\theta'=\exp\{-\{\ln x/[(\ln(x_{\theta=1/e})]\}^n\}$	$G_a=-(n/x\ln x)\cdot(\ln x/\ln(x_{\theta=1/e})^n\cdot\{\exp[-(\ln x/\ln(x_{\theta=1/e})^n]$	$q_{st}=-q_{\theta=1/e}(\ln x/\ln(x_{\theta=1/e})$

The note: $x=P/P$ *is relative* pressure; $\theta=a/a_m$ (a is the current adsorption, a_m is the maximum value adsorption); $\theta'=a/a_0$; K, C, B is constants of equilibrium adsorption; n is adjust parameter; q_{st} is isosteric of differential heat of adsorption; $^*g=1-\beta_{ord}+\alpha_{nord}(\nu-1)$ is the Generalized Non-ideality Factor, β_{ord} and α_{nord} is thermodynamic probability of an order (association) and the disorder (dissociation) in system, the ν is number of particles to which breaks up (dissociates) a system element; "By the way ***g*** can be defined from the relation of experimentally found and theoretical values P, ΔP, ΔT_C,, π following of classical laws, i.e. $\boldsymbol{g}=\mathrm{P}_{real}/\mathrm{P}_{id}=\Delta\mathrm{P}_{real}/\Delta\mathrm{P}_{id}=\Delta\mathrm{T}_{real}/\Delta\mathrm{T}_{id}=\pi_{real}/\pi_{id}=(\sigma_0-\sigma_{real})/(\sigma_0-\sigma_{id})=(S_m^{real}-S_m^o)/(S_m^{id}-S_m^o)=(C_m^{real})/(C_m^{id})=\ldots$ here P,π is a pressure, T – abs. temperature, σ – a surface tension, S_m– "square of molecule", C_m – heat capacity, indexes "*real* " and "*id*" are real and ideal processes accordingly. In principle the way of experimental definition ***g*** is indicated"; $q_o=-RT\ln[(C\cdot\rho_l/\rho_v)+1]$ is beginning (first) heat of adsorption, ρ_v and ρ_l are according to density adsorptive in a condition of vaporous and a liquid.

Relationship between reconstituted vesicle size and the transmembrane protein to lipid ratio

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Reconstitution of detergent-solubilized transmembrane (TM) protein into lipid vesicles is performed by the extraction of the detergent from the mixture of detergent/protein/lipid in a buffer [1]. We reconstituted halorhodopsin (NpHR) that is the trimer of the 7TM protein and the light-driven Cl^- pump originated from Natronomonas pharaonis [2] to study the change in the membrane permeability induced by the protein insertion and control the trimer formation of the 7TM proteins in the membrane. When NpHR was reconstructed using 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), it was found that the size distribution of the resultant vesicles depended on the molar ratio of NpHR and DMPC. To clarify the relationship between the vesicle size and the TM protein to lipid ratio, the present study was devoted.

NpHR (ca. 3 μM) solubilized by the 2.25 mM TritonX-100 was mixed with DMPC in the 0.1 mM Tris-HCl buffer (pH 7.5) containing 150 mM NaCl. To remove the TritonX-100, the detergent-adsorbent (Bio-Beads) was then added (4 times) every one hour until the weight ratio of TritonX:Bio-Beads was reached to 1:40. All the procedures were made at room temperature.

The distribution of the vesicles reconstructed without NpHR depended on the DMPC concentration. At 0.3 or 0.6 mM DMPC, the distribution peak was ranged from 100 to 150 nm (Fig. 1a, b, black), but the size was distributed in a wide range at 1 mM (Fig. 1c, black). When the reconstruction was carried out with NpHR, the distribution differed. Aggregations were observed at 0.3 mM DMPC (NpHR:DMPC = 1:104), indicating that the amount of DMPC was too less to form vesicles with NpHR (Fig. 1a, green). At 0.6 mM DMPC (NpHR:DMPC = 1:208), the distribution was rather narrow (peak at 500 nm), suggesting that uniform amount of NpHR was inserted into each vesicle (Fig. 1b, green). At 1 mM DMPC (NpHR:DMPC = 1:346), the broad distribution was observed (Fig. 1c, green). This would imply that, together with the vesicles inserted with NpHR, an excess DMPC formed vesicles without NpHR with the broad size distribution as in Fig. 1c black. These results suggest that the insertion of NpHR narrows the size distribution of the reconstructed vesicles at 500 nm at a certain NpHR/DMPC ratio. To discuss whether the above interpretation is fair or not, the reconstructions using a different lipid at a different temperature were also performed.

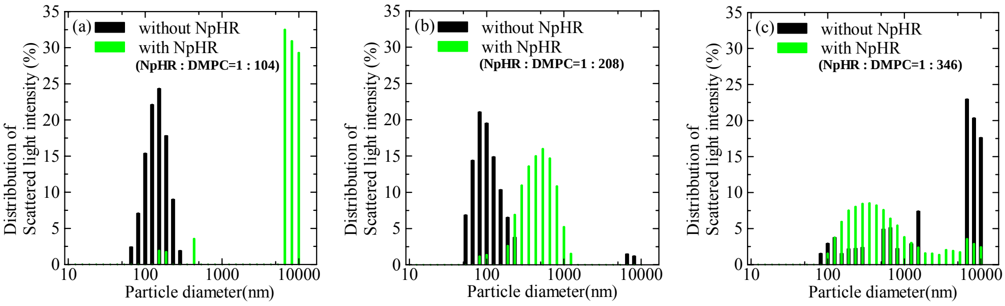

Fig.1 Size distribution of the reconstructed vesicles. The concentrations of DMPC were (a) 0.3, (b) 0.6, and (c) 1.0 mM.

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2. T. Sasaki, N. W. A. Razak, N. Kato, Y. Mukai *Biochemistry* 51 (2012) 2785-2794.

Control of Helical Peptide Orientation in the Langmuir-Blodgett Monolayers

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Polypeptides self-organize into functional proteins, such as transmembrane proteins, due to their advanced self-organization ability. To introduce such self-organization ability to the Langmuir-Blodgett (LB) technique, we are aiming to obtain the LB films consisting of α-helices with controlled orientation. We had proposed amphiphilic peptides (AP), which are constituted by the hydrophilic and hydrophobic domains, and their helical orientation in the LB films had been investigated [1,2]. When the polyelectrolytes were used as the cross-linking agent for the APs, the vertical oriented helical APs were obtained. However, without the polyelectrolytes, the control of their orientation was not successful. The present study has been showed that the use of the subphase (41.5 °C), whose temperature was rather high in the ordinal LB technique, provided an opportunity to control the orientation of helical APs without the cross-linking agent.

The amino-acid (AA) sequence of the AP used was NH_2-KKKALALAAAALWLAAAALALA -$CONH_2$ (AP3-19). Three lysine (K) residues consist of the hydrophilic domain and the underlined AAs indicate the hydrophobic domain. The 5 mM citric acid buffer (pH6.0, 41.5°C) was used as the subphase, and the AP LB monolayers (Z-type) were deposited by the vertical dipping method. The orientation of the helices in the LB monolayers was analyzed by the circular dichroism (CD) spectroscopy, and their surface morphologies of the monolayers were observed by the atomic force microscope (AFM).

The π-A isotherm (Fig. 1) showed a plateau around π = 24 mN/m, suggesting that a phase transition occurred. Such clear plateau was not observed below 41.5°C. According to the CD spectra of the AP LB monolayers, the orientation of the helices was dramatically changed around the plateau region, and the tilt angles of the helical axis from the normal axis of the monolayer were 90, 66 and 52° at the deposition pressures of 22, 24, and 26 mN/m, respectively. The AFM images (Fig. 2) revealed that the significant change in the surface morphology also occurred around 24 mN/m. The structures of the obtained LB monolayer as well as the further possibility of control of the helix orientation using AP3-19 and its analogues will also be discussed.

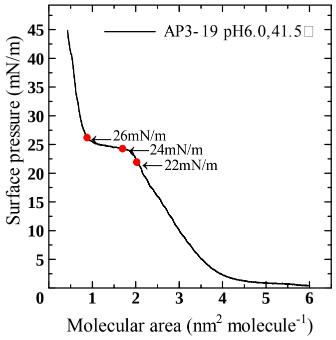

Fig. 1 π-A isotherm of the AP3-19 monolayer.

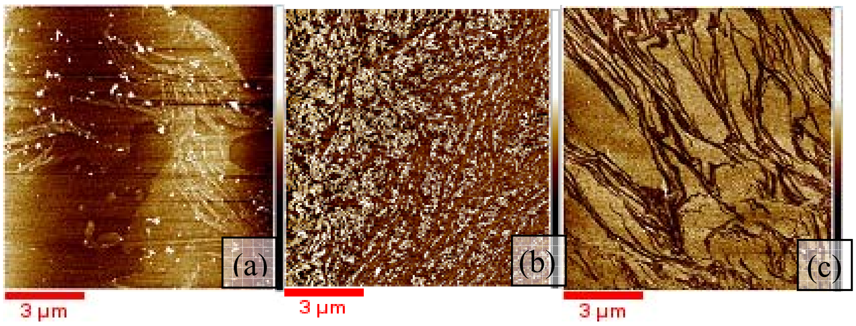

Fig. 2 AFM images of the AP3-19 LB monolayers deposited at (a) 22mN/m, (b) 24mN/m, and (c) 26mN/m.

Literature:

1. K. Togashi, et al, *Journal of Nanoscience and Nanotechnology* 12, 568-572 (2012)
2. K. Togashi, et al, *e-Journal of Surface Science and Nanotechnology* 10, 379-387 (2012)

Thermodynamics and Structure of Nonionic Surfactant Monolayers at the Air/Water Interface. Quantum Chemical Approach

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Morphological features of surfactant crystalline monolayers at the air/water interface are of interest for such spheres as biology and physics of membranes and interfaces as the structural arrangement of molecules defines the properties of obtained films and their further use. The aim of present study is to show that using quantum chemical approach it is possible to reproduce the structural parameters of the unit cells for a number of nonionic surfactants. This is illustrated on the example of two classes of amphiphilic compounds: fatty carboxylic acids $C_nH_{2n+1}COOH$ (n=7-16) and fatty alcohols $C_nH_{2n+1}OH$ (n=6-16).

The simulations are carried out using quantum chemical semi-empiric software package Mopac 2000 and Mopac 2012 in the framework of PM3 method. It is shown that the molecules of carboxylic acids can orientate either angularly t_1=15° (‘tilted’ monolayer) or t_2=2° (‘untilted’ monolayer) with respect to the normal to the air/water interface. The parameters of the hexahonal unit cells for these films are the next: $a_1 = 8.0 – 8.2$ Å; $b_1 = 4.2 – 4.5$ Å and $a_2 = 7.7 – 8.0$ Å; $b_2 = 4.6$ Å respectively. Calculated data for both ‘tilted’ and ‘untilted’ monolayers are in good agreement with corresponding experimental data[1]: $a_1 = 8.4 – 8.7$ Å; $b_1 = 4.9 – 5.0$ Å, $t_1 = 20°$ and $a_2 = 8.4$ Å; $b_2 = 4.8 – 4.9$ Å, $t_2 = 0°$. As opposed to carboxylic acids, fatty alcohols form the hexagonal monolayer with only nearly up-right oriented molecules. It can be caused by the fact that the size of the alcohol functional group is the smallest among the number of the amphiphilic compounds. The geometric parameters of alcohol unit cell are calculated to be: a = 7.4 Å; b = 4.3 Å, t = 3°, agree well with available experimental data[2]: a = 7.5 Å; b = 5.0 Å, t = 7°.

For mentioned film structures the thermodynamic parameters of cluster formation are calculated. On the basis of this array the correlation dependencies of enthalpy, entropy and Gibbs’ energy of cluster formation on the number of intermolecular pair CH···HC interactions and functional group interactions are obtained. It is shown that the spontaneous cluster formation of carboxylic acids at the air/water interface at standard temperature is thermodynamically preferable for molecules possessing at least 13 carbon atoms in the chain. For fatty alcohols this threshold is 11 carbon atoms. These values also agree well with existing experimental data.

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Dynamic Surface Properties of Mixed Protein-Polyelectrolyte Solutions

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The interaction between proteins and polyelectrolytes can lead to the formation of soluble complexes, aggregates and coacervates. The interest in these systems is caused by their applications in various branches of industry. The dynamic surface elasticity of the solutions of the mixture of bovine serum albumin (BSA) with sodium polystyrene sulfonate (PSS) or poly(dimethyldiallylammonium) chloride (PDMDAAC) was measured by the oscillating ring method [1]. A local maximum of the kinetic dependencies of the dynamic surface elasticity and the increase in the rate of change of surface properties were observed in the range of pH corresponding to opposite charges of the protein and polyelectrolyte. The acceleration of the adsorption can be connected with the decrease of the charge of protein/polyelectrolyte complex and hence with the decrease of the electrostatic adsorption barrier. The maximum of the surface elasticity indicates the beginning of the partial destruction of protein tertiary structure in the surface layer. At pH values corresponding to the same charges of the protein and polyelectrolyte, the additions of PSS and PDMDAAC have different effects on the dynamic surface properties of BSA solutions. The addition of PDMDAAC does not influence the dynamic surface properties of protein solution at pH below the isoelectric point of BSA. The PSS addition to the protein solution leads to the decrease of the rate of the change of surface properties. The strong deceleration of the adsorption process in this case is probably caused by the increase of the negative charge of the complex. The dependence of the surface elasticity on the surface pressure for the mixed solutions coincides with the corresponding dependency for the solutions of pure protein thereby indicating that the polyelectrolyte influences only the adsorption kinetics but not the surface structure.

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Acknowledgements:

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Micellar behavior of gemini surfactants of bis(tetradecyldimethylammonium)hexane and bis(tetradecyldimethylammonium)decane

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We have synthesized gemini surfactants of bis(tetradecyldimethylammonium)hexane (14-6-14,2Br$^-$) and bis(tetradecyldimethylammonium)decane (14-10-14,2Br$^-$). Their solution properties were investigated by surface tension measurement at 288.2, 298.2, and 308.2 K. The surface tension measurement was employed the drop volume method, not the Wilhelmy method. From change in surface tension against concentration, the critical micelle concentration (cmc), surface excess amount (Γ), apparent molecular surface area (A), and –log (concentration to reduce surface tension of water by 20 mN m^{-1}) (pC_{20}) were determined. The surface tension of aqueous solutions of gemini surfactants at quite low concentration is known to be difficult to be accurately measured. In the present study, the modified drop volume tensiometer produced the value near 70 mN m^{-1} at low concentrations as seen in typical surfactant solutions. In addition, electrical conductivity of aqueous solutions of the two surfactants was measured at 288.2, 298.2, and 308.2 K. The cmc and the degree of ionization of the micelles were determined from the slopes of the two intersecting lines below and above the break in the conductivity − concentration plot. The cmc values determined by the tensiometer are agreed well with those by the conductivity. The standard Gibbs energy, enthalpy, and entropy of the micellization process were also estimated.

Double chained amphiphilic polyoxometalate: self-aggregation in water

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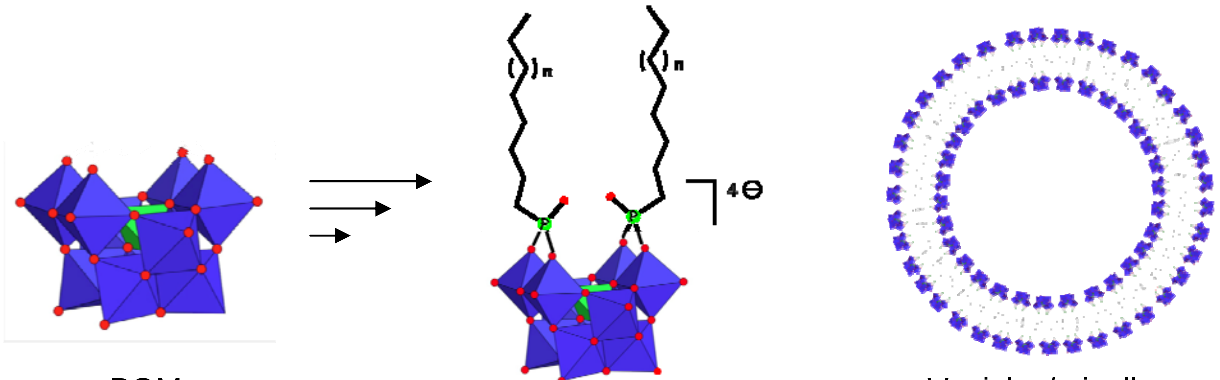
Development of surfactants exhibiting catalytic properties is a crucial issue since their localisation at liquid interfaces is likely to increase both the water-oil compatibility and the kinetics of the catalytic reaction [1]. Polyoxometalates (POMs) are oxo-clusters with versatile structure and properties (shape, size, charge, etc…)[2].They have shown numerous applications in medicine, analytical chemistry and materials science thanks to their relevant properties among them catalytic properties are noteworthy.

New class of POMs surfactants composed of two alkyl chains covalently bound to a tungstosilicate POM ($[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ or $[\alpha\text{-A-SiW}_9O_{34}]^{10-}$) by varying the alkyl chain length (C8, C10 and C12) have been synthesized, see Fig.1. Their aggregation properties are of significant interest for understanding the basics of self-aggregation in relation to their catalytic properties. In water, depending on surfactant concentration, salinity or temperature, vesicles or micelles are formed. By coupling small angle X-rays scattering (SAXS), static and dynamic angle dependant light scattering (SLS/DLS) and freeze fracture - transmission electron microscopy (FF-TEM), aggregation behavior is investigated and resumed in this communication.



POM
$\gamma\text{-}[SiW_{10}O_{36}]^{8-}$

Amphiphilic POM
n=8,10,12

Vesicles/micelles
SLS/DLS, SAXS
FF-TEM

Fig. 1 New class of alkyl covalently bound amphiphilic POM that spontaneously form vesicles or micelles in water.

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A Theta-Shaped Amphiphilic Cobaltabisdicarbollide Anion – A Surprising Self-assembly In Water

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We present a new class of molecules from the family of carborane: the metala-bis-dicarbollide. The cobalta bis-dicarbollide or COSAN is an anionic cluster composed of bore, carbon and hydrogen, highly stable from chemical and thermal points of view with a cobalt cation at the centre. This entity is partly hydrophobic at its two poles and shows hydrophilic behaviour because of its delocalised charge in its equatorial plan that is counterbalanced by hydronium ion (**Fig.1**).

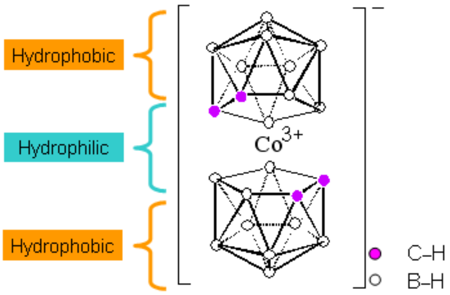

Fig .l Representation of a COSAN

Numerous and important applications have been developed such as in nuclear field the radionuclide co-extraction or in medicine for its inhibition property towards the HIV protease. We present here a fundamental study of this molecule in terms of self-assembly in water. From SANS and SWAXS experiments, absorption spectroscopy and TEM characterization we have evidenced the formation of large vesicles at very low concentrations. COSAN show surface activity and formation of small micelles by increasing concentration caused by a strong Coulombic interaction[1]. The chemistry of substitution on the bore atoms is rich due to the geometric distribution and the availability of the B-H complexing site at the surface of the cage. By exchanging two H by I, a gel with a highly ordered lamellar structure (Lα or Lβ types) of monolayers is observed by SWAXS.

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Study of adsorption behavior of alcohols ethoxylates (C_iEO_j) at the water/dibutoxymethane (DBM) interface. Formation of aggregates in the organic solvent

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The surface activity of a series of alcohol ethoxylates, C_iEO_j ($j = 3 - 8$) at the interface formed by dibutoxymethane (DBM) and water has been evaluated. Plots of interfacial tension γ_{int} against surfactant concentration show a clear breaking point that has been associated to the critical micelle concentration (CMC). The aggregation of C_iEO_j surfactants in DBM is confirmed by fluorescence probing measurements using sodium pyrenesulfonate (Py–S) as fluorescent probe. Similar values of CMC were obtained by both methods. The results show that the effectiveness in decreasing γ_{int} at this interface, Π_{CMC}, of C_iEO_j depends on the surfactant structure i.e. increases by increasing *i* and *j* (see Table 1). The dependence of Π_{CMC} with the effectiveness of adsorption, Γ_m, the efficiency in reducing γ_{int}, pC_{12}, and the critical micelle concentration *CMC* is discussed. The area per molecule in the saturated interface is three times higher for non linear C_iEO_j surfactants (see Table 1). This difference is attributed to the *–iso* group which avoids the parallel orientation of the chains into the DBM phase. For $C_{10}EO_j$ the free energies of adsorption and micellization have been obtained as a function of *j*. The results indicate that adsorption is favored in front of the aggregation process.

Table 1: Π_{CMC}, a_m^{int}, CMC, pC_{12}, linear and iso C_iEO_j surfactants

Surfactant	Π_{CMC}	a_m^{int} (Å^2)^a	CMC, mM^b	pC_{12}
$iso\text{–}C_{10}EO_3$	12.9	97	8.0	2.01
$iso\text{–}C_{10}EO_5$	13.6	104	4.3 (4.2)	2.54
$iso\text{–}C_{10}EO_6$	14.8	88	2.5 (2.6)	2.78
$iso\text{–}C_{10}EO_8$	16.1	86	1.5	2.81
C_8EO_4	10.2 (36.2)	62 (98)	8.5	1.97(5.26)
C_8EO_5	11.3 (42.9)	67 (109)	7.0	2.05(5.46)
$C_{10}EO_3$	18.7 (42.6)	32 (82)	9.0 (10.7)	2.17(5.41)
$C_{10}EO_4$	15.9 (43.3)	46 (87)	5.6	2.20(5.81)
$C_{10}EO_5$	11.5 (42.8)	22 (82)	4.5	2.25(6.11)

a) Values in parenthesis are from reference 2

b) The CMC were determined by fluorescence probing method. Values in parenthesis were obtained from interfacial tension measurements

Micellar and Interfacial Studies of Surface Active Ionic Liquid in Cationic Surfactants

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Many of the room temperature ionic liquids (RTIL's) are emerging as novel surfactants due to amphiphilic nature and have been explored for their self-association behavior. Ionic liquids (ILs) composed of 1-alkyl-3-methylimidazolium cation $[C_n\text{mim}]^+$ have been extensively studied in the field of colloid and interface science. Their physical and chemical properties can be tailored by changing the alkyl chain length; polarizability of head group and the nature of anions present. The influence of 1-tetradecyl-3-methylimidazolium bromide (C_{14}mimBr), a surface-active ionic liquid (SAIL) on the micellar morphological changes of cationic surfactants such as tetradecyltrimethylammonium bromide (TTAB), dimethylditetradecylammonium bromide (DTDAB), alkane-bis(tetradecyldimethylammonium bromide) (14-2-14 and 14-4-14) has been observed. The techniques employed were conductivity, surface tension, fluorescence and ^{1}H NMR. The various micellar and interfacial parameters such as critical micelle concentration (*cmc*), degree of counterion binding (*g*), interaction parameter (β^m), surface excess concentration ($\Gamma_{\max}$), minimum area per molecule ($A_{\min}$), aggregation number (N_{agg}), stern-volmer constant (K_{sv}) as well as some thermodynamic parameters such as standard Gibbs free energy of adsorption (ΔG^o_{ads}) and standard Gibbs free energy of micellization (ΔG^o_{m}) have been evaluated. The interactions for IL+ TTAB mixtures are found to be non-ideal and antagonistic. However when the single chain surfactant is replaced by the double chain surfactants the interactions becomes synergistic for the mixtures. The merging and broadening of the peaks for various protons of IL and cationic surfactants suggests the growth of micelles.

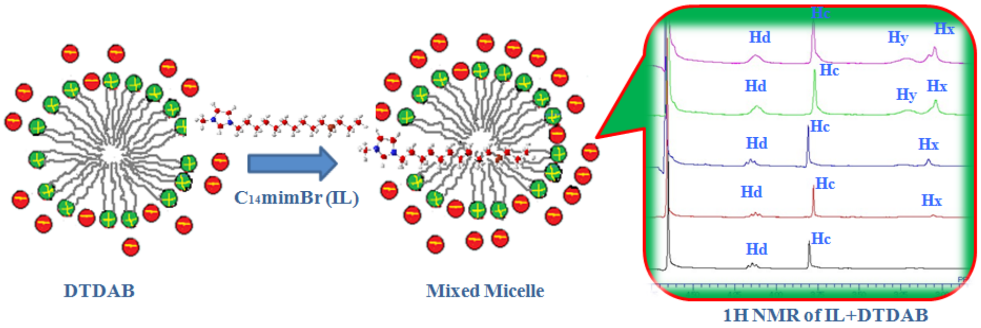

Figure: Penetration of a SAIL in DTDAB micelle and NMR spectra of these mixed systems.

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Influence of Cholesterol on the Elastic Properties of Lipid Membranes

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Thermally induced shape fluctuations of giant quasi-spherical lipid vesicles are used to study the influence of the cholesterol, incorporated in the lipid membranes, on the bending elasticity modulus k_c of the lipid membrane. The influence of cholesterol is investigated throughout a considerably wide interval of concentrations. The values of the bending elastic modulus for 10, 20, 30 and 50 mol% of cholesterol in the SOPC membrane are obtained as a mean weighted value of 6-11 vesicles for each system. The dependence of the bending elasticity modulus on the concentration of cholesterol in the lipid membrane is obtained. At low concentration of cholesterol in the SOPC membrane (10 mol %) a decrease of the bending elasticity modulus is observed, compared to pure SOPC membrane. At high cholesterol content (50mol% and above) a twofold increase of the bending modulus is obtained. The data for k_c for mixed SOPC - cholesterol membrane is compared to the results obtained by different methods on different lipid matrices.

Surfactants type C_iE_j Investigated by SANS Method

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The aim of experiment was investigated of aggregation of three non-ionic classic surfactants type CiEj - heptylethylene glycol monodecyl ether ($C_{10}E_7$), heptaethylene glycol monododecyl ether ($C_{12}E_7$) and heptaethylene glycol monotetradecyl ether ($C_{14}E_7$) in D_2O solutions by tensiometric and small angle neutron scattering (SANS) method. The size and shape of micelles in dilute aqueous solutions was determined at finite surfactant concentrations by SANS at several temperatures below the critical point. The SANS results were successfully analyzed with the PCG 2.1 program (from Graz University, prof. Glatter Otto and co-workers) for micellar solutions formulated with the spherical and ellipsoidal and cylindrical micelles. For investigated solutions we used concentrations c=0.17%, 0.5% and 1% at temperatures 10^o, 15^o, 20^o, 25^o, 30^o and 35^oC. The small angle neutron scattering measurements for two surfactants $C_{10}E_7$ and $C_{12}E_7$ were carried out on the "Yellow Submarine" instrument at Budapest Neutron Centre (Hungary) but for surfactant $C_{14}E_7$ was made on 'YuMO' spectrometer of the IBR-2 on pulsed neutron source in the Laboratory of Neutron Physics, JINR, in Dubna (Russia). Measurements have covered Q range from $7x10^{-3}$ to 0.4 $Å^{-1}$. The micellar solutions were prepared in D_2O since the contrast between the micelles and the solvent in neutron experiments is better with D_2O than with H_2O.

Artificial Lipid Membranes on Graphene Oxide (GO) and the Effect of the Reduction degree of GO

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A lipid bilayer is a fundamental structure of plasma membrane, and experimental methods are desired to clarify the behaviors of lipids and proteins during membrane reactions such as the transportation of information, materials and energy [1]. Artificial lipid membranes on graphene and its derivatives are attractive sensing platforms for biomembranes by applying unique graphene-based techniques such as fluorescence quenching assay and solution-gated FET. Here we describe the fabrication of planar lipid membranes on graphene oxide (GO) and reduced GO (r-GO) by the vesicle fusion method, and the effect of the degree of the reduction. The GO flakes were deposited on SiO_2/Si substrates (Fig. 1A), and incubated in the suspension of zwitterionic dioleoylphosphatidylcholine (DOPC) vesicles. The topographies of atomic force microscope (AFM) shows that planar single or double DOPC bilayer membranes were formed on the GO flakes (Fig. 1B and C) [2]. We prepared r-GO by exposing the GO flakes on SiO_2/Si to the vapor of hydrazine monohydrate. XPS spectra showed that oxygen components decreased with the reduction time and temperature. The vesicle fusion of DOPC on r-GO resulted in the formation of single bilayer, adhesive vesicles, monolayer, and bilayer/monolayer stacking structures depending of the reduction degree of r-GO. We also describe the results of fluorescence recovery after photobleaching and single fluorescence molecule tracking of the lipid bilayers on GO to evaluate the membrane fluidity.

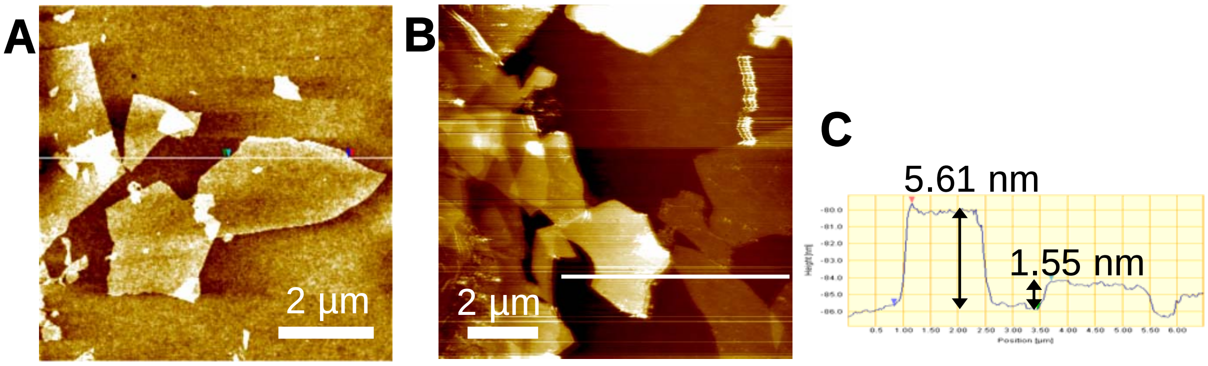

Fig. 1 AFM images of GO flakes on SiO_2/Si (A) before and (B) after the incubation in the suspension of DOPC vesicles. (C) The cross section profile of the white line in (B)

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Synthesis and Investigation of Surface Active Properties of Counterion Coupled Gemini Surfactants

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Three counterion coupled gemini (cocogem) surfactants in the series 1, 6- bis(*N*, *N*-alkyldimethylammonium) adipate, referred as *n*-6-*n* (*n*=12, 14, 16), were synthesized, purified and characterized by ^{1}H NMR and ^{13}C NMR. Their physicochemical properties were investigated by electrical conductivity and surface tension measurements. The degree of ionization, critical micelle concentration (cmc), surface excess at the air/solution interface ($\Gamma_{\max}$), minimum area per surfactant molecule at the air/solution interface ($A_{\min}$), surface tension at the cmc (γ_{cmc}), and pC_{20} (negative log of the surfactants' molar concentration, required to reduce the surface tension by 20 mNm^{-1}) were calculated. Increase in tail length of the surfactants increases the efficiency of surfactants to decrease the surface tension of water. Thermodynamic parameters, viz. molar free energy at the maximum adsorption attained at cmc ($G_{\min}$), standard Gibb's energy of micellization ($\Delta G^{\circ}_{\text{mic}}$), and standard Gibbs energy of adsorption ($\Delta G^{\circ}_{\text{ad}}$), were also calculated. Additionally, fluorescence measurements were used to find the aggregation number. Other relevant surface properties (Krafft point, emulsion stability, foaming ability, micellar stability and dye solubilization ability) were also evaluated. These results suggest that with respect to emulsion formation and micellar stability, the cocogem with 16 carbon chain gives better results and produces more stable foams.

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Discovery of the Unique Solution Behavior of Hydrophilic and Lipophilic Polyglycerol Fatty Acid Esters Generated By the Strong Liopophobicity of Polyglycerols

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Efficient surfactants are generally said to be strongly lipophobic as well as hydrophobic [1, 2]. In this study, two categories of hydrophilic and lipophilic polyglycerol fatty acid esters were investigated to demonstrate the particularly unique solution behavior generated by the strong lipophobicity of polyglycerols compared with polyoxyethylene alkyl ethers. Regarding hydrophilic polyglycerol fatty acid esters of tetraglycerol, hexaglycerol and decaglycerol dodecanoates (nG-D, n=4, 6 or 10), these showed the cmc in *n*-decane, which was 1/200-1/500 lower than that of polyoxyethylene dodecyl ethers ($R_{12}EOn$, n=4, 5, 6, 7 or 8) having the nearly equal Griffin's HLB. In addition, the cmc of nG-D in *n*-decane was almost equal to that in water. However, the cmc of $R_{12}EOn$ in *n*-decane was 10-800 times higher than that in water. These results described that polyglycerol fatty acid esters were extremely lipophobic related to the lipohobicity of polyglycerols as hydrophile parts and these formed self-assemblies such as micelles at the low concentration in not only water but also oils. Moreover, the cloud temperature of nG-D more drastically increased with increase in the HLB than that of $R_{12}Eon$ (**Fig.1**). It meant that the solubility of nG-D in water was largely insensitive toward temperature.

The other category of lipophilic polyglycerol fatty acid esters was also investigated. In the category, polyglycerol phytylacetates (PPA, 5,9,13,17-tetramethyl-4-octadecenoicacid polyglycerolesters) were demonstrated the formation of lipophilic self-assemblies. Of these compounds, diglycerol ester (DGPA) stably formed reversed hexagonal phase (H_2) mixed with water and oil (volatile silicone) at the specific ratio (**Fig.2**). This H_2 when mixed in oil phase with the addition of water achieved W / O emulsion having high internal phase ratio (approximately 90 wt. %). Moreover, the recovery of this W / O emulsion to the original form of H_2 through the phase transition caused by evaporation of water and oil phases was identified.

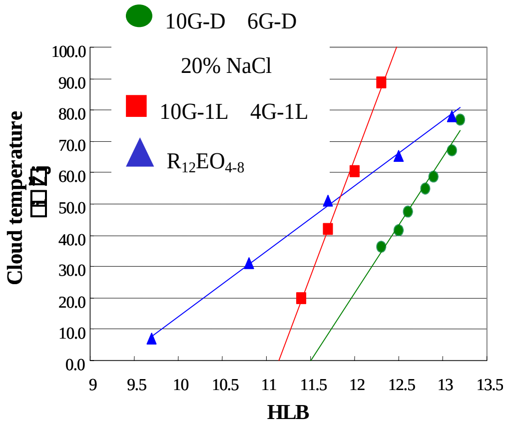

Figure 1 Changes in the cloud temperature as a function of the Griffin's HLB

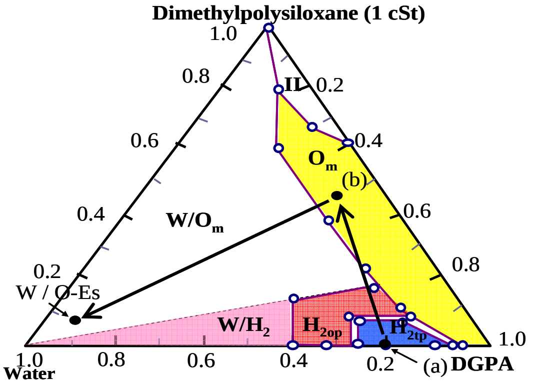

Fig. Phase diagram of DPGA / oil / water system at 25°C
H_{2tp} : Transparent reverse hexagonal phase
H_{2op}: Opaque reverse hexagonal phase
O_m : Reversed micellar phase
II : Isotropic oil phase

Figure 2 Phase diagram of DPGA / oil / water system at 25°C.

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Solubilization capacity of a gemini surfactant of bis(tetradecyldimethylammonium)decane

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Solubilization of *n*-alkylbenzene such as benzene, toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, and *n*-pentylbenzene into micelles of bis(tetradecyldimethylammonium)decane (14-10-14,2Br$^-$) has been investigated, where equilibrium concentrations of all the solubilizates were determined spectrophotometrically at 288.2, 298.2, and 308.2 K. The concentration of the solubilizates remained constant below the critical micelle concentration (cmc) and increased linearly with an increase in 14-10-14,2Br− concentration above the cmc. The Gibbs energy change (ΔG^0) for their solubilization was evaluated by the partitioning of the solubilizates between the aqueous phase and the micellar phase. Furthermore, enthalpy and entropy changes for their solubilization were evaluated from the temperature dependence of the ΔG^0 values. The hydrodynamic diameter of micellar aggregates with or without the solubilizates was also measured by dynamic light scattering. The micellar aggregates greatly grow in size from 3 (no solubilizates) to 100−300 nm (solubilized in equilibrium) at 288.2 K. On the other hand, the size of aggregates become much larger to more than 1000 nm (solubilized in equilibrium) in diameter. From these thermodynamical parameters and the change in absorption spectra of the solubilizates due to their incorporation into the micelles, the detailed solubilization site in the micelles was also examined.

Influence of cobalt ferrite nanoparticles on the bending elasticity and fluidity of lipid membranes

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In recent years, liposomes encapsulated with nanoparticles (NPs) have found tremendous applications in various biomedical fields and medicine, such as drug design and delivery, diagnostics and therapy **(Papazoglou and Parthasarathy 2007)**, **(Tang, Russell, and Khatri 2009)**. These applications require a clear understanding of the effect of encapsulated particles in altering the mechanical properties of lipid membranes. The present work aims to investigate the effect of encapsulation of neutral cobalt ferrite ($CoFe_2O_4$) nanoparticles on elasticity and fluidity of synthetic 1-stearoyl-2-oleoyl-sn-glycero-3-phosphocholine (SOPC) lipid membranes. Thermally induced shape fluctuations of giant quasi-spherical lipid vesicles **(Faucon et al. 1989)** are used to study the influence of NPs, incorporated in the liposomes membrane on the bending elasticity modulus k_c of the membrane. The experimental equipment is improved by the implementation of stroboscopic illumination based on a xenon flash lamp **(Genova and Pavlič 2012)**. The obtained results show that the NPs, encapsulated in the lipid membrane decrease the value of the bending elasticity modulus of the lipid membrane in comparison to the pure lipid membrane. Through the temperature dependent fluorescence anisotropy measurements **(Ota et al. 2012)**, we have found that the entrapment of nanoparticles in the bilayer decreases the lipid transition temperature and increases the membrane fluidity of lipid membranes.

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Acknowledgements:

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Influencing the BSA adsorption to oil-water interface by the use of pH dependent polymer surfactants

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Pharmaceutically active proteins are introduced to various interfaces in most pharmaceutical preparations both during processing and in the final product. The amphiphilic nature of proteins, the folding of hydrophobic groups towards the center in aqueous medium, results in unfolding when introduced to hydrophobic interfaces, in order to reduce the energy in the system. This unfolded form of the proteins can have reduced therapeutic efficacy and in worst cases can induce unfavorable immune reactions. Protein adsorption to interfaces is inevitable but can be reduced using various excipients.

In this study two pH dependent polymers are introduced to the system in order to hinder the model protein, bovine serum albumin (BSA), from adsorbing to the oil-water interface. The two polymers are; a water soluble poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA), and a water insoluble $\text{PDMAEMA-PBuA}_{38700}\text{-PDMAEMA}_{33000}$ (PBuA). Phosphate buffer at pH of 6.6, 7.0 and 7.4 (50 mM) was used as the aqueous phase and Miglyol 812 (coconut oil; medium chain triglycerol) as the oil phase. The protein adsorption was monitored by the utilization of pendant drop for surface tension measurements, and interfacial rheology using double wall ring geometry to study the shear deformation. The oscillatory shear measurements were conducted at 0.1 Hz and strain of 0.1% (within the linear viscoelastic regime). The secondary structure of BSA was investigated using FTIR spectroscopy.

The measured interfacial rheological parameters for BSA were not significantly influence by pH over the range used in this study. The presence of the PDMAEME and the PBuA resulted in a decrease of the adsorption with increasing pH where PBuA was more efficient. The greatest reduction of the interfacial complex viscosity was reached in the presence of PBuA at pH 7.4. Neither the protein alone nor the polymer-protein combinations showed any changes in the interfacial tension regardless of the pH. The secondary structure of the protein was not altered in the presence of the polymers.

PDMAEME and PBuA show promising effect on the hindering of BSA adsorption to oil-water interfaces. This effect was, as expected, dependent on the pH of the formulation. Therefore, strategic choice and design of polymers can be used to prevent the protein unfolding and aggregation when exposed to interfaces and thus potentially improve the therapeutic efficacy of protein drugs.

Surface adsorption properties and liquid crystal formation of nonionic surfactants in ionic liquids mixture

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Surface adsorption properties and phase behavior of nonionic surfactants, phytosterol ethoxlates (BPS-n) in aprotic ionic liquids (ILs) mixture of 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF_6) and 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) were investigated by surface tension measurement, dynamic light scattering (DLS), and small angle X-ray scattering (SAXS).

For surface adsorption properties, the critical micelle concentrations (cmc) were determined in different molar ratio of ILs mixture by surface tension measurement. The obtained cmc values increased almost linearly by increasing bmimPF_6 molar ratio. The size of molecular assemblies evaluated by DLS was about 4-10 nm irrespective of the composition of ILs, suggesting the formation of normal spherical micelles. In addition, the effect of the ILs composition on the adsorption of the surfactant was discussed in terms of the surface adsorption parameters calculated by Gibbs adsorption isotherm.

Regarding phase behavior, the formation of various liquid crystalline phases such as cubic, hexagonal, and lamellar phase was confirmed by SAXS measurement. The mechanism of this phase transition dependent on the IL composition is also discussed in the presentation.

Effect of the Different Amino Acid Hydrophilic Head in the Adsorption Behavior of Eco-Friendly Glycerol Ether Surfactants at the W/A Interface

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Environmentally friendly surfactants are gaining ground in the last decades. Two novel non conventional biocompatible and biodegradable molecules with a glycerol skeleton were synthesized. Both, new molecules have a hydrophobic alkyl chain of 12 carbon atoms conjugated with two different amino acids in the hydrophilic head: phenylalanine ($PhGE_{12}$) and tyrosine ($TyrGE_{12}$). $TyrGE_{12}$ molecule has a phenolic group, viz. a benzene ring with a hydroxyl group, instead of a simple benzene ring in $PhGE_{12}$ molecule. Measurements of dynamic surface tension by maximum bubble pressure tensiometry and drop profile tensiometry are carried out for alkali aqueous solutions over a wide concentration range and for surface ages spanning from milliseconds to hours. CMC values, standard free energies of adsorption and other physicochemical properties are calculated based on static (equilibrium) surface tension measurements. Interfacial dilatational storage modulus and loss modulus measurements have also been conducted. It is found that $TyrGE_{12}$ not only reduces surface tension to much lower values than $PhGE_{12}$ but it also exhibits much faster interfacial adsorption than $PhGE_{12}$. Thus, different polar heads in glycerol ether surfactants can give appreciable differences to adsorption kinetics comparable to effects commonly expected for surfactants with different alkyl chain length.

Aqueous Phase Behavior of Oleic Acid-Based Gemini Surfactants with Alanine-Type Chiral Headgroups

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Gemini surfactants are dimers of monomeric surfactants linked with a spacer at the level of headgroups. One of the key properties of gemini surfactants is the remarkably low critical micelle concentration (cmc) in aqueous media, which enables us to reduce the total consumption of surfactants in waterborne chemical products. Nevertheless, the number of commercially available gemini surfactants is very limited because the synthesis and subsequent purification process is generally more complicated than that of conventional monomeric surfactants.

Based on this background, we have developed oleic acid-based gemini surfactants in the last several years in order to provide cost-effective gemini surfactants in the market[1)]. In this study, we introduced alanine-type headgroups to the *cis* double bond of oleic acid. Chemical structures of the surfactants synthesized in this study are shown in **Fig. 1**. We obtained two surfactant samples whose chirality of the headgroups is different with each other. These samples are abbreviated as DiAla-L-ODEs and DiAla-D-ODEs.

The aqueous temperature-concentration phase diagrams of the surfactants were examined through the combination of visual appearance observations, optical and polarized microscope observations, and small angle X-ray scattering (SAXS) measurements. From these measurements, for both of the two surfactants we observed a micellar solutions below 54wt %, and then the micellar phase was changed to a lamellar phase. We will demonstrate such phase transitions in order to see if the difference in the chirality makes a significant impact on the phase behavior.

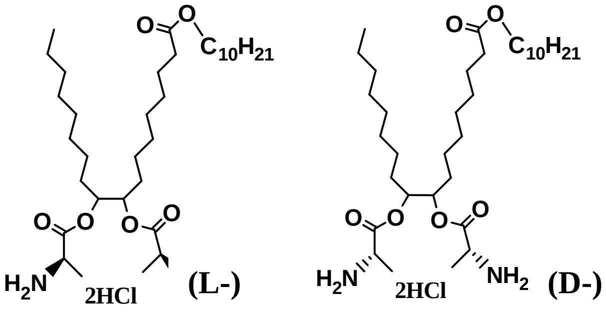

Fig.1 Chemical structures of DiAla-L(D-)ODEs

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Preparation of Water-toluene Nanoemulsion Stabilized by β-sheet Network of Amphiphilic Peptide-blockpolymer

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Emulsions with droplet size at the nanoscale, so-called nanoemlusions, have promising application in various nanotechnologies such as nanoreactor, DDS, and so on. Formation of nanoemulsions needs rational design of surfactants which can stabilize oil-water interface effectively. We consider to use spontaneous, hierarchical self-assemble property of peptides and considered to incorporate such peptide domain into amphiphilic polymer surfactants, which is a new class of surfactants. In this study, novel ABC type peptide-polymer amphiphile with β-sheet peptide segment as a center unit, poly(styrene)-oligo(leucine)-poly(ethyleneglycol) (PS-oligoleucine-PEG)(**1**) was designed in order to apply its peptide-guided interaction in oil-water interface. Triblock polymer **1** was synthesized via Fmoc solid phase peptide synthesis and atom transfer radical polymerization, amd characterized by GPC and 1H-NMR. Its aggregation property in water or toluene was characterized through FT-IR, AFM, SEM and TEM. Firstly, aggregation behavior of **1** in water dispersion was investigated. CAC was evaluated to be 50 μM by surface tension measurement. Ellipsoidal vesicular aggregates with diameters of 30-100 nm were observed in TEM and AFM images. ATR FT-IR spectrum showed that the peptide segments took parallel β-sheet structure in such aggregates. Subsequently, self-assembling property of **1** in toluene, which was good solvent for PS and PEG, was examined. Spherical aggregates of 50-100 nm in diameter were observed in AFM on mica substrate casted from toluene solution of **1**. ATR FT-IR indicated that triblock polymer **1** also formed parallel b-sheet structure in toluene. From these results, it is concluded that **1** assembled into spherical aggregates both in water and toluene through β -sheet formation. Finally, surface behavior of **1** in O/W system was examined to confirm stabilization at oil-water interface through β-sheet formation of peptide segment. Peptide free PS-PEG was also employed for comparison. **1** and PS-PEG was dissolved in water-toluene (1:200 v/v) emulsion with fluorescent dye Eosin Y as a probe for water droplets dispersed in toluene. Water-toluene dispersion without any surfactants shows phase separation in a few hours but **1** and PS-PEG kept stable dispersion state after 24 h. Interestingly, as shown in Fig. 1 (c), triblock polymer **1** gave clear solution even after 20 days while PS-PEG emulsion showed phase separation, indicating contribution of the β-sheet network on long-term stability of nanoemulsion.

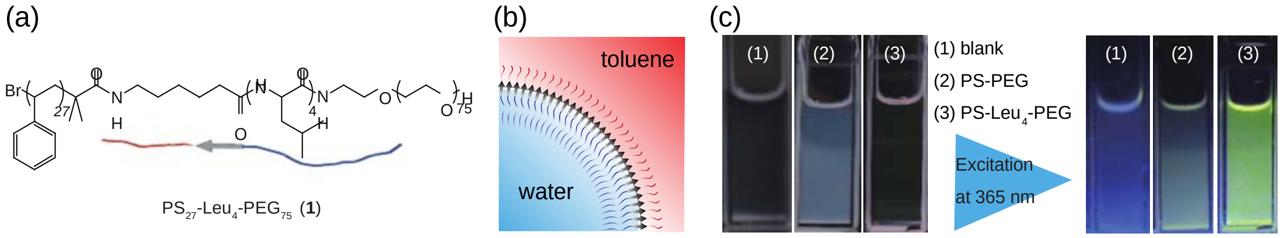

Fig. 1 (a) Molecular design of 1. (b) Schematic representation of nano-droplet stabilized by **1**. (c) Fluorescence of Eosin Y in water-toluene nanoemulsion stabilized with **1** (1), PS-PEG (2), (3) 20 days after prepatation.

Phase Properties and Emulsification Abilities of Long-Chain Monoalkyl Phosphates

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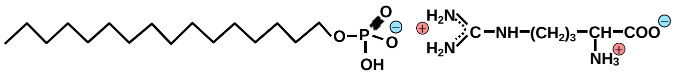
Monoalkyl phosphates are well-known as surfactants for cosmetics and toiletries because of the mildness to skin. However the most industrially available products were sesqui-type in which the chemical composition is the mixture of mono- and dialkyl type. Two types of high purity monoalkyl phosphates, linear hexadecyl phosphate (R_{16}MP) and β-branched hexyldecyl phosphate (R_6R_{10}MP), were synthesized and the phase behavior and emulsification abilities were investigated. Both of them showed unique phase properties by using L-arginine as the counterion.

From the phase study of L-arginine hexadecyl phosphate (R_{16}MP-Arg)/water system, it was found that R_{16}MP-Arg forms stable α-gel below the phase transition temperature (T_C) of 55-60°C whereas it forms hexagonal liquid crystals at above T_C. Though in general, the α-gel is thermodynamically unstable, R_{16}MP-Arg crystal formed the α-gel spontaneously by swelling with coexisting water without heating up to T_C. This suggests the formation of stable α-gel. The α-gel formed the lamellar structure and the long-spacing increased linearly against C/(1-C), where C is the weight ratio of R_{16}MP-Arg. This α-gel forming ability was maintained in the system of R_{16}MP-Arg and fatty alcohol (R_{16}OH) mixture.

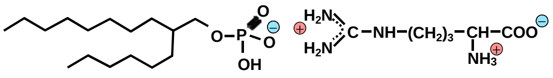
In case of L-arginine hexyldecyl phosphate (R_6R_{10}MP-Arg)/water system, the lamellar LC was formed in quite wide temperature (0 to 100°C) and concentration (about 5 to over 90 wt %) range of R_6R_{10}MP-Arg by reflecting the double chain configuration and ionic property.

These unique properties of phase behavior were considered to be generated due to the bulkiness of L-Arginine as a counterion, and the strong electrostatic interaction between the neighboring molecules which arise from the amphoteric character of ω-moiety of amino acid residue (Fig. 1).

When the LC of R_6R_{10}MP-Arg was used as a medium of continuous phase of emulsions, gel-like O/LC emulsions were formed with wide variety of oils including hydrocarbon, ester oil, triglycerides, dimethylpolysiloxane and etc. The oil-retaining capacity of O/LC emulsions varied with glycerol content in liquid crystals. O/W emulsions were prepared by water addition to O/LC emulsions. The droplet size of emulsions varied with the oil/surfactant ratio and the efficacy of stirring during the formation of O/LC emulsions. This emulsification was also available by using lamellar LC systems composed of R_{16}MP-Arg and amphiphilic lipid, like mono hexadecyl glyceryl ether and hexadecyl alcohol. Emulsification was performed at temperatures above T_C to form O/LC gel-like emulsions and followed by dilution with water to form O/W emulsions. The O/LC emulsions changed to O/Gel emulsions in which emulsion droplets were retained in α-gel at below the phase transition temperatures of the mixed system.



R_{16}MP-Arg



R_6R_{10}MP-Arg

Figure 1 Dissociation state of R_{16}MP-Arg and R_6R_{10}MP-Arg.

Molecular Dynamics Simulations for Alkane Oils Characterization

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Simple hydrophobic systems such as hydrocarbon oils have high importance in many areas of industry, pharmacy and nanotechnology [1,2]. Liquids consisting of n-alkane molecules, in particular, are valued for their simple structure and additive variation in their physical characteristics upon carbon chain elongation. Derivation of explicit molecular models for these fluids allows us to obtain a deeper understanding of a number of processes at the oil-water interface [3]. Moreover, theoretical approaches can easily be validated, as heterogeneous environments containing aqueous and oil phases are well described experimentally [4-6].

Atomistic molecular dynamics simulations of liquid normal pentane, hexane and heptane, modelled with different number of molecules, were undertaken. In order to extract the optimum parameters, the statistical averages and the variations of a set of structural, thermodynamic and transport properties were estimated and compared to empirical data. The results prove to be insensitive to the model size and they coincide with the experimental values. The optimal algorithm was further tested through simulations at three different temperatures. The obtained trends in the evolution of all parameters upon temperature increase and hydrocarbon chain elongation were correct. The atomistic models proved to be reliable for further applications in different studies of hydrophobic systems, solutions and liquid surfaces or liquid-liquid interfaces.

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Effects of Nanoparticles on Interfacial Behaviour of Natural Pulmonary Surfactant

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According to recent studies, cardiorespiratory diseases which may lead to death are associated with the inhalation of NPs. Inhaled NPs whose size are especially below 100 nm cannot be defeated by the immune system of the lung and interact with lung surfactants (LS). LS exist at the alveoli surface, where the gas exchange occurs. This mixture is adsorbed at the air-water interface of alveoli to facilitate breathing by reducing the surface tension to very low values during respiration and prevent lung collapse [1]. Systematic investigation of functional disorders due to interaction of NPs with LS is important. The purpose of this study is to investigate the effects of widely used three different NPs, on the LS function. LS is obtained by bronchioalveolar lavage of calf lungs [2]. Vesicular suspension is formed by vortexing the dried material film in buffer [3]. Hydroxyapatite NPs (HA-NP) and different sizes of gold NPs are synthesized and characterized by appropriate methods. Titanium dioxide NPs are obtained commercially. By using Langmuir-Blodgett (LB – trough) device, pressure-area isotherms of pure LS is obtained at the air-water interface. To simulate the interaction of NPs with LS, different approaches have been used. First, NPs with various concentrations are injected to the sub-phase after the formation of pure LS monolayer and pressure-area isotherms are obtained at the air-water interface with respect to time. HA-NPs penetrate to the LS film at the air-water interface and the film is inhibited. When LS is inhibited by NPs, required area compression to reach the certain pressure is increased when compared to pure LS. It indicates that irreversible loss of LS at the interface occurs when inhibited with NP. The effect of HA-NPs is also investigated at different time intervals. The loss of LS from the interface reaches 9.5% at the end of third hour. In the second approach, LS and NPs are incubated together and then the mixture is injected to the sub-phase at selected time intervals. Similar behavior is also observed when the NPs are interacted with LS in the stock solution. Monolayers are transferred to the solid surface at specific pressures and monitored with Atomic Force Microscopy (AFM) in order to get more information about the molecular level interaction. AFM images show that the morphology, in terms of the number and size of the lipid domains at the interface of LS film, is altered upon the interaction of HA-NPs with LS. Similar behavior is observed for gold NPs and titanium dioxide NPs. When these results are considered for actual systems, it is seen that inhaled NPs can disrupt LS may cause irreversible fatal lung diseases. Also, NPs can easily penetrate from alveolar surface to blood stream and this situation is also thought to lead to other health problems.

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Correlative relationships between some spreading parameters and properties of surfactants and surfaces: Spreading of water droplets containing alkyl ether surfactants

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Dynamic three-phase contact (TPC) angles of aqueous surfactant solutions (C_nEO_m) were measured in the pre- and micellar concentration ranges on polymer surfaces of different hydrophobicity. A special emphasis was put on possible evaporation effects at ambient humidity that was varied between 40 and 80%.

The interpretation of the experimental data and the observed spreading regimes were analysed in the frame of Blake-Haynes model for the TPC line velocity. The analysis is based on the assumption that the droplet keeps its spherical cap shape during wetting and evaporation processes. According to this assumption, from three geometric parameters measured – the droplet volume V, TPC radius r and TPC angle θ only two are independent. Similarly, only two of the observed rate processes – evaporation rate (dV/dt), spreading rate (dr/dt) and contact angle change rate (dθ/dt) can be independent. The role of relative humidity, surfactant type and concentration as well as substrate surface energy on the spreading velocity dr/dt and the evaporation rate dV/dt is discussed. The interaction between the two processes (spreading and evaporation) is analyzed. The measured and calculated dynamic contact angle of a water droplet containing $C_{12}EO_5$ surfactant at c = cmc is shown in **Fig. 1** for a moderately hydrophobic PET surface and in **Fig. 2** for a highly hydrophobic TeflonAF surface.

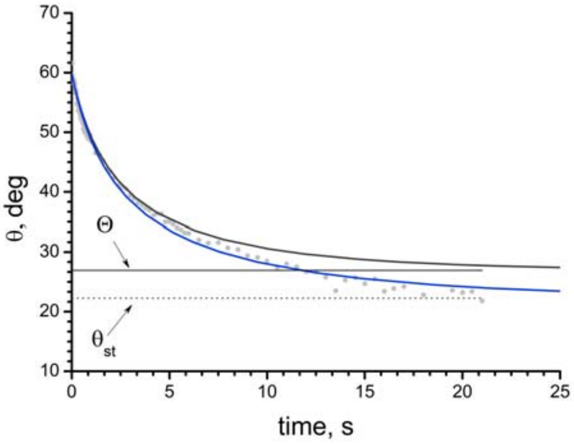

Fig. 1 Contact angle of aqueous $C_{12}EO_5$ solution on PET: measured values – grey dots; calculated values without considering evaporation – blue curve; calculated values when evaporation considered – grey curve; θ_{st} – static contact angle, Θ – equilibrium contact angle.

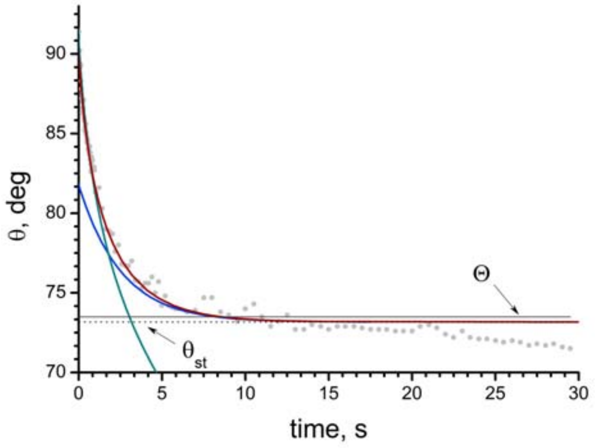

Fig. 2 Contact angle of aqueous $C_{12}EO_5$ solution on TeflonAF: measured values – grey dots; calculated values without considering evaporation – red curve; calculated values when evaporation considered – blue and green curves according to different spreading regimes assumed.

Acknowledgements: The authors thank Radomir Slavchov (Sofia University) for carrying out numerical approximations

Lyso- and ω3-containing phosphatidylcholines affect the elastic properties of lipid membranes

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The docosahexaenoic polyunsaturated fatty acid (22:6n3) is known as an ω3-fatty acid and is found at high concentration levels in the frontal cortex of mammalian brains. It is believed to play a highly protective role against the aging processes in the brain [1]. The lysolipids represent another class of molecules reported to be related to the proper functioning of the central nervous system by serving as lipid mediators and modulators of the neural function [2]. They are also a part of intracellular regulation mechanisms [3,4] and are involved in the cell-cell communication [5]. The molecular mechanisms of the above effects remain still unknown. In order to picture the roles of docosahexaenoic acid and lysophosphatidylcholine as structural components of the lipid bilayer, a comparative study of their influence on the membrane bending rigidity was performed here. The bending modulus of bilayers was deduced from thermal fluctuation analysis of the shape of quasispherical lipid vesicles [6] with monounsaturated phosphatidylcholine membranes containing various molar fractions of an ω3-containing phosphatidylcholine and/or a lysophosphatidylcholine. Strong evidences of their softening effect on lipid bilayers were provided together with data suggesting different strengths of the influence of the two molecules on the membrane bending elasticity.

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Acknowledgements:

This study was supported by Grant DMU03-80/2011 from the National Science Fund at the Ministry of Education and Science of Bulgaria.

Rheology of self-assembled systems derived from vitamin C

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Ascorbyl-alkanoates (L-ASCn) are a class of vitamin C-derived surfactants that makes the anti-oxidant properties of ascorbic acid available in lipophilic environments[1].

ASCn are biodegradable and biocompatible, thus possible candidates for pharmaceutical, cosmetic and food-processing industries, as they are able to disperse and protect from oxidation hydrophobic substances in aqueous environments, or act as preservatives for lipids[2].

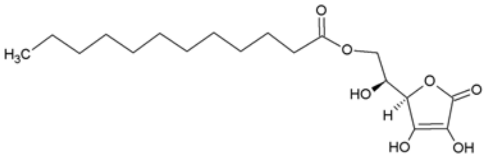

Fig. 1. Ascorbyl-6-O-dodecanoate (L-ASC12)

L-ASCn (with n>10) surfactants are of scientific interest also because of their peculiar self-assembly properties in water, as they exist as "coagel" (semicrystalline lamellar mesophase) at room temperature, and turn into a "gel" phase if heated above their Krafft point (about 47°C for L-ASC12 systems).

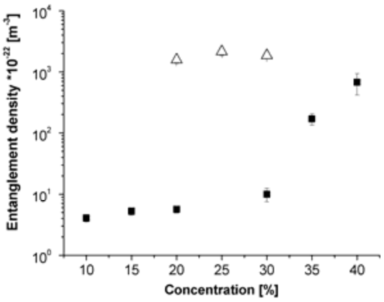

Fig. 2. Entanglement density of the gel (full symbols) and coagel (empty symbols) phases.

After the setup of an experimental procedure that could give reproducible results, oscillatory and rotational tests (plate-plate geometry) were performed on L-ASC12/water gels and coagels.

All the samples showed a shear-thinning behaviour, and their response to the oscillatory tests indicates that the interactions between their aggregates are of the same kind but different in number. The entanglement density was calculated (Fig.2), and we hypothesize that a phase transition of the gel packing occurs between the 20% and the 30% concentrations. Rotational tests performed at different temperatures allowed us to calculate the flow activation energies of the two phases.

Optical microscope observations confirmed the effectiveness of our experimental method, and the gel to coagel transition was recorded and interpreted according to the Avrami-Erofe'ev kinetics, concluding that the phase transition is characterized by a mono-dimensional growth under phase boundary control.

This work investigated the rheological properties of L-ASC12/water systems in-depth, formulating structural hypotheses to be verified by LS techniques. The rheological characteristics confirm these systems as interesting candidates to be employed in controlled-release applications.

Fig. 3. 20% L-ASC12 coagel, parallel Nicols.

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The effect of fragrances on the viscoelastic properties of anionic wormlike micelles

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The viscoelastic properties of aqueous solutions of sodium lauryl ether sulphate (SLES) in the presence of salt (NaCl) are significantly altered by the addition of fragrances[1]. Generally, as the salt concentration increases, the viscosity of the surfactant solutions passes through a maximum, referred to as the 'salt curve'. Adding hydrophobic fragrance molecules does not change the shape of the salt curve, but they can shift the maximum to lower salt concentrations and alter the peak viscosity. Dynamic rheological measurements revealed a detailed picture of how these molecules affect the different length scales and relaxation times in the entangled wormlike micelles. The two effects on the viscosity of surfactants have different molecular origins and are uncoupled from each other. The shift in the salt curve can generally be understood as due to either flattening of the interface, i.e. a reduction of the spontaneous curvature, caused by insertion of amphiphilic molecules into the surfactant layer, or micellar swelling, caused by solubilization of very hydrophobic molecules in the micellar core. The viscosity decrease at the salt curve maximum is inversely proportional to the hydrophobicity of the added molecules, so less hydrophobic compounds cause larger decreases. These molecules interact with the surfactant headgroups and thereby soften the interfacial film. As a consequence the persistence length is reduced resulting in an effective shortening of the micelles. Fragrance molecules typically show a combination of the two effects, and the extent of each one of them is tightly related to molecular descriptors such as amphiphilicity and hydrophobicity.

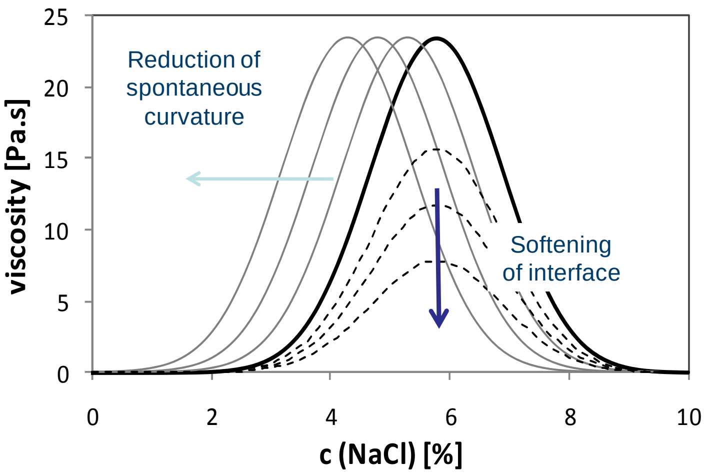

Fig. 1 Effect of fragrances on the zero-shear viscosity of aqueous solutions of SLES.

Literature:

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Surface Freezing in Surfactant/Alkane/Water Systems

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Pseudo-partial wetting is an intermediate wetting state of a liquid oil droplet placed at the air/surfactant solution interface. A recent systematic study on the pseudo-partial wetting film of alkanes at the aqueous surfactants solutions shows two types of freezing transitions[1]. For shorter chain alkanes, a transition occurs from a 2-D liquid state to a hexagonally packed solid state with upright chains (type I). For longer chain alkanes, an unusual transition (type II) occurs from a 2-D liquid state to a bilayer with a hexagonally packed upper monolayer of pure alkane and a liquid-like lower monolayer containing both surfactant and alkane. Ellipsometry is a sensitive technique for studying these 2-D phase transitions.

Fig. 1 shows the variation in coefficient of ellipticity with temperature for *lyso*-palmitoylphosphatidylcholine (*lyso*-PPC) + alkane (C_m) with m = 14, 19, 20, 28. The change in the ellipticity at the transition temperature indicates a type I transition for $m \leq 19$ and a type II transition for $m \geq 20$.

Further, we measured the ellipticity of the system SDS and $C_{16}E_8$ with several alkanes. We will discuss the effect of alkane chain length on the type I/II boundary from a thermodynamic point of view.

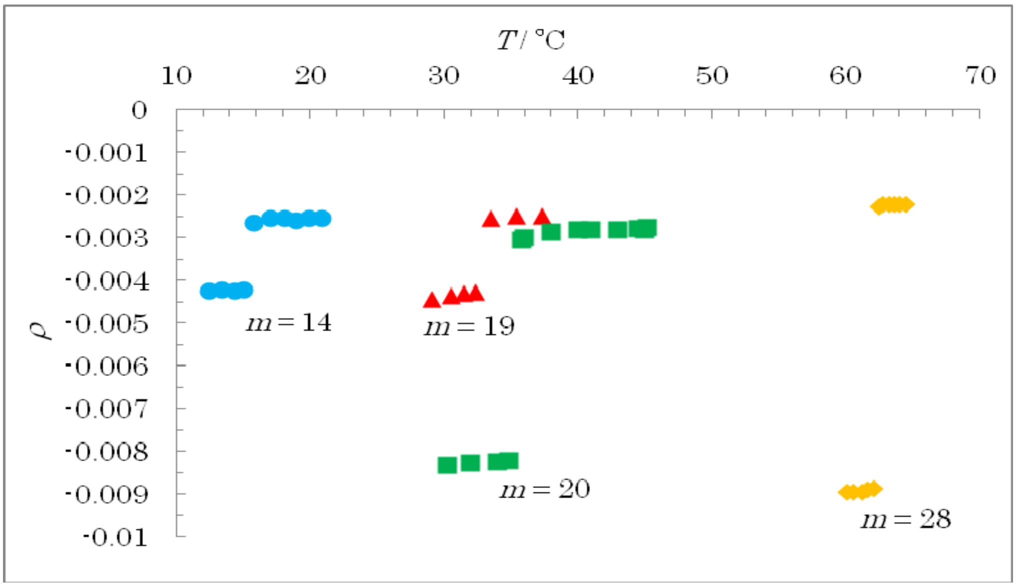

Fig. 1 Variation in the coefficient of ellipticity with temperature for surface of aqueous solutions of 0.4 mM *lyso*-PPC in the presence of lenses of alkane with chain lengths, *m*.

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Miscibility and Distribution of Binary Counterions of Different Valences in Surfactant Adsorbed Films

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To investigate the specific ion effect on the distribution and miscibility of binary mixed counterions in surfactant adsorbed films, the surface tension and total reflection XAFS were measured similarly to our previous study [1] for the aqueous solution of dodecyltrimethylammonium bromide (DTABr) − bis-dodecyltrimethylammonium sulfate (DTA_2SO_4) mixture with varying the total molality $\hat{m}$ and the composition of DTA_2SO_4 in the bulk solution $\hat{X}_2$ at 298.15 K under atmospheric pressure.

The compositions of DTA_2SO_4 in the adsorbed film were evaluated using two ways, i.e., by the thermodynamic analysis ($\hat{X}_2^H$) and the jump value XAFS analysis ($\hat{X}_2^{XAFS}$) and shown in Fig. 1. Fig. 1 is the phase diagram of adsorption and expresses the relation between $\hat{X}_2^H$ and $\hat{X}_2$. At 55 mN m^{-1}, $\hat{X}_2^H$ is larger than $\hat{X}_2$ and smaller than $\hat{X}_2^H$ of ideal mixing at all bulk compositions, which means the SO_4^{2-} ions have higher affinity to the surface than Br^- ions and the miscibility of counterions is improved. At 45.5 mN m^{-1}, the phase diagram is an azeotrope type, and the miscibility is greatly improved. These results indicate that SO_4^{2-} ions are firmly hydrated but interact strongly with DTA^+ ions due to their higher ionic valence, while Br^- ions are relatively easily dehydrated and bound to DTA^+ ions especially when the surface density of surfactant ions is higher.

This consideration is supported also by the surface density, excess Gibbs energy of adsorption from thermodynamic analysis and the counterion distribution from EXAFS analysis for hydration structure of Br^- ions in the adsorbed film.

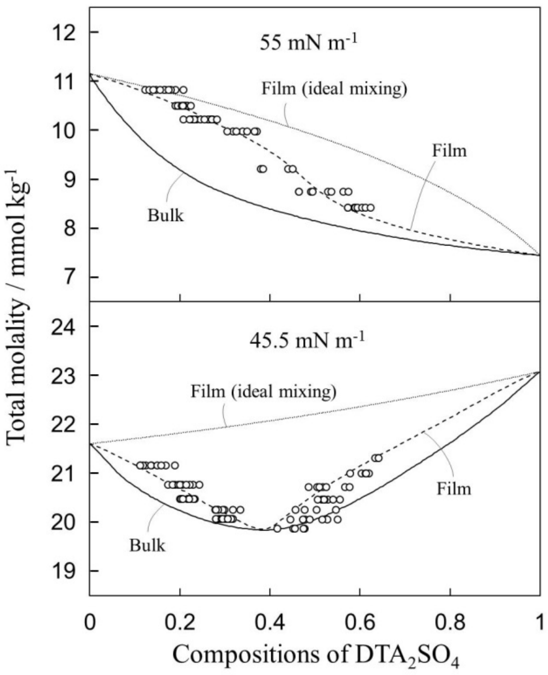

Fig. 1 Phase diagram of adsorption at constant surface tension. Solid, dashed and dotted curves represent $\hat{m}$ vs. $\hat{X}_2$, $\hat{m}$ vs. $\hat{X}_2^H$ and $\hat{m}$ vs. $\hat{X}_2^H$ of ideal mixing, respectively. Open circles represent $\hat{X}_2^{XAFS}$.

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Acknowledgements:

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Effect of Condensed Film Formation at Alkane Mixture/Aqueous Solution Interface on Its Composition and Emulsion Stability

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Adsorbed films at oil/water interface stabilize emulsions to some extent. So far, it has been reported that the adsorbed films of ionic surfactants at oil/water interface are in the expanded state due to the electrostatic repulsions between head groups. However, Lei et al showed condensed film was formed at the hexadecyltrimethylammonium bromide (HTAB) aqueous solution/tetradecane (C_{14}) interface [1]. This is due to that the penetration of C_{14} molecules into HTAB adsorbed film strengthen the interaction between hydrocarbon chains without decreasing the distance between head groups.

In this study, we examined the effect of the condensed film formation not only on the interfacial composition of oil in an alkane mixture system but also on the stability of oil in water (O/W) emulsions. We adopted C_{14} – hexadecane (C_{16}) mixture as oil phase and measured interfacial tension (γ) and ellipticity ($\bar{\rho}$) as a function of temperature (T) at fixed HTAB molality in the aqueous phase (m) and C_{16} composition in the oil phase (x_2).

Figure 1 shows the results of ellipsometry. As temperature decreases, $\bar{\rho}$ was decreased across the phase transition at x_2 = 0 to 0.8. However, $\bar{\rho}$ in the condensed films of alkane mixtures were significantly different from those of pure C_{14}. This indicates that C_{16} molecules are adsorbed preferentially in the condensed film region due to stronger lateral van der Waals interaction between HTAB and C_{16}. The conclusion was also confirmed by the thermodynamic analysis of interfacial tension data.

Figure 2 shows the time dependence of the phase volume of emulsions prepared by stirring of HTAB aqueous solution and C_{14} with VORTEX MIXER. The volume of emulsion phase did not change appreciably when the adsorbed films are in the expanded state, while decreased gradually with time when they are in the condensed one. The results at different m and x_2 will be also displayed and discussed.

Literature:

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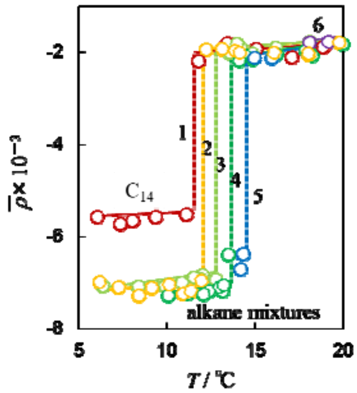

Figure 1 : The $\bar{\rho}$ vs T curves at m = 0.6 mmol kg^{-1}. The x_2 was fixed at 1) 0, 2) 0.2, 3) 0.4, 4) 0.6, 5) 0.8 and 6) 1, respectively.

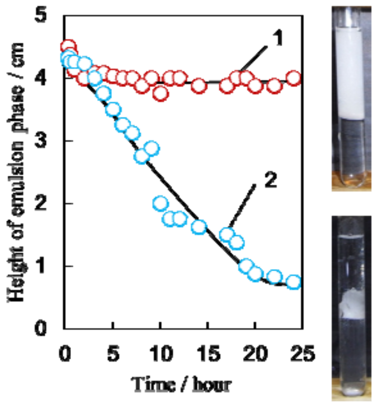

Figure 2 : Stability of O/W emulsions in the expanded state (1) and in the condensed state (2).

Evaluation of Surfactant Potency by TLC: Alternative Indexation to HLB Number

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HLB is a very practical concept to identify the properties of surfactant as an emulsifier. Many methods to calculate HLB had been proposed, but some are restricted for general use and others are too complicated in practice. Davies's method, as one of the typical methods to calculate the surfactant characteristic, referres certain unit value to each functional group as either hydrophilic or hydrophobic element, and HLB of the molecule can be calculated as a summation of total unit. Such calculated HLB, however, is empirically known not to be applicable to many types of surfactants, especially for ionic surfactants, because HLB was established on the basis of polyoxyethylene (EO) type non-ionic surfactants.

It seems noteworthy that thin layer chromatography (TLC) gives hydrophilic and hydrophobic character of the molecule by using normal phase or reversed phase method, respectively. We have originally investigated the empirical method for amino acid-based surfactants by using TLC.[1] For pure polyoxyethylene (EO) alkyl ethers, Esquena and Solans further indicated that combination of two experimental values measured by the reversed and normal phase TLC well expressed surfactant characteristic, compatible to HLB.[2] With reviewing our previous procedure, the present study shows the novel method to evaluate potency not only for the pure non-ionic surfactants but the commercial ones with a chain distribution, and eventually would propose a practical index of surfactant characteristic. In addition, it is shown that the new parameter would be responsible for specific surfactant properties in solution which were often inconsistent with the common HLB numbers. In the presentation, we will look back to the intrinsic sense of the HLB number and reconsider a useful parameter demanded by industry.

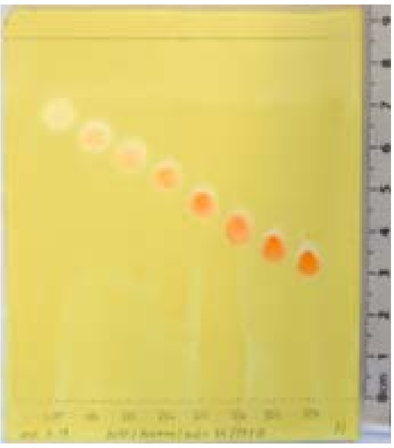

Fig. 1 TLC measurement of the series of pure polyoxyethylene-type nonionic surfactants using the normal phase plate. The spots are placed downward with increasing the EO chain length.

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Clustering of Charged Colloidal Particles in the Coexistence of Ionic Surfactants

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Clustering of colloidal particles has attracted considerable attention[1,2] in recent years. Here, we report a novel method to control the clustering by using ionic surfactants. We used positively and negatively charged polystyrene particles (PS(+) and PS(-), respectively), which form clusters when mixed in aqueous dispersions due to Coulombic attraction. By using adsorption of cationic surfactants, we could vary the surface charge of PS(-) to be positive, and control the clustering behavior. We also examined clusters of PS(-) and negatively charged silica particles using cationic surfactant.

We synthesized PS(+) by emulsifier-free polymerization, using styrene (monomer), 2-vinylprydine (comonomer), and 2,2'- azobis (2-methylpropion- amidine) dihydrochloride (polymerization initiator). The particle diameter *d* was 420 nm. An aqueous dispersion of PS(-) (*d* = 1200 nm) were purchased from Thermo Fisher Scientific Inc. Cetylpyridinium- chloride (CPC) was used as the cationic surfactant. Silica particles were purchased from Japan cataryst Co., Ltd.

It was confirmed by zeta potential measurements that the charge numbers of PS(-) could be controlled from negative to positive by adsorption of CPC. The mixture of PS(+) and PS(-) particles formed the clusters at sufficiently low CPC concentrations (C_{CPC}), while clustering was not observed at high C_{CPC}s. An illustration of the cluster formation is shown in Fig.1. At PS(+) and PS(-) concentrations = 0.05 % and 0.4 %, for example, the clustering was observed at C_{CPC} <10 μM. Fig.2 shows micrographs of the sample where the clusters were formed (A, C_{CPC} = 5 μM) and not observed (B, 20 μM). The clustering was reversible, that is, the clusters were formed on increasing C_{CPC}, while they separated into free particles upon decrease in C_{CPC}. We also report effect of temperature on the clustering behavior.

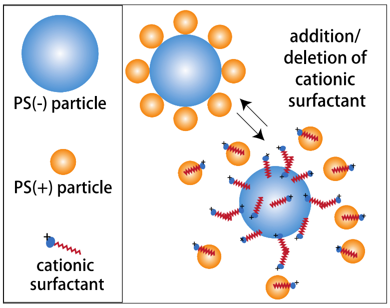

Fig. 1 Illustration showing clustering of positively/negatively charged PS particles in the coexistence of cationic surfactants.

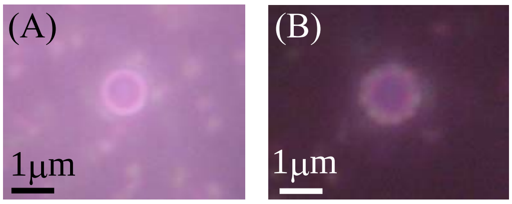

Fig. 2 Micrographs of (A) free particles and (B) the cluster.

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Spontaneous Chiral Segregation of a Hybrid Surfactant upon Aqueous Micelle Formation

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Chirality has been actively studied for a long time, since the discovery of molecular chirality by Pasteur in 1848. In particular, researches on chiral amplification, spontaneous chiral segregation, and chiral recognition have attracted significant attention in an attempt to clarify the origin of biological homochirality. In the field of interface and colloid science, there is little difference in the critical micelle concentration (cmc) of each enantiomer because the physicochemical properties of two enantiomers are generally the same. Also, a racemate, which is the mixture of equal parts of two enantiomers, has properties similar to both enantiomers. This phenomenon results from the formation of mixed micelles that consist of both enantiomers in an aqueous solution of the racemate. In this paper, the properties of aqueous micelles formed from chiral and racemic hybrid surfactants (F6H5PPhNa), which have a fluorocarbon and hydrocarbon chain in the molecule, are reported.

Racemic F6H5PPhNa (*rac*-F6H5PPhNa) was synthesized by a method previously reported, whereas the chiral surfactants [(*S*)- and (*R*)-F6H5PPhNa] were synthesized through five steps in an enantioselective reaction. The solution properties of these hybrid surfactants were evaluated by surface tension and NMR measurements.

The synthesis of (*S*)- and (*R*)-F6H5PPhNa was successful and had an optical purity of 95%. The Krafft point, which is the surface tension at the cmc, of (*S*)-F6H5PPhNa, and the occupied area per molecule of (*S*)-F6H5PPhNa were similar to those of *rac*-F6H5PPhNa. However, it was found that the cmc of (*S*)-F6H5PPhNa is different from that of *rac*-F6H5PPhNa. The cmc of (*S*)-F6H5PPhNa was 0.12 mM and the cmc of *rac*-F6H5PPhNa was 0.23 mM. This indicates that (*S*)-F6H5PPhNa and (*R*)-F6H5PPhNa molecules do not form mixed micelles consisting of *S* and *R* forms in water. In other words, *rac*-F6H5PPhNa molecules may discriminate between *S* and *R* forms in the formation of micelles. There was no difference in the chemical shift of the protons on the hydrocarbon chain in the molecule between the racemate and enantiomer at any concentration above the cmc in ^{1}H-NMR experiments. In addition, pulsed-gradient spin-echo NMR (PGSE-NMR) experiments indicated that *rac*- and (*S*)-F6H5PPhNa formed small micelles with a hydrodynamic radius of ca. 3.5 nm in water. These results indicate that *rac*-F6H5PPhNa molecules form individual micelles of each enantiomer in aqueous solutions.

It was also theoretically proven whether (*S*)-F6H5PPhNa and (*R*)-F6H5PPhNa molecules form mixed or demixed micelles in an aqueous solution of racemate. The interaction parameter between (*S*)-F6H5PPhNa and (*R*)-F6H5PPhNa in the aqueous racemate solution indicates that *rac*-F6H5PPhNa molecules form demixed micelles in water. In conclusion, all results in this study suggest that the racemic hybrid surfactant is spontaneously discriminated by its individual enantiomers upon micelle formation.

Light Control over the Morphologies of Aggregates Containing a Photoresponsive Amphiphilic Compound

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Surfactants of amphiphilic molecules form various aggregates (e.g., micelles, vesicles, and lamellar phases) in water. Recently, researches on controlling the morphologies of aggregates formed from photoresponsive amphiphiles using light have been reported. In this study, reversibly wormlike micelles were formed using ultraviolet (UV) light irradiation and then disrupted with visible light irradiation for mixtures of sodium [4-(4-butylphenylazo)phenoxy] acetate (C4AzoNa) and cetyltrimethylammonium bromide (CTAB) in water. In this paper, the photoinduced transition of the aggregate formed from mixtures of CTAB and azobenzene derivatives is reported, along with detailed mechanisms for the photoinduced transition of aggregates and further transitions through alterations of the alkyl chain length of the azobenzene derivatives.

Azobenzene derivatives (C*n*AzoNa, *n* = 2, 4, 6, **Figure 1**) were synthesized. Photoisomerization of the *trans* to *cis* isomer was performed with UV light irradiation of aqueous solutions of the CTAB/C*n*AzoNa mixtures for at least 180 min. Interfacial curvatures of aggregates in the aqueous solutions of the CTAB/C2AzoNa mixtures increased with UV light irradiation, indicating transitions from wormlike micelles to spheroidal micelles and bilayers to wormlike micelles. On the other hand, interfacial curvatures of aggregates in aqueous solutions of the CTAB/C4AzoNa and CTAB/C6AzoNa mixtures decreased with UV light irradiation, indicating spheroidal micelles to wormlike micelles and wormlike micelles to bilayers. In addition, the solubility of C*n*AzoNa in water decreased with increasing alkyl chain length in C*n*AzoNa. In general, the hydrophilicity of the *cis*-isomer is higher than that of the *trans*-isomer because *cis*-isomers of amphiphiles containing an azobenzene group have larger dipole moments than the *trans*-form. Therefore, the *cis*-isomer will barely penetrate into surfactant aggregates. Past studies on the photoinduced transition of surfactant aggregates report that photoresponsive amphiphiles have a tendency to desorb from aggregate interfaces in bulk solution with UV light irradiation because of their increasing hydrophilicity. However, C4AzoNa and C6AzoNa will effectively penetrate into surfactant aggregates because of their low solubility in water. Therefore, the azobenzene derivatives were photoisomerized in mixed aggregates without desorbing to the bulk solution. This brings about a decrease in the interfacial curvatures of aggregates, resulting in a change in the effective critical packing parameter.

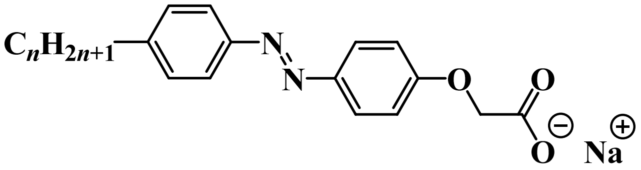

Figure 1: Chemical structures of C*n*AzoNa.

Studying Complex Nanoparticle Self-Assembly at Liquid Interfaces Using Pendant Drop Tensiometry, Micro-rheology and Fluorescence Correlation Spectroscopy

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Trapping at the interface, combined with lateral mobility and the presence of specific interactions, makes self-assembly of colloidal particles at liquid-liquid interfaces (SALI) a process with huge potential for the creation of controlled structures, including novel ultrathin membranes and capsules.

It has recently been demonstrated in our group that superparamagnetic iron oxide nanoparticles (NPs) stabilized by low molecular weight poly(ethylene glycol) (PEG) shells [1,2], can be self-assembled into saturated monolayers at the water/n-decane interface [3,4]. Understanding the basics of SALI is a keystone in turning these NP assemblies into composite membranes suitable for applications. In particular, measuring the viscoelastic properties of the interfacial assemblies *in situ* and on the micro-scale is of paramount importance [5].

Particle characterisation using pendant drop tensiometry (PDT) has been completed at different concentrations to compare the effects of different PEG shells on the interfacial adsorption behaviour of the particles. Particles with longer linear PEG chains show the highest surface activity and the fastest adsorption kinetics. Master curves have been created for the different particle types, demonstrating the concentration dependence of adsorption speed.

To further investigate the behaviour of the nanoparticles at the decane-water interface, the mechanical properties have been characterised via the tracking of probe particles with very different sizes. Micron-sized tracer particles observed with fluorescence optical microscopy still show diffusive behaviour at the interface upon adsorption of the NPs. Fluorescence correlation spectroscopy, using quantum dots as tracers [6], was used to investigate the interface on the same length scale as the NPs. Surprisingly, these tracers also showed purely diffusive behaviour, with a progressive slowing down ascribed to NP adsorption. It was thus possible to follow the build-up of the NP monolayer with time, and to obtain master curves for the diffusion coefficient as a function of a concentration-dependent effective time, similar to the PDT master curves.

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Surfactant Induced Charging of PMMA in Nonpolar Solvents

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Charges in nonpolar solvents are not as easily stabilized as in polar media but are important in technologies such as electrophoretic displays. Poly(methyl methacrylate) (PMMA) spheres sterically-stabilized with poly(12-hydroxystearic acid) graft copolymer (PHS-*g*-PMMA)[1] can be charged in organic solvents using sodium dioctylsulfosuccinate (AOT).[2] While previous results demonstrate that surfactants can charge PMMA particle surfaces, it is unclear whether AOT adsorbs on the surface as aggregates or in the stabilizer layer as monomers.

Contrast-variation small-angle neutron scattering (CV-SANS) has been employed to understand the interaction between surfactants and polymer surfaces. The interaction of AOT with PMMA particles has been measured along with model systems for the surface of the particles based on the PHS-*g*-PMMA stabilizer copolymer. The CV-SANS experiments involved measuring the scattering of particles and polymers with deuterated AOT-D_{34} in either particle or surfactant contrast-matched solvent. By studying the simplified model systems, it has been possible to determine the contribution that the chemical interactions between surfactant and polymer and the particle surface conformation make to the charging of PMMA particles in nonpolar solvents.

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The Influence of Salt on Zwitterionic Lipid Bilayers

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Calcium ions play a central role in a number of physiological processes, both indirectly as a messenger spreading excitation between an array of receptors leading to gene activation and directly involved in specific ion channel membrane depolarisation.[12] Similarly, cellular fusion involves a complex interplay of proteins[3] and protein receptors[4] but this is all thought to be triggered and regulated by the concentration gradient of Ca^{2+} ions present.[5] Often the role of salt in protein interactions with lipid bilayers is neglected. This work presents a detailed neutron reflectivity study of both monolayer and floating lipid bilayer systems to understand the extent to which $CaCl_2$ influences the membrane of zwitterionic lipid systems as a function of concentration and temperature.

Six distinct regimes have been identified in the mechanism of membrane change as the $CaCl_2$ concentration is increased in the bulk solution. These can be explained by considering the contributions of steric, electrostatic and Helfrich repulsions to the overall three dimensional bilayer structure. The data is presented within the wider context of a number of biophysical examples, where the conclusions of this study can be used to more efficiently design membrane studies in the future.

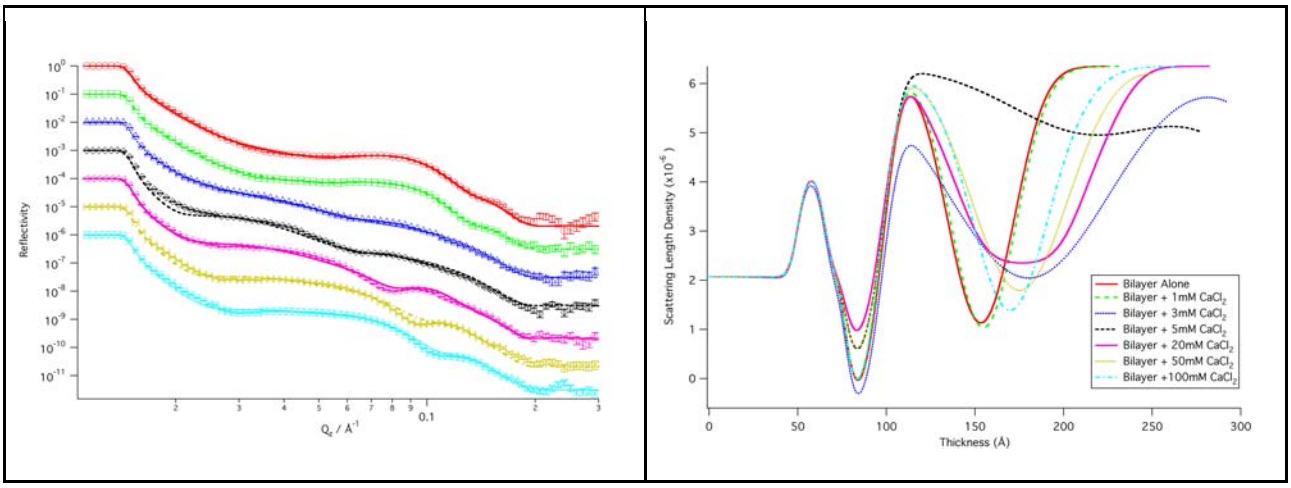

Fig. 1 Neutron reflectivity data sets with fit (Left) and SLD profiles (Right) comparing a DPPC Bilayer with as a function of salt concentration against D_2O at 50°C. Each data set represents a different regime the membrane experiences under the influence of salt.

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Interfacial Mechanisms in Complex Biosystems

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Supported Lipid Bilayers (SLBs) are important substrates for the study of interactions involving biological molecules such as drugs, DNA, proteins and nanoparticles. SLBs are commonly employed in studies using surface-sensitive techniques such as neutron reflectometry (NR). We have widely investigated the interaction of PAMAM dendrimers with lipid vesicles and SLBs using NR and have found contradictory results depending on whether the interface under examination is located above or below the bulk liquid [1,2]. Recently we have carried out work involving a novel comparison of neutron reflection up vs down measurements on the same samples (using an approach pioneered recently on synthetic polymer/surfactant mixtures [3]), which demonstrated that phase separation and gravity massively influence the interfacial properties according to the location of the interface. In Fig. 1, mixtures of PAMAM dendrimers with 9:1 POPC/POPG vesicles resulted in the production of a lamellar phase on the top surface and a floating bilayer on top of dendrimer molecules on the lower surface. Issues concerning (1) the role of bound vesicles, (2) the influence of the charge of the substrate and (3) the underlying mechanism of surface nanostructure formation will be discussed. This work demonstrates that a better understanding of the effects of gravity and bulk phase separation is required in order to rationalize results concerning the interfacial properties of complex mixed biological systems relevant to fundamental biology and applications such as drug or gene delivery.

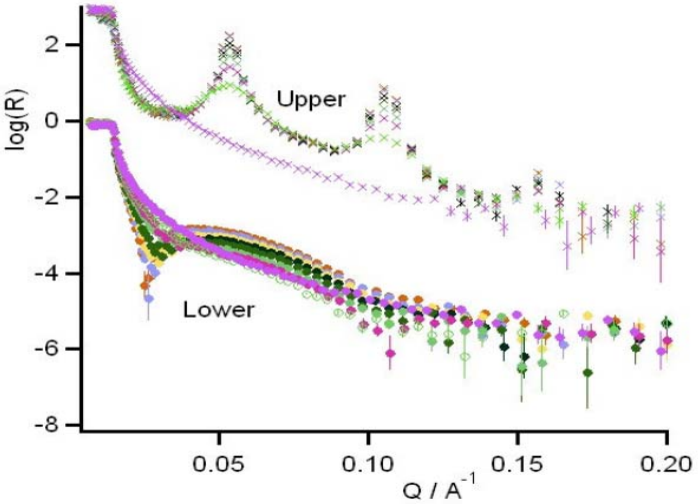

Fig. 1. Neutron reflectivity of PAMAM/9:1 POPC:POPG vesicle mixtures at the silicon/liquid interface where the solid surface is located above (upper) and below (lower) the solution.

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Oxidation of Organic Surfactant at the Air-Water Interface

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Organic surfactants are key components of atmospheric aerosols, both in the bulk and at the surface. The exposure to oxidising agents, *e.g.* ozone (O_3) and nitrate (NO_3), affects their fate and thus their impact on the Earth's radiative balance and on cloud formation. The understanding of the ageing of organic films on atmospheric aerosols is still incomplete.
We present a surface study of the oxidation kinetics of pure and mixed films of oleic acid (OA) and stearic acid (SA) by nitrogen oxides. While bulk studies suggest that OA is more reactive than SA due to the presence of unsaturation, its surface reaction scheme and related kinetic parameters to feed into atmospheric models are missing. Films at the air-water interface of a Langmuir trough, contained in a new miniaturised reaction chamber were exposed to the oxidant and the material loss at the surface during the reaction is followed by neutron reflectometry (NR). The oxidants were produced *in-situ* by a well established procedure. A range of concentrations have been accessible by tuning the conditions of the reaction between O_3 and NO_2. We measured the concentrations off-line trough UV-Vis and FTIR spectroscopy and we optimised the reaction conditions to obtain reproducible values. The thermodynamic behaviour of the organic films were previously investigated by isotherms and Brewster angle microscopy. A lifetime of the OA surface layer was shown to be at least two orders of magnitude shorter than that of the SA surface layer. The rate coefficients are used to refine the surface reaction schemes involved. We also found that 15% surface coverage remained even at long reaction times for OA. Oxidation of recompressed films is discussed to determine the nature of the residual material (products vs reoriented reactant) and its atmospheric implications.
Lastly, the oxidation by nitrogen oxides of mixed OA/SA films has been studied for the first time to measure the relative reaction rates of the components in more realistic model systems.
So far, we used completely deuterated molecules to gain information on the rate coefficient in the future we intend to selectively deuterate the molecules in order to study the mechanism of the surface reaction.

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Development of Novel Hydrocarbon Low Surface Energy Materials (LSEMs)

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Low surface energy materials (LSEMs) are obtained by attachment of surface layers to substrates. The cause of low surface energy is the underlying chemical structure of the interfacial layers: the ability to control surface properties being the direct consequence of chemical structure. There are numerous applications of LSEMs today, such as printing, painting, adhesion, metal-plating emulsification/suspension (medical, cosmetic, food packaging, etc.), washing (electronics, clothes, etc), antifogging and repellent surfaces (self-cleaning windows, water-proof textiles, anti-snow, anti-fog surfaces, papers, fibers, etc.).

Therefore, development and optimization of LSEMs has attracted much attention, and a wide variety of useful LSEMs can be obtained by Fluorinating surfaces. Unfortunately, this has dramatic environmental consequences because of the persistence and bioaccumulation of Fluorocarbons (FCs)[1,2] Therefore, new surfactants have been synthesised using commercially-available Hydrocarbon (HC) compounds with various low surface energy hyperbranched "hedgehog" tails to establish the best substitutes for FCs and to explore how surfactant chain length and branching affects adsorption at the air-water interface (surface excess and hence surface tension/energy).

Adsorption/self-assembly behavior of these surfactants has been studied by tensiometry γ, and small angle neutron scattering (SANS). A comparison of the individual cmc's shows that they follow the expected general trend of decreasing cmc with increasing effective chain length (i.e., the length of the longest linear portion of the chain only). However, because the surfactants differ in terms of degrees of chain branching, the exact relationship between the cmc and the alkyl chain length is more indirect.[3] Analyses of tensiometric data indicate the subtle structural modifications in the tails, feed through to significant effects on surface tension of complete monolayers. Higher branching factor and closeness of the branch to the head group promotes an effective surface tension reduction and an increase in the effective molecular area, while increase in the chain length reduces solubility of the surfactants in aqueous solutions.

A structural study of these surfactants at a range of concentrations using SANS revealed the formation of spherical micelles with radius of about 10-12 Å (Fig.1).

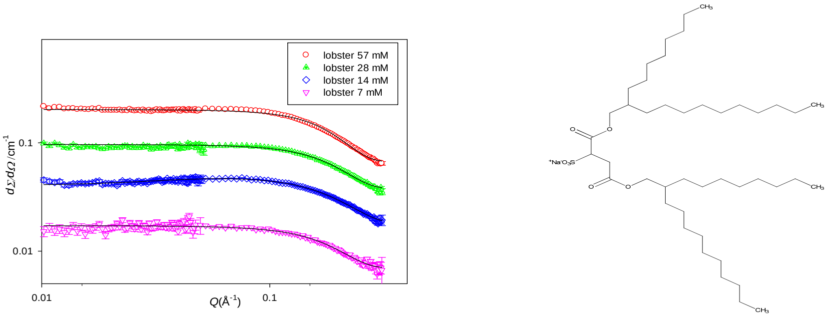

Fig. 1: SANS from a branched surfactant in various concentrations. Solid lines are fits to the spherical model.

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Novel Structural Changes During Temperature-Induced Self-Assembling and Gelation in Aqueous solutions of the Copolymer $PLGA_{1170}$-PEG_n-$PLGA_{1170}$

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It is well established that certain polymers undergo conformational changes in response to changes in temperature, pH, magnetic field, electrical field, or the wavelength of light. In one type of stimuli-responsive polymer, thermogel polymers, the polymer aqueous solution undergoes sol-to-gel transition as the temperature increases. Drugs or cells can be mixed into the polymer aqueous solution when it is in its lower viscosity solution state. After injection of the solution into a target site, heating prompts the formation of a hydrogel depot in situ, which can then act as a drug releasing system or a cell growing matrix.

In this presentation, we have employed small-angle neutron scattering (SANS) technique to study temperature-induced structural transitions of water-soluble triblock copolymers of the type [1,2] poly(D,L-lactic acid-*co*-glycolic acid)$_{1170}$-*block*-poly(ethylene glycol)$_n$-poly(D,L-lactic acid-*co*-glycolic acid)$_{1170}$ ($PLGA_{1170}$-*b*-PEG_n-$PLGA_{1170}$). The length of the PEG spacer assumes two values (n =1000 and n =1500) and this gives rise to fundamental different structural features of the polymer complexes in dilute and semidilute concentration regimes at different temperatures.

The length of the PEG spacer has dramatic implications for the structures formed in *dilute* aqueous solution (1 wt %). For the longest PEG chain (n = 1500), temperature-stable spherical micelles are created. These micelles are probably stabilized due the fact that the PEG chain is long enough to turn back on itself so that both PLGA-ends of one chain can be incorporated into the same micelle. For the PEG block with n = 1000, the micelles cannot be stabilized like that with n =1500, and the equilibrium conformation at low temperature (10 ^{o}C) is an elongated micelle (prolate) with the PEG chains extending into solution. At high temperatures, these disk-like particles will easily aggregate and start to sediment at the highest temperature of measurement. In *semidilute* solutions (20 wt%) of the copolymer with n=1000, intermicellar interactions with the formation of core-shell structures is observed at 10 ^{o}C. At 20 ^{o}C, the correlation peak in the SANS scattering curve disappears, because a gel network is formed; at 30 ^{o}C rod-like entities are created (cylinder length: 34 nm and radius 6 nm) and at 40 ^{o}C, close-packing (hexagonal packing) of micelles to thick "cylinders" (d = 16 nm) occurs (see Figure 1). For the copolymer with n=1500, similar scattering profiles evolve but in this case flower-like micelles can be formed and they are more stable than those formed for n = 1000, and the gel network is formed 40 ^{o}C as compared with 20 ^{o}C for n=1000. These novel structural features for this type of copolymer in aqueous solution have not been reported previously.

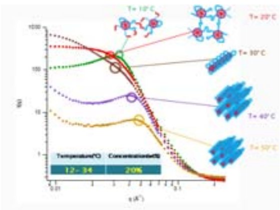

Fig. 1. SANS scattering data for 20 wt% aqueous solution of $PLGA_{1170}$-*b*-PEG_{1000}-$PLGA_{1170}$ at different temperatures and the change from spherical micelles to cylindrical micelles and the formation of gel at 20 ^{o}C.

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Electrostatic interaction between charged colloids trapped at an interface

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Self-assembly of stably trapped sub-micrometer colloidal particles at oil-water interfaces has attracted much interest in recent years because of its applications in the study of two-dimensional melting and investigations of mesoscale structure formation. For charge stabilized colloids at the interface, the attractive part of the interaction is dominated by strong van der Waals forces which is balanced by a repulsive part coming from the electrostatic repulsion between the colloids. For large separations between the particles, this repulsive part can be compared to a dipole-dipole interaction. However for distances close to the particle this simple dipolar picture cannot be applied. For a single colloidal particle trapped at the oil-water interface, a complete expression for the electrostatic potential was derived by Domínguez *et al.* [1]; however for a multi-particle system they essentially used the superposition approximation which corresponds to the limit of large separations. In this contribution we will consider the case of colloids situated very close (~50-100 nm) to each other at an oil-water interface by going *beyond the superposition approximation* [2]. The electrostatic potentials obtained within these two approaches show significant deviations for typical experimental situations. This implies significant deviations of the surface tensions at the charged walls and of the line tensions at the three-phase contact lines (line where oil and water phase meets at the wall).

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Models of Pseudolinear Surface Electrostatics for Gas-Liquids

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As known, a considerable interest to the interface electrostatics has been provoked mainly from the open questions for the mechanism of phenomena, called surface nucleations – in gas-liquid (in particular, lipid) systems. The importance of the questions on surface phenomena has became clear from their active presence both in related basic topics of Physical Chemistry (e.g. [3]) and ecological problems. Here we goal to find expressions for the electric potential, as the key quantity for a given heterogeneous system that integrates the basic electrostatic parameters of the medium. The actual interest accent however on the complex case of heterogeneity – when the system is considered as a material composition of distinct bulk (3D), surface (2D) and line (1D) phases (via models, well enough adequate to the phenomena). A basic case of 3-2-1 D heterogeneity is presented by gas (air)-electrolyte systems with highly ionic surface monolayers. The schematic structure of the said type systems can be described as follows. The interface (of the gas-liquid medium) is given as the plain $z=0$ (regarding a Cartesian (x,y,z) - coordinate system). It consists in two (homogeneous, but materially different) 2D sub-phases, known as LC/LE (liquid condensed/liquid expanded) nucleation components, where LC fills a bounded set and LE – the exterior to LC. The said LC, LE phases are separated by a circle contour, with radius ***r***, recognized as an electrostatic autonomous 1D material phase. The air (treated as vacuum) bulk phase fills the upper semi-space, $z>0$, and the lower one, $z<0$, is homogeneous and filled by the liquid matter.

Applying the classical Gibbs approach (for the idealized description), we derive a mathematical model for the electrostatics of the above type of gas-liquid systems, and find an explicit formula regarding the electric potential at the separating (2D) interface. It is done in the generally open case of a surface charge distribution, (quadratically) nonlinear regarding to a suitable integral mean value of the surface potential. Thus a view point of pseudolinear surface electrostatic is proposed. An extension is used of the Gibbs ([2]) idealizing approach and the Bedeoux-Vlieger ([1]) singular formalization of step transitions, for mathematical modeling.

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Thermodynamics of liquid film nucleation on a solid dielectric particle with a charge localized not at the particle center

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Though intensive studies of nucleation of under- and supersaturated vapor on charged solid particles had been started from the end of XIX century,[1] there are still some thermodynamic questions which have to be answered. Considering the droplet as a thin liquid film covering the spherical particle surface, we have studied the joint effects of (*a*) capillary forces, (*b*) surface forces of the solid particle, and (*c*) electric field of the particle charge on the shape and thermodynamic properties of the droplet. By contrast to the case of a central or uniformly distributed charge[2], here we have considered the influence of a *non-central axisymmetrical electric field* which is produced by an absorbed/adsorbed ion.

We have considered a spherical solid nanoparticle (phase γ) covered by a thin condensate (phase α) film isothermally formed out of the surrounding vapor-gas phase β. Mathematically, we were solving the electrostatic Laplace equation $\Delta\varphi = 0$ for the electric potential φ with corresponding boundary conditions at infinity, close to the point charge and at the phase boundaries. The ion represented by a point charge was considered to be close to the particle surface (at some distance above or below it). The shape of the droplet was determined by[3,4]

$$2H\gamma^{\alpha\beta} - \Pi\, h_{1\mathrm{n}} h_{2\mathrm{n}} / h_1 h_2 = P^{\alpha}_{\mathrm{NN}} - P^{\beta}_{\mathrm{NN}} \,. \qquad (1)$$

Here H is the mean local curvature in the arbitrary point on the droplet surface, Π is the local disjoining pressure of a liquid film, h_i and h_{in} ($i = 1, 2$) are the Lamé coefficients for a curvilinear coordinate system on outer and inner shells of the film. Single superscripts mark the phases, double ones mark the interfaces; $\gamma^{\alpha\beta}$ is the liquid-vapor surface tension, P^{α}_{NN} and P^{β}_{NN} are the normal components of pressure tensor in the same point on the droplet surface from the liquid and vapor-gas sides.

We have developed a numerical scheme for solving this problem and calculating shape as well as thermodynamic characteristics of the droplet (the chemical potential of the condensate molecules and the work of droplet formation) as functions of the droplet equivalent radius. We have applied it to different model disjoining pressure isotherms and demonstated that *axisymmetrical electric field produced by the electric charge, absorbed/adsorbed at the condensation nucleus surface, strengthened the electric effect on nucleation characteristics* in comparison with the case of the central field[2] at nucleation on nanosized condensation nuclei. For a realistic model system, this can give a *significant correction to the effect of the surface forces* (with no charge present).

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Polyelectrolyte adsorption on solid surfaces: theoretical predictions and experimental study

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Polyelectrolytes find many applications in colloid science, often related to their ability to absorb at solid/liquid interfaces. Polyions have very strong tendency to absorb on oppositely charged surfaces, usually generalizing overcharging. This means that some distance away from the surface, the potential will have a sign opposite to the bare surface charge. The overcharging generates an electric double layer repulsion at long range, while bridging and ion correlations mediate a strong attraction at short separations. The free energy barrier can be reduced, or removed, by the addition of simple salt.

In this work, we shall use a correlation-corrected classical polymer density functional theory to predict how the adsorption of highly charged polyelectrolytes at a silica surface varies with the concentration of simple salt. We shall compare these predictions with data from ellipsometry measurements, by using two different polyelectrolytes with a similar linear (and high) charge density: Poly(diallyldimethylammonium chloride) (PDADMAC) and Poly(4-vinyl N-methylpyridinium iodide) (PVNP). We shall demonstrate that the theory captures the overall adsorption behaviours of these, even under the assumption that the adsorption is of purely electrostatic origin. However, a nearly quantitative agreement is obtained, for both polymers, if a short-ranged non-electrostatic surface affinity is added in the theoretical treatment.

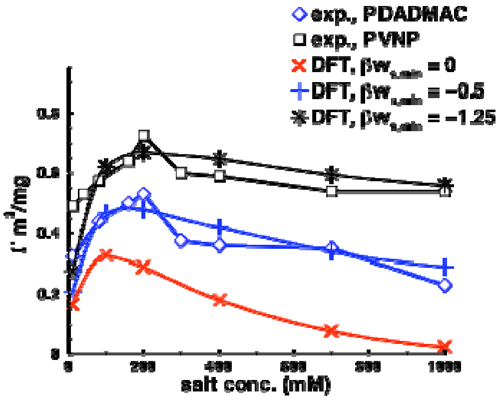

Fig. 1 Comparing net adsorption of PDADMAC and PVNP, as measured by ellipsometry, and calculated by density functional theory, respectively. In the latter case, the pure electrosorption curve is also given, as reference. Values of $w_{s;min}$ are chosen so as to generate a similar slope of $\Gamma(cs)$, at high salt concentrations (where these contributions start to dominate).

Ion distributions in critical solvents probed by X-rays

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In recent years, there has been a significant theoretical interest in ion distributions close to surfaces suspended in critical solvents. However, experimental verification of the theoretical predictions is challenging. Here, we address this question by studying interfacial ion distributions at the hydrophobic liquid-gas interface of a critical binary mixture consisting of water and 2,6-lutidine by simultaneous grazing-incidence X-ray fluorescence (GIXF) and X-ray reflectivity (XRR) experiments. We have probed ion distributions for different concentrations of potassium chloride (KCl) within a range of 10-100 mM and for temperatures below the critical temperature for demixing (T_C = 304 K). Quantitative comparison with theoretical predictions is in progress.

Droplet oscillations driven by electric field for studying rheological and interface properties of liquids

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Innovative experimental technique is proposed for studying wide range of rheological and interface properties of pendant spherical and hemispherical droplets of pure and complex liquids. The technique is based on the study of forced resonant oscillations of droplets in a modulated electric field and allows examining the bulk and interface properties as well as their dynamic changes. Preliminary results [1,2] show that surface tension and bulk viscosity can be measured precisely. Further experiments are aimed to examine the influence of free and bound surface charges, as well as the structure of the interfacial electrical double layer on the resonant behaviour of the droplet. The oscillating drop technique for measuring properties of liquids and interfaces has been analyzed and reviewed widely in literature [3-5]. The frequency of the n-th resonant mode for a perfect sphere, calculated by Rayleigh, is: $f_n^2 = n(n-1)(n+2)\sigma / 4\pi^2 \rho R^3$. Theoretical analysis claims, that the resonant frequency modes of a hemispherical droplet with poor wetting of the supporting surface are almost the same as for an ideal sphere [6].

Recently [1,2] we have shown that pendant droplets can easily be driven into oscillations by applying external electric field. Forced oscillations disturb the equilibrium state of the droplet and the deviation amplitudes are detected by an optical system comprising low power laser beam and photodiode. To avoid the influence of precise optical adjustments, the laser beam is widened to a cross section larger than the size of the examined droplet. As a result amplitudes of droplet oscillations less than 10^{-6}m can be detected. The resonant curve depends on surface tension, on droplet volume and on force frequency. Keeping two of these parameters constant and scanning continuously the third parameter allows one to describe the resonant curve which gives flexibility of experiments to obtain different information for the liquid.

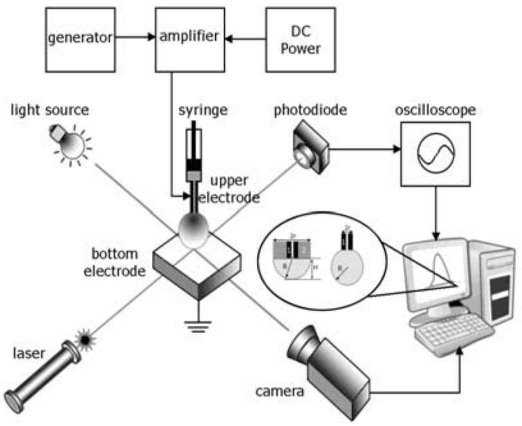

Fig. 1 Experimental setup

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Interactions between Charged Particles at the Air-Water Interface: Effect of External Electric Field and Surface-Pressure Isotherm

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Electrically charged micron-sized particles at the air-water interface form hexagonal lattices of constant, which is much greater than the particle diameter. This is due to the long-range electrostatic repulsion between the particles across the nonpolar fluid (in this case – air). This phenomenon has found application for the creation of non-densely packed particle monolayers that can be used to reduce the reflectivity of solid surfaces, e.g. solar panels. Here, our first task is to investigate whether it is possible to control the distances between the particles in the two-dimensional lattice. First, we examined the interactions in pairs of floating particles, which represent a superposition of electrostatic repulsion and capillary attraction [1]. If an external uniform electric field is applied normal to the interface, the capillary attraction between the particles is enhanced because of the additional electric deformations of the liquid surface around the particles. In addition, we investigated also multi-particle interactions in a particulate monolayer spread on the air-water interface in a Langmuir trough. Surface-pressure vs. area, $\Pi(A)$, isotherms have been obtained. For micron-sized particles, Π increases with the monolayer compression solely due to the interparticle electrostatic repulsion. For large A, the experiment yields $\Pi(A) \propto A^{-3/2}$, which cannot be explained with the available theoretical isotherm for charged particle monolayers. For this reason, using the Bakker formula and the Maxwell tensor, we developed a new theoretical model, which excellently compares with the experiment (Fig. 1).

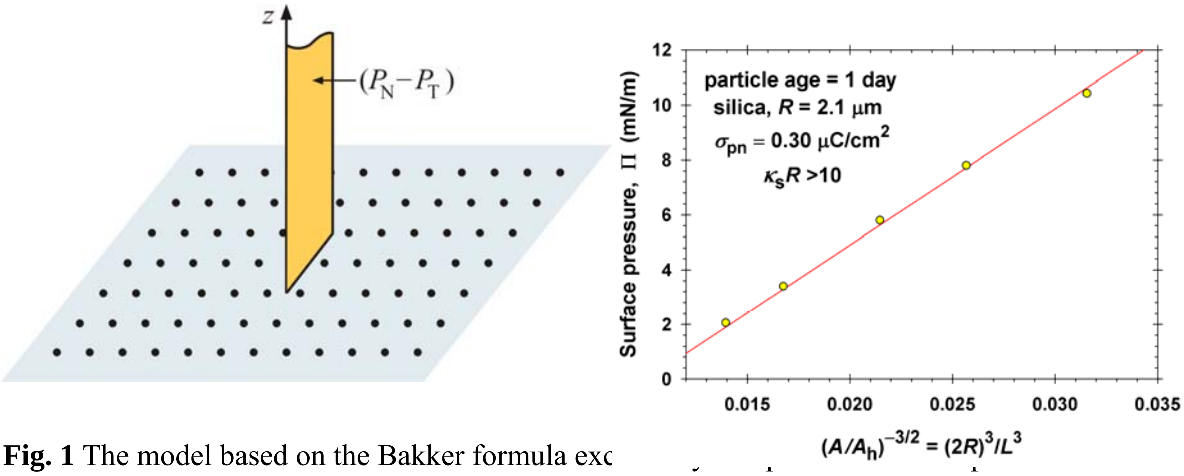

Fig. 1 The model based on the Bakker formula exc

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Effect of the prolonged electrode potential cycling on the impedance response of poly(o-aminophenol) (POAP) film electrodes

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The aim of this work was to study the effect of prolonged potentiodynamic cycling (-0.2 V $< E <$ 0.5 V vs. SCE) on the conducting properties of poly(o-aminophenol) (POAP) film electrodes. The Electrochemical Impedance Spectroscopy (EIS) was employed in this study to obtain dependences of charge-transport parameters on the degree of deactivation (θ_c^d) of the polymer after prolonged electrode potential cycling. Impedance diagrams of POAP films were analyzed on the basis of two different models [1,2]. While diffusion coefficients for electron (D_e) and ion (D_i) transport decrease, interfacial resistances related to ion ($R_i^{f|s}$) and electron ($R_{m|f}$, $R_e^{f|s}$) transfer across the different interfaces involved in the metal/polymer film/solution system increase as the degree of deactivation increases. Fig. 1 shows the $R_{m|f}$ vs. θ_c^d dependence. The slower electron transport with the increase in the degree of deactivation was attributed to the increase of the electron hopping distance between redox sites. Transport parameters, such as, $R_i^{f|s}$ and D_i, were associated with proton movements. POAP films maintain their conducting properties almost unaltered for about 500 potential cycles at a scan rate of 0.010 V s^{-1}. However, a loss of conductivity was observed as the number of potential cycles was extended beyond 500.

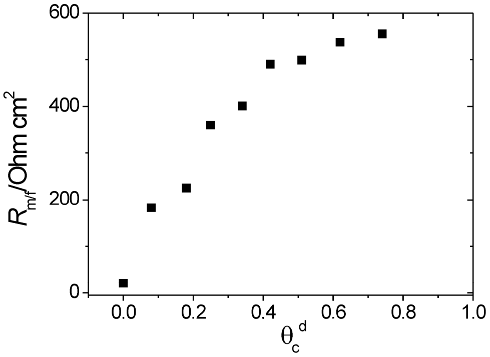

Fig. 1. Metal-polymer interfacial electron-transfer resistance ($R_{m/f}$) as a function of θ_c^d. Electrolyte: 0.1 M $HClO_4$ + 0.4 M $NaClO_4$ + 2 x 10^{-3} M (HQ/Q) solution.

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The role of citrate in the stabilization of gold nanoparticles. Conformational analysis of citric acid

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To prevent the aggregation of synthesized gold nanoparticles, some sort of stabilizing agent that sticks to the nanoparticle surface is usually added. The method pioneered by J. Turkevich et al. in 1951 and refined by G. Frens in 1970s, is one of the most widely eused to produce relatively monodisperse spherical gold nanoparticles suspended in water of around 10–20 nm in diameter [1]. It involves the reaction of small amounts of chlorauric acid with small amounts of sodium citrate solution. The colloidal gold will form because the citrate ions act as both a reducing agent, and a capping agent.

The present work has focused on the conformational study of citric acid and its dissociated forms using computational methods. The conformational analysis is performed with DFT calculations at B3LYP/6-31+G* level of theory in the aqueous phase and in gas phase. The obtained low energy conformers were found to be in close match with their corresponding crystal structures. The results suggest that the calculations are reasonably accurate for predicting the low energy conformers for citric acid and its dissociated forms.

The information gathered in the present work would be valuable for studies involving citric acid or its different dissociated forms adsorbed on the surface of the gold nanoparticle. The adsorption properties and the distribution of citrate molecules over the gold surface is analyzed to identify the role of this molecule in the stabilization of gold nanoparticles.

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Acknowledgements:

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Surface tension and surface $\Delta\chi$-potential of concentrated Z+:Z– electrolyte solutions

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Our aim is to explain the ion-specific surface properties of concentrated electrolyte solutions. Our explanation is based on an extension of the classical model of Schmutzer [1,2]. The model involves hydration and image forces between the ion and the interface and predicts the specific desorption, the surface tension σ and the surface $\Delta\chi$-potential of Z_+:Z_- electrolytes. The thickness of the ion-free layer is calculated from the experimental values of the so-called "hydrophobic gap" thickness at the water surface and the radii of the first and the second ionic hydration shells [2].

It is shown that the ion-specific dependence of the bulk activity coefficient $\gamma_\pm$ on c strongly influences σ, and its contribution to the ion-specificity of σ most often prevails over the specific effect of the ion-surface interactions. Thus, the surface tension of potassium salts follows the order $\sigma_{KOH} > \sigma_{KCl} > \sigma_{KNO_3}$, which turns out to be a direct corollary of the corresponding activity coefficients series: $\gamma_{KOH} > \gamma_{KCl} > \gamma_{KNO_3}$ [1].

The negative value (towards air) of the $\Delta\chi$-potential of most 1:1 electrolytes is shown to originate from the dipole moment of the water molecules at the surface. The negative χ-potential due to water dipoles is inversely proportional to the dielectric permittivity ε of the solution. Since ε diminishes as c_{el} increases, most 1:1 electrolyte solutions exhibit a more negative χ-potential than pure water ($\Delta\chi < 0$) even when the cation stands closer to the surface than the anion. The Hofmeister series of $\Delta\chi$ of 1:1 salts ($\Delta\chi_{LiCl} \approx \Delta\chi_{NaCl} < \Delta\chi_{KCl} < \Delta\chi_{KF}$) follows the corresponding series of ε ($\varepsilon_{LiCl} \approx \varepsilon_{NaCl} < \varepsilon_{KCl} < \varepsilon_{KF}$) [2].

The model is compared with a large amount of data for various symmetric and asymmetric electrolyte solutions. If the bulk ion-specific effects are correctly evaluated, our model predicts accurately their surface properties in a wide concentration range (up to 5-10 mol/kg), without adjustable parameters.

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Electro-optics of complexes between ferric oxide particles and pectins with different distribution of charged units

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Complexation between ferric oxide particles and pectins with degree of methylation 50%, but having ordered or random arrangement of free carboxyl groups, is investigated by means of electro-optics and electrophoresis. The influence of charge distribution in pectin chain on the electrical properties of oppositely charged oxide particles and stability of their suspensions is examined as a function of pectin concentration. We found small but measurable difference in the behavior of both oxide/pectin complexes, which is attributed to condensation of counterions near the chains of pectin with ordered distribution of charges. This leads to a decrease in the effective charge density of this pectin and to a corresponding decrease in the contour length of its adsorbing chains.

At particle charge reversal, two parameters are found sensitive to conformation of the adsorbed pectin chains. The electro-optical effect is higher for the complex between ferric oxide particles and less charged pectin, which is explained with larger amount of chains, adsorbed in a more coiled conformation than the chains of pectin with random distribution of free carboxyl groups. The addition of small amounts of $CaCl_2$ has no significant influence on the thickness of the layer from the less charged pectin in agreement with a more compact conformation of the chains in this adsorbed layer. In contrast, the thickness of the layer from pectin with random distribution of charged units decreases with increasing concentration of $CaCl_2$, indicating more loose structure of this layer.

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Electronic Structure Properties of the Inhomogeneous System Composed of a Ni Doped YVO_4 Photo-catalyst in Contact with Water

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The material YVO_4 is known as a promising photo-catalyst which can produce both oxygen and hydrogen from water by ultra violet (UV) light irradiation like a well-known TiO_2[1]. However, the photo-catalytic performance is much reduced if the co-catalyst based on Ni is not accompanied. To elucidate the role of the Ni-based co-catalyst, we performed dynamical simulations at room temperature within first-principles approaches of the inhomogeneous photo-catalytic system, including H_2O molecules at the density of the ordinary liquid water, the YVO_4 metal oxide photo-catalyst and the Ni co-catalyst.

Simulations have been done by modeling the inhomogeneous photo-catalytic reaction system with a supercell approach where a Ni doped YVO_4 slab is in contact with H_2O molecules at the typical density of bulk liquid water. The exposed surface of YVO_4 is the (010). The simulated system contains Ni doped YVO_4 slab composed of 4 conventional YVO_4 unit cells as a slab substrate and a few H_2O molecular layers on the slab surface.

Main results of this work are as follows; (i) Although the V sites exposed on the surface often contribute to enhance water molecule dissociation at the surface, Ni sites as well as Y sites do not promote the dissociative adsorptions very much. (ii) The relative weight of O_2p orbitals of exposed O atoms is rather large in proximity of the highest occupied molecular orbital (HOMO). This reflects the under-coordination affecting O sites at the surface. These atoms form the thick band of the so-called surface levels. On the other hand, the weight of O_2p orbitals of adsorbed water molecules in the states around the HOMO is relatively small. (iii) The Ni_3d atomic orbital components are well merged in the occupied levels formed by the O_2p of YVO_4 slab substrate. The Ni dopant exchanging Y also provide two kind of unoccpied states. The one kind of them is located in the energy gap of the pristine substrate (Ni-undoped), just below the V_3d unoccupied band, and the other kind of them is located quite close (by roughly 20 ~ 30 meV) to HOMO, which is the so-called hole level. In the YVO_4 system, generally three electrons are transferred from Y to O, so that Y^{3+} cations are present in the system. Conversely, the inclusion of Ni introduces a chemical species which is less electron rich and can donate only two electrons. As a consequence, one hole is introduced in the valence band for each Y-Ni substitution. The most interesting feature here is the fact that the hole levels include not only the components of O_2p of the ophoto-catalyst and Ni_3d but also those of O_2p of the water molecules as dominat components. This implies that the holes are created partially at O sites of water molecules and is possible to promote to oxidize the water molecules located near the surface.

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DNA Focusing in Silica Nanofluidic Channels

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Within the last decade electroosmotic flow has emerged as a promising biochemical analysis technique for molecular detection [1], focusing, separation [2] and purification. Under this technique target molecules that enter a nanochannel experience two opposing forces: a drag force, due to the local electroosmotic velocity within the nanochannel, and an electrostatic force, due to the applied field acting on their charge. Molecules are trapped where the net force is zero. As the concentration gradient varies along the nanochannel, both the electric field and electroosmotic velocities vary, resulting a complex relationship between ion concentration, applied field, device geometry, molecule type and trapping performance. In this study, we use Computational Fluid Dynamics simulations to examine how DNA molecules are trapped in a concentration gradient-based electroosmotic-flow silica nanochannel. The simulations reveal that the electroosmotic velocity within the channel reverses near the trapping location, increasing the efficiency of the trap, but also hindering its ability to discriminate between different DNA lengths (Fig. 1). Qualitatively, the behaviour is observed experimentally (Fig. 2).

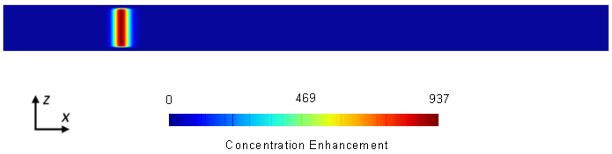

Fig. 1 Contour of the concentration enhancement (CE=DNA concentration/input DNA concentration) from simulation for 600bp DNA in a rectangular nanochannel.

Fig. 2 Image of DNA trapping from experiment for a 100-1000 bp DNA solution under similar conditions (2V applied, 3min, 10/141mM salt concentration).

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Electric Double Layer Expansion by Solution Exchange. A Source of Clean Energy

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Blue energy, or energy associated to salinity differences has recently gained interest as a true potential route for obtaining renewable energy by clean methods. Several procedures have been proposed to take this possibility to practical grounds [1-3], known under the common name of Capmix (*Capacitive Mixing*) techniques. In one of them (CDLE, [3]), a pair of porous electrodes (typically, activated carbon) are externally charged in contact with salty water (sea for example) and discharged in fresh water (river, for example). Since the interfacial potential increases when the ionic concentration is reduced at constant charge, the charge returns at higher potential, hence, gaining an amount of energy roughly equal to the product of the charge transferred times the potential increase. In practical terms [1,4], the typical values are, respectively, 100 mC and 50 mV, so the energy amounts to some hundred µJ. In this work, we present a model of the processes involved, and give clues as to the optimum working conditions. We will provide results of the simulations carried out at steady state and on the kinetics of the charging-discharging process, assuming cylindrical, parallel pores. As illustration, Fig. 1 shows the cycle and the predicted energy production as a function of the charging voltage for different values of pore radius. Experimental data will also be considered, and in particular we will analyse the main characteristics of the electrode material (pore size distribution, wettability) aimed at maximizing energy production.

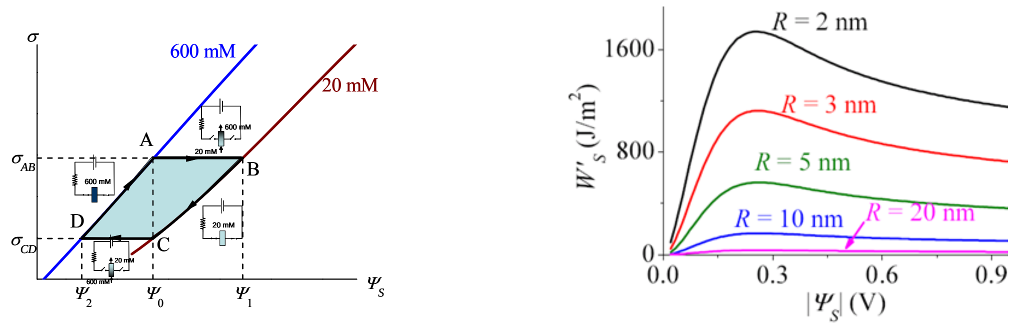

Fig. 1. Schematics representation of the working cycle and predicted energy production.

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Ultrasonic Approach for Nanoparticles in Water

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Acoustic cavitation is widespread in both research and industry with the emphasis on water purification, cleaning of surfaces and formation or design of novel materials as a green and environmentally friendly technology. The remarkable effects of cavitation arise from tiny bubbles that act as hot spots with supersonic extremes far above molecular level in otherwise cold bulk. Typically the surface energy of ultrasound is transformed into chemical (sonochemistry), mechanical (shock waves or jets) or thermal (thousand K and atm) energy avoiding chemical pollution, expensive apparatus and long time processing.

Here we demonstrate several designed ultrasonic approaches to form amorphous materials (relevant for catalysis),[1] modify plasmonic surfaces[2] (important for SERS) and synthesize fluorescent geometries[3] at the nanoscale of colloidal solutions in water. Figure 1 shows electron images of ultrasonic amorphous platinum nanoparticles, gold-silver nano-alloys and fluorescent erbium oxide nanoparticles in organic-free water. To note, the latter normally requires organic substances to form well-defined morphology that exhibit optical properties.

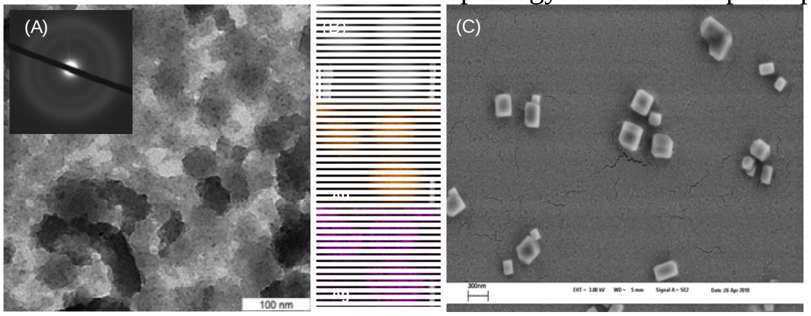

Fig. 1 In water (A) TEM image of amorphous Pt nanoparticles after 20 min of sonication, (B) STEM images of ultrasonic Au-Ag alloy and (C) SEM image of erbium oxide nanoparticles.

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Drops impacting water- and oil repellent coatings

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Impact dynamics of liquid drops is of high importance in a variety of industrial processes such as rapid spray cooling, spray painting and coating, or deposition of pesticides on plant leaves. Of special importance is the transition regime between complete rebound and pinning since it goes in hand with a change of the wetting behavior.

Here, we study impact dynamics of drops on so called "superamphiphobic" coatings, i.e. coatings that repel both, water and oil.[1] Superamphiphobic coatings extend the properties of superhydrophobic coatings towards low interfacial tension liquids. Both, water and oil drops do not wet a superamphiphobic surface but roll-off, when tilting the coating by less than 5°.

We fabricated superamphiphobic coatings that consist of a fractal-like fluorinated silica network.[2] Mixtures of ethanol-water and glycerin-water are chosen to investigate the influence of interfacial tension and viscosity on spreading and retraction dynamics. At low impact velocity the drops completely rebound. However, the contact time increases with impact velocity. Now, the drops temporarily impale the superamphiphobic coating (Fig. 1). Further increase of the impact velocity causes partially pinning. An increasing amount of liquid remains on the coating. The depth of impalement increases with impact velocity, where impalement is confined to the initial impact zone of the drop. From an estimate of the pressure is can be concluded that impalement is dominated by depinning.

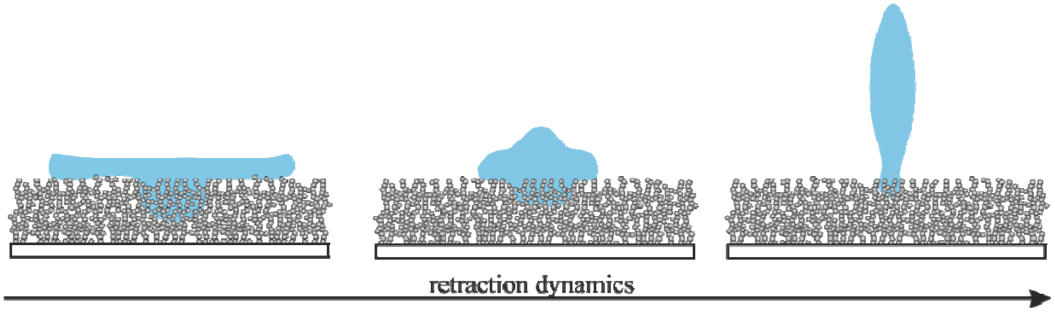

Fig. 1 Sketch of the evolution of a retracting drop, after impacting a superamphiphobic surface

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Viscoelastic instabilities of core annular flows

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Making materials via an extrusion step usually involves complex liquids that are known to exhibits bulk and interfacial instabilities. Here, we present an experimental study on the stability of the co-extrusion of two miscible liquids. The existence of a liquid core that is miscible with the surrounding layer, which is more viscous or has viscoelastic features, leads to a partial mixing inside the injector. Then, a flapping instability of the resulting free compound jet, which is formed in air at rest, is observed. Understanding and controlling such instabilities should enable to create new kind of core-shell materials.

We use concentric round glass capillaries in order to visualize the primary destabilization before formation of the compound free jet. Moreover, a harmonic perturbation of the flow rates can be superimposed. In that way, the frequency response of this co-flow can be assessed. The interface position between the two liquids, which is controlled by the flow rate ratio, is a key parameter that controls the transition between a stable regime towards an unstable one. Different flow patterns have been identified as a function of the liquid and flow properties. In particular, we observe a spiral motion of the core when polymers are added into the shell liquid.

The destabilization of the core directly impacts on the formation of the resulting compound jet in air. A flapping motion is observed when the core is subjected to azimuthal fluctuations. The polymer chains of the shell fluid are elongated under shear inside the injector. Then, in air, the relaxation of the associated normal stress induces a swelling of the free jet. The spiraling motion of the core leads to an anisotropic stress relaxation that deviates laterally the jet and thus induces a flapping movement. All these flow instabilities preclude any controlled fragmentation of the resulting compound jet for making core-shell objects. By damping the flow fluctuations inside the injector and by using a polymer solution that can be further solidified, we managed to produce monodisperse micrometric capsules having a liquid core.

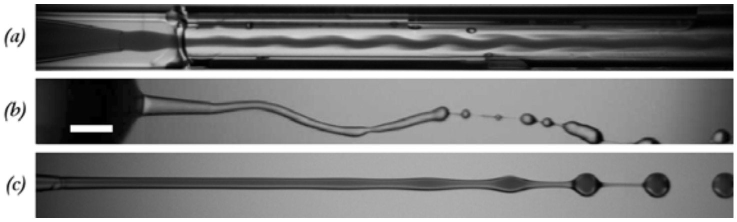

Fig. 1 The core fluid is water with ink and the shell one is a polymer solution. Scale bar = 500µm. (a) Spiraling mode of the shear instability of a confined co-flow. (b) Flapping instability of a compound free jet. (c) Controlled fragmentation of the compound free jet without the flapping motion.

Shear microrheology ofcomplex fluids using magnetic wires

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Rheology is the study of the deformation and flow of matter. It is usually performed on macroscopic samples to determine a value of the viscosity, or a frequency-dependent response. Rheology on biological fluids is more challenging because of the small amounts of fluid available. Living cells for instance have volumes of the order of 10^{-12} L, and can only be studied with specific micro-rheology techniques, e.g. by embedding colloids in the cell interiors and monitoring their motion by microscopy [1]. Here, we present amicro-rheology technique based on the use of magnetic wires. Micron-sized wires of diameter 0.5 µm were synthesized followingthe electrostatic assembly of iron oxide nanoparticles. Passive/active micro-rheology was first conducted on model liquids, such as Newton and Maxwell fluids. These experiments reveal excellent agreement with theory [2].

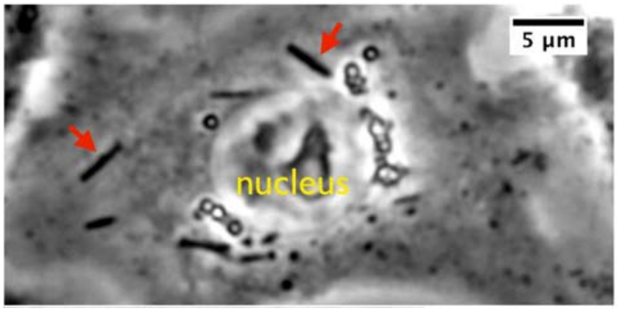

Figure*1: Phase contrast microscopy images of NIH/3T3 fibroblasts cells treated with 4 μm wires for 24 h at a concentration of 10 wires/cell. The arrows indicate internalize nanowires.*

Experiments were then carried out with wires embedded in the intracellular medium of murine fibroblasts [1] and of canine kidney epithelial cells (Figure 1). The mean-squared angular displacement (MSAD) of wires was obtained as a function of the time using an originaltracking technique. The MSAD reveals a Brownian-like diffusive regime and a rotational diffusion constant varying as $1/L^3$, where $L$is the wire length. This scaling suggests that for the fibroblasts and for the epithelial cells, an effective viscosity of the cell interior can be determined.Values of viscosity were found at 0.16 and 1.4 Pa s, respectively, i.e. 200 and 1800 times the viscosity of water (T = 37°C). These results are discussed in the light of previous cell mechanics experiments, and demonstrate the importance of innovative probes for studying fluids in confined environments.

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Laplace Equation of Capillarity Extension for Non-Localized Situations to Included Capillary Systems Containing Surface and Line Boundaries

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Classical expressions for mechanical equilibrium in capillary systems such as the Laplace, Young and Neumann triangle relation can be derived using a calculus of variations approach that minimizes the composite system's free energy subject to constraints to obtain extremals. These free energy expressions are functionals of the equations that characterize the system's boundaries and they yield localized expressions between the intensive properties (e.g. pressure, surface tension, etc.) and the boundary geometry. However, for very small systems with nonlocalized behaviour new approaches or extensions are required. These extensions provide for consideration of functionals of functional that lead to Euler-Lagrange equations that are integro-differential in character. This expands the ability to describe capillary systems beyond solely differential equations and permits a description of interfacial forces such as disjoining pressure, etc. within a consistent formulation

Supramolecular Solvent-Free Nanofluids

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We show that auto-condensation of organoalkoxysilanes, followed by suitable anion exchange, produces solvent-free nanoparticle nanofluids we call organosiloxane supramolecular liquids. We find that classical liquid properties are exhibited with some distinct differences. We observe heat capacity anomalies manifested as lambda transitions in excess heat capacity centered around a glass transition (T_g) and around a freezing transition. The T_g-proximal lambda transition is the first experimental realization of an enthalpic phase transition overlying a glass transition. The existence of such a connection or coincidence has undergone decades of theoretical conjecture. The second anomaly spanning the melting/freezing range is the first reported excess enthalpy ever reported for an experimental particulate fluid undergoing a phase transition. The integral enthalpy from these lambda transitions is quantitatively accounted for by the loss of specific surface area of the particles, and the associated surface free energy, upon freezing and upon cooling beneath the glass transition temperature. This new material and cousins to be similarly derived promise to become useful in developing soft-sphere potentials in the thermodynamics of polymeric liquids.[1]

Similarly composed nanofluids obtained by condensation on nanosilica core templates and surface decorated with both ionic liquid organic salt groups and with various reactive groups are exotic cross-linking agents that define new types of resins. Such agents can be used to counter embrittlement provided by nanofillers while increasing toughness. We show that such materials can be used to produce thin films including UV protective clearcoats and an interesting new family of adhesives.[2,3]

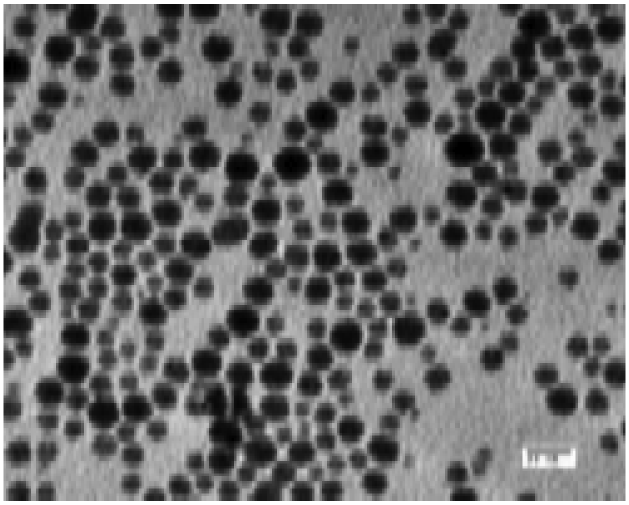

Fig. 1 TEM of nanofluid (20 nm scale bar)

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Adsorption properties of surfactants and their mixtures – potential components of industrial degreasing agents

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Eco-friendly degreasing agents useful in various branches of industry should be effective at very low dosage, should exhibit a low tendency to foaming and should possess very high emulsion stability at any pH. Furthermore, it should be readily biodegradable. The main components of degreasing agents are surfactants which are responsible mainly for the decrease of surface /interfacial tension and increase of the wettability. Usually degreasing systems contain two or three surfactants because the mixed systems exhibit much better adsorption/wetting properties than the individual components. In order to obtain a recipe of effective degreasing agent, a selection of suitable surfactants is required.

The main goal of presented investigations was the determination and comparison of adsorption properties at the air/water interface of selected commercial surfactants and their binary mixtures which are potential components of the industrial degreasing compositions. Surface and micellar properties of surfactants and their mixtures were discussed on the basis of equilibrium surface tension measurements and study of kinetics of adsorption.

Five commercial surfactants were investigated: two anionic compounds and three non-ionic derivatives. All measurements were carried out at 294 K. Equilibrium surface tension at the air/water system for individual compounds and their binary mixtures was measured by du Noüy ring method using K12 Krüss and KSV Sigma 701 tensiometers. Dynamic surface tension measurements were performed using the bubble pressure tensiometer (Sita t60, Germany), which registered change of surface tension in time from 30 ms to 60 000 ms.

The application of Frumkin's equation to approximate the experimentally obtained equilibrium surface tension isotherms allows estimation of adsorption parameters, as: the partial molar area of a surfactant molecule at the surface (ω), surface excess at the saturated interface (Γ^{∞}) and free energy of adsorption (ΔG_{ads}). On the basis of the dynamic surface tension data for micellar solution the magnitude of micelle dissociation rate constant were estimated.

The experimentally obtained surface tension isotherms in the air/water system for all surfactants investigated allowed to compare the surface activity of these compounds. Observed differences of the kinetics of adsorption and the abilities for lowering the surface tension are significant. Compounds studied reveal both different efficiency as well as different effectiveness of adsorption in the air/water system. The results of study of surface activity for binary systems indicated that some of investigated mixtures showed strong synergistic effect in reducing of surface tension in the air/water system.

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Gravity effects on particle-bubble interactions in granulometric separation processes

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The influence of the gravity effects on the behaviour of fine particles in the boundary layer of rising bubbles is presented. By scaling analysis the role of the gravity in addition to the dynamic interaction, caused by the finite dimensions of the particles is explained. An asymptotic model for the disturbance field caused by fine heavy solid is obtained and solved analytical. The trajectories of sub- and micron sized heavy particles in the boundary layer are calculated. It is found that the rejection outside of the boundary layer or “capturing” particle-bubble effect is observed (may be expected) with increasing the density of the solid. An idea it is also given about granulometric separation of particles by the bubble. A criterion for separation, which may be experimentally clarified is found.

Uptake of six heavy metal cations by synthetic goethite

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Synthetic goethite [1] was characterized by means of XRD, SEM, BET, electrophoretic mobility, electric sonic amplitude, and Mössbauer spectroscopy [2-4]. The particles had an acicular shape (470 nm long, and 66 nm wide), the specific surface area was 40 m^2/g, and the IEP was at pH 9.4. The uptake of heavy metal cations at various pH and initial concentration of metal cations of 10^{-2} M was studied by ASA. The uptake decreased in a series Cu>Pb>Zn>Co>Ni=Cd, which is typical for other studies of uptake of metal cations by iron (hydr)oxides [5], and which is correlated with the 1st hydrolysis constants of metal cations.

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Highly water repellent coatings in marine environment

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Highly water repellent coatings with wettability properties known as superhydrophobicity (SH) are related to surfaces with contact angle above 150° and a very small hysteresis.
The small area available for these surfaces when in contact with water address to be exploited in many applications where interactions with aqueous environment are usually strongly to be avoided like for protection and friction reduction in marine environment.
With the aim to provide more resistant and long lasting coatings, the SH surfaces under investigation have been prepared by different preparation methods and studied in presence of pure water, marine waters, solutions and dispersions.
Depending on the preparation SH surfaces show different aging resistance due to the composition and thickness of the coating.
Wetting studies and surface characterization show how the use of patterned and non patterned surfaces can be used to achieve different aims in terms of fouling prevention and protection of metals in underwater conditions.

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Acknowledgements:

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Gold and silver nanoparticles: green synthesis, immobilization onto silica spheres and analytical applications

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In this work, aqueous dispersions of silver (Ag NPs, D_{av}=14 nm) and gold (Au NPs, D_{av}=11 nm) nanoparticles were synthesized by green chemical reduction method using carbohydrates as reducing and stabilizing agents. The colloid mixing method were applied to immobilize the starch-coated Ag NPs and Au NPs onto the surface of amine-functionalized silica (SiO_2) submicrospheres (D_{av}=400 nm). The size, morphology, structure, surface and optical properties of nanoparticles and nanocomposites were characterized by transmission electron microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, dynamic light scattering, zeta potential measurements, UV-vis spectroscopy.

Simple, fast and low cost procedures were developed for highly sensitive and selective quantitative sensing of Hg (II) and Cr (VI) using aqueous dispersions of starch-stabilized and raffinose-stabilized silver nanoparticles as optical sensing systems. Colorimetric probes developed are based on various mechanisms including sorption of analytes, redox reaction and/or aggregation of silver nanoparticles. The sensitivity and selectivity of colorimetric sensors proposed towards interferent transition-metal ions, alkali metal ions and alkaline earth metal ions were studied. The effect of the analyte concentrations to the Ag NPs optical response was considered and the LODs for analyte determination were defined.

Nanocomposite particles SiO_2-AgNPs and SiO_2-AuNPs were characterized as sorbents for speciation and determination of iHg and methylHg in surface waters. Several parameters such as acidity of the sorption media, amount of sorbent, time of sorption, type and concentration of the eluent were optimized in order to define chemical conditions for selective separation and enrichment of both iHg and methylHg. Analytical schemes for speciation and determination of Hg were developed.

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Starch-assisted green synthetic route of nanosized zinc oxide with promising photocatalytic properties

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Gel matrix of the natural polysaccharide starch has been employed as a template for the sol-gel synthesis of zinc oxide nanoparticles via solution-solid technique. The template offers selective binding sites for Zn (II) under aqueous conditions. Controlled solvent-exchange, further isolation of solid product by microfiltration and drying, and subsequent removal of the template backbone enable the synthesis of spatially separated zinc oxide nanocrystals with smaller crystallite size and higher surface area.

The crystalline character of the zinc oxide and near narrow particle size distribution pattern have been confirmed through powder XRD measurements and TEM with SAED observation. The average crystallite size of the particles obtained at optimal synthesis conditions was found to be 16 nm irrespective of the nature of the template. The morphology, surface and optical properties of ZnO samples were characterized by SEM observation, BET-surface area and ζ-potential measurements, UV–Vis and PL spectra.

The UV photocatalytic activity of zinc oxide nanoparticles was studied and compared with TiO_2 (P25) by analyzing the degradation of methylene blue (MB) in aqueous solution. The nanosized ZnO sample showed greater photocatalytic activity than commercial TiO_2 photocatalysts. The size and shape factors seem to be of great importance in the observed photocatalytic performance.

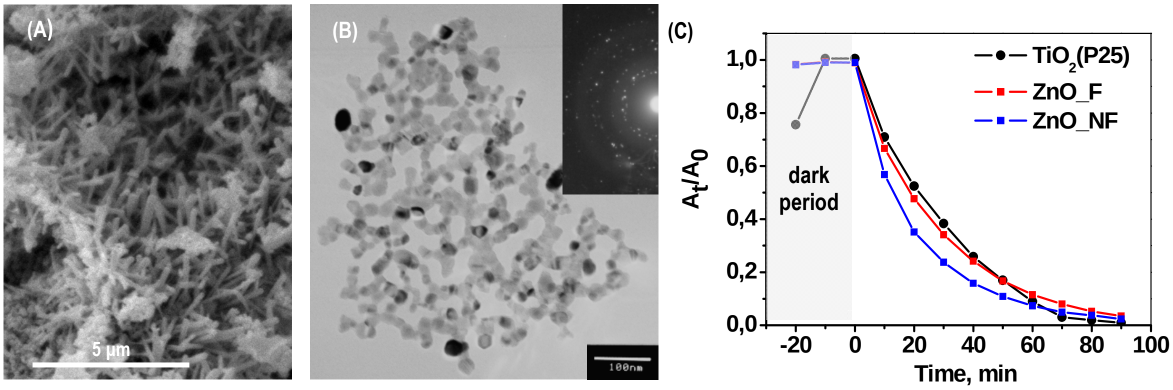

Fig. 1 (A) SEM and (B) TEM images of nanocrystalline ZnO; inset in (B): SAED pattern; (C) Evolution curves of MB photocatalytic degradation on TiO_2 (Degussa P25) and ZnO nanoparticles.

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Rotational diffusion in concentrated platelet systems measured with X-ray Photon Correlation Spectroscopy

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Using X-ray Photon Correlation Spectroscopy (XPCS) we have measured the rotational modes of concentrated charged gibbsite platelets in the isotropic regime. This has been done by analyzing the data qualitatively using available theories for non interacting systems. The relaxation spectra do not follow the same pattern as for spherical particles at larger wave vectors. It will be shown that this deviation from the behavior of spherical systems arises from the influence of the rotational modes. In addition, in the isotropic state a pre-transitional peak in the static q-dependent intensity at large q values is discussed. We suggest that this peak originates from a strong local alignment between platelets before the actual phase transition takes place.

Barrier properties of natural polyelectrolytes studied by diffusion experiments in model hydrogels

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Humic substances form the key constituent of natural organic matter in numerous natural environments (soils, sediments, water aquifers), where they take responsibility for crucial ecological effects (e.g. self-detoxification of soils). As they are formed primarily from the biodegradation of plant residues, they are characterized by a complex molecular structure with plenty of diverse functional groups which result in unusual and versatile reactivity and sorption ability of natural humic matrices. This interesting nature of humic substances stands behind their ability to control the transport of low-molecular compounds in the environment (e.g. transport of nutrients, pollutants or pesticides in soils) and motivate reactivity-mapping studies on humics. Recently, various laboratory diffusion techniques were introduced [1-2] in order to illustrate an effect of interactions with humic substances on the transport of ionic compounds in model humic matrices (i.e. humic hydrogels). This contribution summarizes most recent experiments utilizing diffusion cells technique and non-stationary diffusion experiments (Fig. 1) in reactivity-mapping on humic substances, applied in agarose-supported hydrogel. In the experimental part, effect of numerous experimental parameters (concentration of humic substances in the hydrogels, pH, ionic strength, selective masking some reactive groups) on representative transport parameters of low-molecular compounds (effective diffusion coefficients, partition coefficients) have been systematically studied. As was experimentally confirmed, two opposing effects take place in these reactive systems– on the one side, interactions between HAs and the diffusing dyes causes improved partitioning of the dye in the gel (characterized by high concentration jump at the solution-gel interface) but at the same time, it strongly suppress the mobility of the dye in the gel (characterized by value of diffusion coefficient)

Fig. 1 Picture of diffusion cells apparatus (left) and samples from non-stationary diffusion experiments (right)

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Penetration of dissolved humic fertilizers to leaves studied by simple diffusion technique

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Simple laboratory diffusion technique was designed in order to study transcuticular movement of dissolved humic substances, which form the crucial component of modern agricultural foliar preparations. In the experiments, the rate of transport of liquid potassium humate (Lignohumate A, Amagro, Czech Republic) through mechanically, chemically and enzymatically isolated leaf cuticles and through the respective original leaves of several higher plants (*Rhododendrone*, *Bryophyllus calcynium*, *Prunus laurocerasus*, *Epipremnum pinnatum*) was observed in diffusion couple apparatus, in which cuticle (or leaf) sample was sandwiched between two agarose hydrogels (1% wt.) with different concentration of dissolved humate (0% wt. and 1% wt., respectively). Concentration of the humate at different positions of the "receiving" hydrogel was determined photometrically at various times. From such concentration profiles, corresponding values of diffusion coefficients were estimated in order to compare the rate of transport of the humate for different plants and different cuticle isolation procedures.

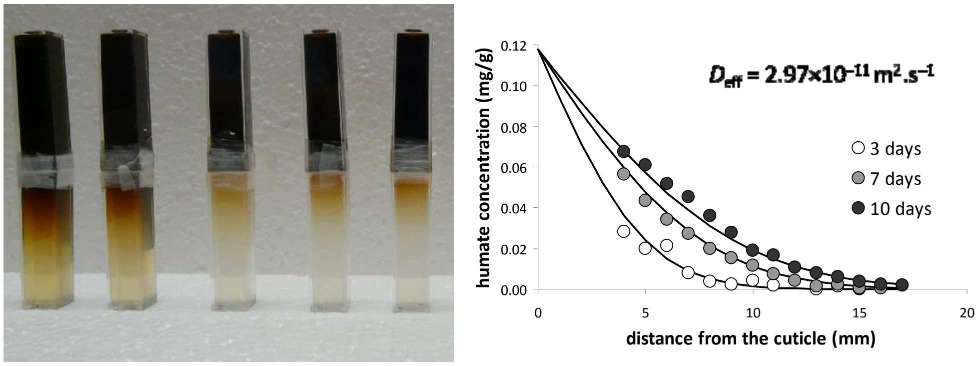

Fig. 1 Diffusion couples, in which potassium humate had diffused through leaf cuticles into "receiving" (lower) agarose hydrogel (left picture, different penetration depths are obvious). Example of concentration profiles in "receiving" hydrogels (right picture): experimentally determined (circles) and calculated using estimated diffusion coefficient D_{eff} (solid curves).

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Synergism by Co-assembly at the Origin of Ion Selectivity in Solvent Extraction

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In solvent extraction, synergism emerges when for a defined formulation of the solvent phase, there is an increase of distribution coefficients for some cations in a mixture. To characterize the synergistic mechanisms, we determine free energy of mixed co-assembly in aggregates. Aggregation in any point of a phase diagram can be followed not only structurally by SANS, SAXS and SLS, but also thermodynamically by determining the concentration of monomers coexisting with reverse aggregates. Using the industrially used couple HDEHP/TOPO forming mixed reverse aggregates, and the representative couple U/Fe[1], we show that there is no peculiarity in the aggregates microstructure at the maximum of synergism. Nevertheless the free energy of aggregation necessary to form mixed aggregates containing extracted ions in their polar core, is comparable to the transfer free energy difference between target and non-target ions, as deduced from the synergistic selectivity peak.[2] The effect of extracted ions and solvents on aggregation will be discussed in this talk.

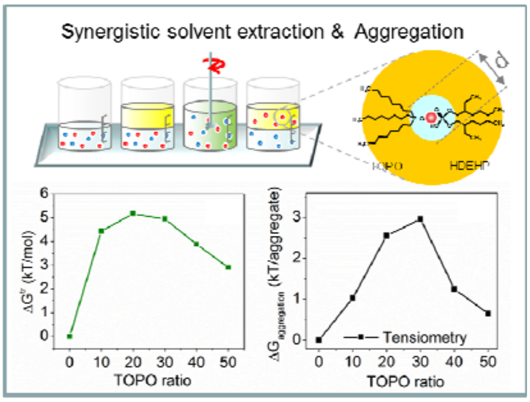

Fig. 1 Aggregation and transfer energy correspondence in and out of synergism.

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Microemulsions as carrier media for environmentally friendly enzymatic decontamination of lipophilic toxic compounds

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Decontamination is the process of removal or neutralization of surface hazards resulting from a chemical attack or an accidental release of toxic chemicals, e.g. organophosphates as insecticides and chemical warfare agents. Modern decontamination media have to match requirements, which allow to reconstitute personnel and equipment rapidly. Their ability to extract penetrating chemical agents and industrial chemicals out of sorptive surfaces is of importance and they have to be noncorrosive, nontoxic and environmentally friendly. In recent years natural surfactants, e.g. alkyl polyglucosides attract increasing interest for new applications of liquid decontamination agents. For example, microemulsions based on sugar surfactants and plant and food grade oils combine a soft and "green" performance with a phase behaviour of low temperature sensitivity.

For a series of such bicontinuous microemulsions, we discuss extraction and wetting properties for model and realistic surfaces of different degrees of hydrophobicity. These systems overcome the problem of solubilisation of the hydrophobic contaminant. Additionally, the effect of enzyme addition to these microemulsions was investigated. The enzyme Diisopropyl fluorophosphatase (DFPase) from the squid *Loligo vulgaris* efficiently detoxifies highly toxic organophosphorus compounds. DFPase can be used in bicontinuous microemulsions where it remains catalytically active which can be shown by the use of NMR and FTIR spectroscopy. Scattering techniques allow us to confirm that structure and dynamics of the amphiphilic interface are not affected by the presence of the enzyme. Hence, these sugar surfactant based bicontinuous microemulsions are promising environmentally friendly compartmentalized reaction media providing interesting properties for biotechnological applications in general.

Refined Classical Theory of Coagulation of Aerosol Nanoparticles

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The classical theory of the laminar electro-Brownian coagulation of charged particles in the transition regime has been founded by N. Fuchs and based on his “boundary sphere” concept. However, this theory missed the hydrodynamic factor, i.e., dependence of a diffusion coefficient of closing particles on their separation. First, this factor was proposed by B. Derjaguin in his theory of colloidal stability. But its relevant incorporation into the theory of coagulation of aerosol particles is still under a question. In our theoretical studies, we considered this problem and proposeda“refined classical model” (RCM) of coagulation of charged nano-sized aerosols with correct including this missed factor. In an initial model, we consider van der Waals’, Coulomb’s and “image” driving forces. The RCM and the corresponding refined classical theory (RCT) of aerosol coagulation are used for describing coagulation and stability of charged and uncharged nano-aerosols in the transition Knudsen range (0.1 <Kn< 10)that is typical for motion of nanoparticles in the air.

The major new results of this approach are (1) the criteria of RCM/RCT validity and their limits, (2) the exact steady-state charge distribution function describing aerosol ensemble in the bipolar ion atmosphere, (3) the DLVO-type criterion of preventing coagulation of charged particles, and (4) the refined electro-Brownian coagulation coefficient with the enhancement factor in the Knudsen transition regime. A comparison of the theory with other theoretical and experimental data on soot nanoparticles shows a good semi-quantitative agreement in most important cases [1,2].

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Electrokinetic Properties of Biodegradable Conducting Polyaniline-*graft*-Chitosan Copolymer in Aqueous and Non-aqueous Media

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Zeta (ζ)-potential measurements are one of the most powerful tools to investigate the colloidal properties. Electrokinetic data are used to determine the ζ-potential characteristics of the materials [1,2]. In this study, electrokinetic properties of polyaniline-*graft*-chitosan (PAni-*g*-CS) copolymer, synthesized by chemical oxidative radicalic polymerization, were investigated. The effects of time, pH, electrolytes, various surfactants, and temperature onto ζ-potentials of the dispersions prepared in polar (water) and non-polar (silicone oil) media were examined. The ζ-potential of PAni shifted to more positive regions after grating with chitosan (Fig. 1). Concomitantly, the isoelectric point of the PAni homopolymer shifted to higher pH value. In acidic medium, ζ-potential of the copolymer was observed to increase up to +44 mV. It was concluded that the presence of monovalent ($NaCl$) electrolyte had no impact on ζ-potentials of the copolymer whereas; divalent ($BaCl_2$) and trivalent ($AlCl_3$) electrolytes caused the ζ-potentials to shift to more positive regions. Mastery of this study will be very helpful for designing, fabricating, and developing further new materials based on biodegradable chitosan and conducting polymers.

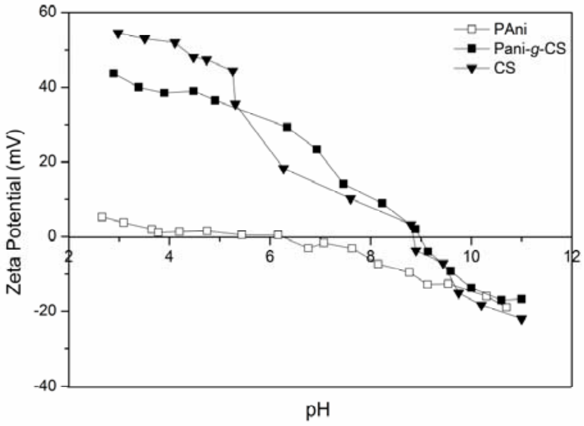

Fig. 1 Effect of pH on ζ-potentials of the materials, c_{samples} = 0.1 g/L, T = 25 ºC

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Acknowledgements:

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Gel Point Determination Thanks to Microrheology Measurement at Rest

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This work presents a new technique of the passive microrheology for the study of the microstructure properties of soft materials like emulsions, polymers, hydrogels. Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. It allows to measure the mean displacement of the microstructure particles in a spatial range between 0,1 and 100 nm and a time scale between 10^{-3} and 10^{5} seconds. Displacement of probe particles is monitored to obtain directly the Mean Square Displacement (MSD) curve, which is the signature of the viscoelastic properties of a product. This technique allows to monitor the evolution of the microstructure, the restructuration after shearing, the variation of the viscoelastic properties versus temperature, pH...

This work focuses on viscoelastic properties evolution and particularly gel point transition. A new method called Time Cure Superposition is used to rescale MSD curves and obtain a master curve. From this curve can be automatically and precisely determined the liquid/solid transition. We will explain this rescaling method and show application examples and advantages of using a non intrusive method for :

- Gelation process of food products to measure gel point of yoghurt
- Carraghenan networks formation and comparison of their viscoelastic properties versus concentration.

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Colloidal Stability of Emulsions and Nanoparticles in Pharmaceutics

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The world of drug delivery is getting every day more efficient with new product forms, which are directly targeting the deficient organs. Colloidal systems such as emulsions (simple or multiple) or nanoparticle suspensions are now widely used as drug carriers or nutritional solutions in this respect. These new product forms allow better targeting and assimilation for the patient, and give rise to new solutions for the drug designers. However, the stability of these inherently unstable colloidal systems makes them complex to formulate and study.

Despite the existence of models and increasing knowledge on physical chemistry to help the formulator to tend towards more stable formulations, he cannot take the risk to select an industrial formula for its sole end-use properties without testing the stability experimentally, when an unstable formulation can risk the life of the patient he is trying to cure. Therefore, the companies developing instruments have worked in collaboration with the physical chemists, from industry and research, to develop new techniques of analysis for either predicting the stability of these mixtures, or reducing times of ageing tests. These techniques, although very powerful, require a good knowledge of measurement to interpret the results. This presentation aims to review the main examples of multiple light scattering to monitor the physical stability of colloidal systems for pharmaceutical applications.

Characterization of PDADMAC monolayers on mica by streaming potential measurements

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Physical properties of the cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) having a molecular weight of 160 kDa were characterized. The bulk characteristics involved the diffusion coefficient (hydrodynamic diameter), and electrophoretic mobility as a function of polyelectrolyte solution concentration for various ionic strengths. The hydrodynamic diameter data suggested that the macromolecules assume an extended, wormlike shape in the bulk. Accordingly, the diffusion coefficient was interpreted in terms of a simple hydrodynamic model pertinent to flexible rods, previously applied for poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) [1]. The thorough characterization in the bulk allowed a proper interpretation of PDADMAC adsorption on mica studied by the streaming potential technique. The obtained results were quantitatively interpreted in terms of the electrokinetic model postulating a 3D adsorption of macromolecules as discrete particles. These measurements allowed one to determine the coverage of PDADMAC as a function of zeta potential of mica. Furthermore, the stability of the polyelectrolyte monolayers against prolonged washing (up to 24 h) also was determined using the streaming potential method. It was demonstrated that PDADMAC layer is resistant to washing. It also was concluded that due to high sensitivity, the electrokinetic method applied can be effectively used for quantitative studies of polyelectrolyte adsorption, desorption, and reconformation.

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Non-equilibrium structure formation in real time at surfactant-polymer interfaces

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The interaction of polymers and surfactants is a well studied phenomena generally studied at equilibrium. Combinations of oppositely charged polymers and surfactants have long been known to form a variety of complex liquid crystalline structures at certain compositions and salt concentrations. However many processes require an understanding of the non-equilibrium aspects of such systems, as structure formation at the interface of eg a polymer solution and a surfactant solution dictate the transport properties of the material, processability and suitability for final application.

Towards understanding the non-equilibrium behaviour at such interfaces we have established spatially resolved kinetic information on structure through the interface using small angle x-ray scattering. Evolution of structure after contact, and the rate and direction of progression of various phases can be readily monitored using this approach. When combined with spectroscopic and microscopic techniques such as crossed polarising microscopy, Raman microscopy and NIR microscopy, the link with composition can be established, providing a powerful means of understanding and hence controlling structure formation and subsequent properties of these systems.

Using polyDADMAC and SDS as an example, hexagonal phase structures formed at the interface were observed to grow towards the micellar surfactant rich region. The diffusive growth indicated greater diffusivity of polymer in the interface compared to surfactant.

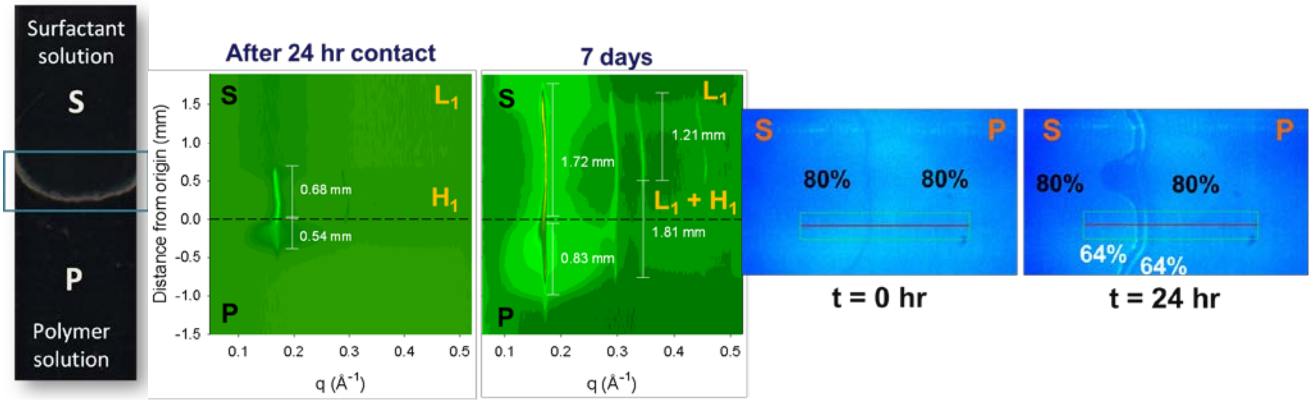

Fig. 1 Interface between polyDADMAC and SDS (i) viewed through crossed polarizing microscopy, (ii) structural profile through interface by SAXS, (iii) water content through interface by NIR

Synthesis and Characterization of Polymer Grafted Silica Nanoparticles

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In this project, we prepare as a starting point well-defined silica nanoparticles (SNPs) by means of amino acid based catalysis (or ammonia) from precursors like tetraethoxysilane (TEOS), which allows to achieve monodisperse SNPs in the size range of 10- 300nm (**Fig.1a**). In the next step they become polymerically modified *where as monomers we employ 2-(dimethylamino) ethyl methacrylate (DMAEMA) or tert-butyl methacrylate (t-BuMA).* The polymer is grafted onto the surface by atom-transfer radical polymerization (ATRP) because this allows good control over the target molecular weight (and its distribution) of the grafted polymers. With this choice we are able to form silica nanoparticles with both cationic and anionic polyelectrolyte shells of variable length, i.e., this allows us to have a very variable functionalization of the surface of the silica nanoparticles. The extent of surface modification and polymerization can then be followed by themogravimetry (TGA) (**Fig.1b**). Furthermore DMAEMA and MAA are weak bases and acids, respectively, thereby allowing in a simple way to tune the charge density of the resulting modified nanoparticles simply by adjusting pH.

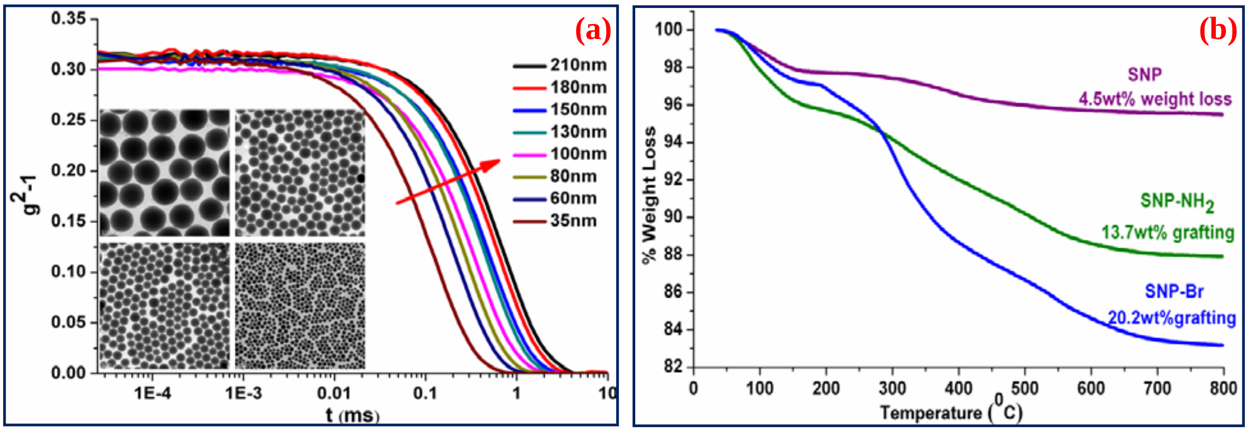

Fig1. (**a**) The narrow size distribution of the synthesized SNPs was observed by DLS and TEM (**b**) TGA curve after each stage of modification, which indicates the amount of initiator grafting.

The resulting product were characterized by Static and Dynamic Light Scattering (DLS), Small Angle X-Ray Scattering (SAXS), Thermal Gravimetric Analysis (TGA), Fourier Transform Infrared (FTIR), and Transmission Electron Microscopy (TEM). These experiments confirm that polymer shells of variable thickness are successfully attached onto the SNPs. Current and future work then will address the interaction of such polymer modified SNPs with membranes and how to use them for purposes of selective drug delivery. For these purposes fluorescently labeled SNPs are prepared and employed in corresponding experiments.

CD-Spectroscopic Assessment of Potential Antigenicity Induced by Negatively Charged Drugs

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Early detection of immune-mediated adverse drug effects is a major challenge in drug development. Towards this goal, complexes made of the positively charged chemokine platelet factor 4 (PF4) and polyanionic drugs have been studied, since these complexes are the target of the most frequent drug-induced immune reaction affecting blood cells, the heparin-induced thrombocytopenia.

By varying the polyanion's degrees of sulfation and polymerization, the exposure of antibody-binding sites (epitopes) on PF4 can be controlled during complex formation. Comparison of the data of circular dichroism (CD) spectroscopy and an enzyme-linked immunoassay shows a strong correlation between changes in the secondary structure of PF4 and epitope exposure, which enables us to predict PF4/polyanion complex antigenicity using CD spectroscopic data only. Based on the observed interaction of polyanions with proteins, a model of the expression of antigenic structures on PF4/polyanion complexes is suggested.

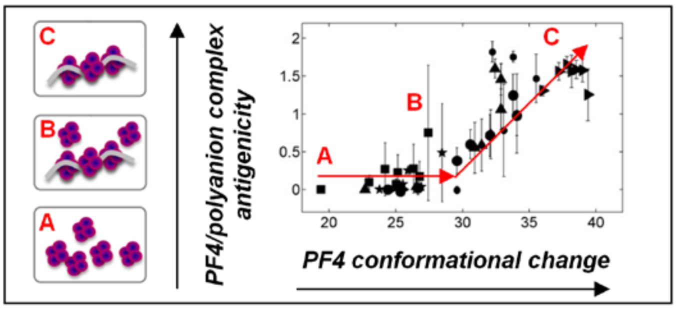

Fig. 1, right**:** The antigenicity of the PF4/polyanion complex as function of the conformational changes of the protein PF4. Antigenicity is measured by an enzyme-linked immunoassay, and the conformational changes by CD spectroscopy. Different symbols correspond to different polyanions. Left: Sketch of PF4/polyanion complexes with different composition. For each polyanion, an optimum ratio between the concentrations of PF4 and polyanion corresponds to the most pronounced conformational changes and the maximum in antigenicity.

Polymeric nanoparticles from thermo-sensitive PNIPAM-g-PEO copolymer: effect of solvent composition and added drug

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In the recent years, polymeric “soft” nanoparticles sometimes called „polymersomes”, self-assembled from amphiphilic copolymers in selective solvents, have attracted much attention for their potential application as multidrug delivery carriers. In selective solvents, polymersomes are formed by controlling the critical molecular factors that affect micellization. For example, the loading of hydrogen-bonding inducing drugs like indomethacin, ibuprofen and ketoprofen, can trigger significant morphological transformations of polymeric self-assemblies based on graft amphiphilic copolymers.

In the present work, we examine the effects of the cononsolvent composition and added model drug, Indomethacin, on the morphologies of PNIPAM-g-PEO graft copolymer aggregates in solvent mixtures of ethanol and water. To evaluate the influence of the solvent composition on the structure of the resulting aggregates, we performed rheological investigations on a series of copolymer solutions as a function of the added ethanol and drug and attempted to correlate these results with experimental data about the interfacial behavior of the same system in respect to changes in interfacial tension and surface dilational viscoelasticity.

Acknowledgements:

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Viscoelastic properties of hydrophobically modified polyacrylates in thin liquid films and bulk solution

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Hydrophobically modified (HM)- or associative polyelectrolytes are widely used as technologic viscosifiers, but to the same measure they benefit from academic interest. This arises from the necessity to understanding their aggregation mechanism and conformation in confined media and in bulk. The properties in solution of such amphiphilic polymers are sensitive to salts, surfactants and moreover to pH, in the particular case of associative polyacids. Still, less is known about their capability of forming thin liquid films and their drainage properties, which should be helpful if they are used as additives in oil transport through pipes. In this respect, the present study investigates two poly(acrylic acids) (PAAs), with MW=25000 (PAA25) and respectively 150000 (PAA150), randomly grafted with 3% (unit moles) dodecyl (C12) chains. Two main pH domains were implied, i.e. pH=3-4 and pH=8-9. The interfacial properties of the polymers were explored by microinterferometry using the Scheludko-Exerowa cell and also, by surface dilational rheology. The data were corroborated with pyrene fluorescence emission and dynamic bulk rheology in the HM-PAAs aqueous solutions. The polymer levels were just below their critical micellar concentration, as indicated by the polarity ratio (I1/I3) of pyrene. We tried to obtain Newtonian black films by tuning the polymer and electrolyte concentration and the pH. The experimental results show that in NaCl presence, the PAA25-C12 could form thin liquid films with a rheologic behavior, while PAA150-C12 forms thick films with slow or without drainage, depending on pH. These things were explained in connection with the polymers pH and consequently with their capacity to develop intra- or inter-molecular interactions, reflected in the viscoelastic properties of film and bulk, as well.

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The role of the porphyrin ring in the fluorescence quenching of conjugated polymers by proteins

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The fluorescence of the water-soluble anionic conjugated polymer, poly[potassium-5-methoxy-2-(4-sulfopropyloxy)-1,4-phenylenevinylene] (MPS-PPV), is quenched in diluted aqueous solution by cytochrome c, a small, naturally occurring electron-transfer protein. This study investigates the mechanism of fluorescence quenching of this process. Experiments with ferrous cytochrome and ferric cytochrome c have been carried out and we found that the Stern-Volmer constant is similar independently of the oxidative state of the iron which seems to indicate that photoinduced electron transfer between the iron atom of the protein cytochrome c and the conjugated polymer does not play any role on the fluorescent quenching. With the aim to know the role of the porphyring ring in this process, we have investigated the fluorescence quenching of the polymer by the precursors protoporphyrin IX and hemin, molecules that constitute the active site of the protein. Our results suggest that the quenching mechanism is based on the resonance energy transfer between the electron-rich MPS-PPV and the electron-deficient porphyrin ring of cytochrome c. Furthermore, this result is supported by the quenching observed using the 5,10,15,20-Tetrakis-(4-trimethylammonio-phenyl)-porphyrin-tetra-(*p*-toluenesulfonate). Due to the controversy found in the bibliography, studies about the quenching mechanism in CPs/heme proteins systems could be very helpful.

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Phase Behaviour of Anisotropic shaped Colloids

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Anisotropic shaped microgels of high uniformity are prepared using dumbbell-shaped poly (styrene) (PS) particles as core and thermosensitive poly (N-isopropylacrylamide) (PNIPA) as shell. Volume fraction and aspect ratio of dumbbell-shaped microgels can be adjusted flexibly through temperature and concentration. Different rheological measurements have been carried out on dumbbells with aspect ratio (the ratio of centre to centre distance to diameter of one sphere, below 0.43) below lower critical solution temperature (LCST). All the dumbbell-shaped microgels are dispersed in 0.05 M KCl solution to screen the electrostatic interactions resulted from residual charges completely.[1] The phase transition has been realized by controlling temperature and concentration. We observe a phase transition of the microgels from fluid to an ordered, crystal-like state which is apparent through Bragg-reflections in the visible range. A biphasic gap for $0.50 < \phi_{eff} < 0.56$ is seen[2] and the comparison with previous computer simulations strongly suggests that the thermosensitive dumbbells can form plastic crystal.[3,4] Rheological measurements demonstrate the crystallization process in microgels suspensions with $\phi_{eff} = 0.51$ and a glassy-like behaviour when ϕ_{eff} is increased up to 0.63. Moreover, double yielding events are investigated in fully crystalline phase.

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Thermoresponsive polymeric micelles as efficient tool for controlled drug delivery

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Recent research efforts on drug release strategies focus, besides liposomes and nanoparticles, on polymeric micellar systems that, thanks to their structural properties, are able to effectively encapsulate and release controlled and localized quantities of drugs in response to external stimuli. According to recent evidences of the importance of polymerosomes for targeted therapies, we studied self-assembled micelles obtained from triblock copolymers of PCL-PEO-PCL with the twofold aim of efficient storage of drug molecules and of sustaining thermodependent processes allowing chemical release on demand. [1]

The thermoresponsive behaviour of drug-free micelles was assessed by means of Dynamic Light Scattering measurements run on PCL-PEO-PCL micelles as a function of temperature and aging time. Zeta-potential measurements for the same samples enabled the determination of the surface charge density of the polymeric micelles. Measurements along the temperature cycles evidenced a micellar phase transition, centred around 40 °C, characterized by decrease of the micellar size at higher temperature paralleled by an increase of the absolute value of zeta-potential. The transition was shown to be reversible for at least 5 temperature cycles in terms of size, distribution and surface charge density of the micellar aggregates.

Two different fluorescent compounds, i.e. Acridine Orange and Rhodamine 6G, were inserted in the polymeric system to mimic the stimulated release of a potential drug upon thermal triggering. Insertion of the probes was demonstrated by fluorescence emission of the micellar solution and confirmed by spatially resolved emission spectra acquired by means of Confocal Laser Scanning Microscopy once the micelles were immobilized in a planar porous biopolymer scaffold. Fluorescence measurements performed on the dye-loaded micelles were recorded in the 15-60 °C temperature range, the results showed that the variation in intensity and position of the emission bands with temperature exhibit a clear-cut discontinuity at 40 °C. These findings were ascribed to a change of the probe microenvironment and to a variation of the aggregation state of the probes prompted by the migration of the fluorescent molecules from the interior of the micelle towards the water phase. Interestingly, this process superimposes with the shrinkage of the micellar aggregates at the transition temperature. The study of the inclusion behaviour in thermoresponsive polymeric micelles was extended to drugs involved in pathologies that span from cancer therapy to neurodegenerative diseases.

Literature:

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Acknowledgements:

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Foamability Of The Amphiphile Copolyelctrolytes And Stability Of The Foams, Produced From Them Without Conventional Surfactants

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Amphiphile copolymers are those which macromolecules contain hydrophobic and hydrophilic monomer units. If the hydrophilic units are ionogenic the copolymers are copolyelectrolytes. Their solubility in water depends on the mole fraction and ionization degree of the ionogenic monomer units. The ionization is a function of pH and ionic strength of solution, and on the copolymer concentration also. It appears that at a certain ionization degree the hydrophobic-hydrophilic balance of the macromolecules provides the surface activity of the copolyelctrolytes. The indicator of the copolyelectrolyte surface activity is its foamability without the addition of any low molecular surfactant. The stability of the polymer foams produced depends on the mentioned above copolyelectrolyte solution characteristics, determining the copolyelectrolyte solubility, and the ionization degree of the ionogenic monomer units. Each of them influences the viscosity of the copolyelectrolyte aqueous solution and on the rheology in the foam thin films.

In the communication presented the results for the stability of the foams, produced from two copolyelectrolytes of methacrylic acid (MA) and metrhyl methacrylate (MMA) with mole fraction of the MA monomer units $m_{MA} = 0.3$ and 0.6, and molecular weight $Mn=1.80x10^5$Da and $1.65x10^5$Da, respectively. The pH intervals for both copolyelectrolytes where the stable polymer foams are obtained are identified. The dependencies of the foam stability as a function of pH, ionic strength (NaCl, KCl concentrations), temperature and copolyelectroilyte concentration are determined. The two-parameter (pH and copolymer concentration) phase diagrams for both copolyelectrolytes are constructed, demonstrating the regions for the 2, 7 and 30 days foam stability duration.

The both copolyelectrolytes are used for the coating of the pharmaceutical tablets. The results obtained reveals new possibilities for the production of the new foam pharmaceutical forms for the drug control release. This is another approach for nanocompartmentalization of drugs, in addition of the amphiphilic block-copolymer self-assemblies [1, 2].

Acknowledgements: The work is supported by the Bulgarian Scientific Research Fund (Grant № 02-43/2010).

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Structural Studies of Low-Molecular Weight Organogels Investigated by Synchrotron Small-Angle X-Ray Scattering

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Low-molecular weight gelators (LMWGs) and their gels have attracted many researchers because of applications in various areas such as cosmetics and petrochemical industries as well as academic interest. The gels are formed by self-assembly of the LMWGs, which is driven by non-covalent bonds such as hydrogen bonds, π–π interactions, van der Waals interactions and so on. The organogel exhibits a thermally reversible behaviour, i.e., the gel melts at high temperatures, and when the solution is cooled again, it gelates. It has been shown that there exist two types of low-molecular weight gels such as crystalline gels and surfactant gels[1]. In the former, the molecular arrangement of the gelators in the gel is similar to that of the crystalline powder[2]. On the other hand, in the latter gels addition of an additive to a surfactant micelle causes gelation. In this study, we compared structures and the gelation process of the above two types of the organogels by using synchrotron small-angle X-ray scattering (SAXS) and polarizing optical microscopy.

Figure 1 presents SAXS profiles of lauroyl-L-glutamic-α,γ-dibutylamide/toluene gels at various concentrations. The scattering intensity increases with concentrations of the gelator, while the profiles in log-log plot show almost the same shape. Figure 2 depicts SAXS profiles of cationic surfactant (trimethylstearyl ammonium chloride, TMSAC) /additive [dodecanedioic acid (DDA), decanoic acid (DA)] /xylene gels and TMSAC precipitated in xylene. All the SAXS profiles have multiple order peaks at q/q_m = 1, 2 and 3, where q_m represents the first peak position. The behaviour indicates that the gels form lamellar structures. When the additive is added, the q_m shifts to smaller q, which means the lamella spacing becomes larger. Moreover, q_m was smaller for the additive molecule with larger size. Thus, it can be concluded that TMSAC /additive /xylene gelates by insertion of additive molecules into the surfactant layers.

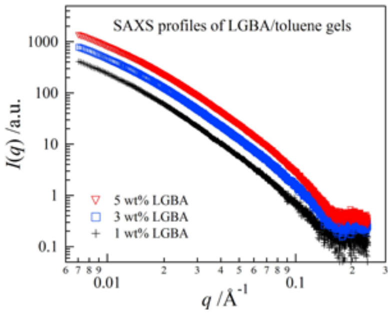

Fig.1 SAXS profiles of LGBA/ toluene gels at various concentrations.

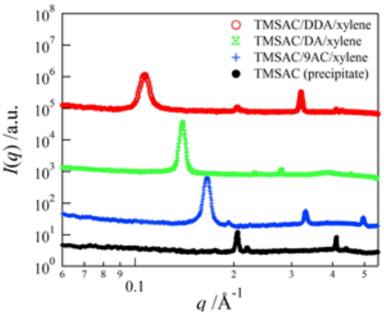

Fig.2 SAXS profiles of TMSAC/ additive/xylene gel.

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Dynamic Swelling and Thermal Properties of Polysulfobetaines Hydrogels

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Polysulfobetaines (PSBs) are class of polymers containing covalently bound positively charged quaternary ammonium group and negatively charged sulfo-group in each monomeric unit. These polymers provoke very low non-specific protein adsorption and thus possess very good haemo- and biocompatibility. The excellent performance of PSBs as biomaterials is explained by their ability to expand more in a low molecular weight electrolyte (LMWE) aqueous solution than in water (antipolyelectrolyte effect). This behaviour of PSBs is due to their structure – clusters, formed by the dipole-dipole interactions between several monomeric units. These clusters are stable in pure water but destroyed by the entrance of LME. Thus the interactions in PSB-LMWE aqueous solutions are interesting in view to understanding their properties and should reveal details about the PSB performance in vivo as the LMEs aqueous solution resembles the body fluids.

The aim of the present study was to investigate the dynamic swelling and the structural mobility of PSBs networks in aqueous solutions as a function of LMWE concentrations. The increase in the LMWE concentration results into an enhanced PSB-water interaction in PSB hydrogels swollen in LMWE aqueous solutions as revealed by the dynamic swelling. Differential scanning calorimetry (DSC) confirms this conclusion as the fraction of bound water in PSBs hydrogels increases with LMWE concentration. These results are in agreement with the data obtained by HR MAS NMR methods.

Kinetics of Colloidal Gelation and Scaling Behavior at the Gelation Point

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We have in-situ investigated the colloidal gelation in the RLCA (reaction-limited cluster aggregation) regime using a small-angle light scattering technique, avoiding any sample handling, in the particle volume fraction range of 0.02 to 0.08, and observed some specific gelation features never indicated previously. The measured structure evolutions clearly show that colloidal gelation follows two stages: (1) clusters growth and (2) clusters interconnection when crowded to form the gel. In Stage 1, the aggregation kinetics in all the cases follows the power-law scaling, as if it is in the DLCA (diffusion-limited cluster aggregation) regime. This indicates that crossover from RLCA to DLCA kinetics takes place along the gelation. When we use a properly defined dimensionless time to account for role of particle concentration and stability, all the kinetic data obtained in Stage 1 at different particle sizes and concentrations and different salt concentrations collapse to form a single master curve. Thus, all the gelation systems follow the same aggregation kinetics and the formed clusters have the same structure. In Stage 2, the average clusters grow only slightly with time. This allows us to distinctly determine the gelation point by the transition from the aggregation kinetics before the gelation point to the slow cluster growth in the gel. It is found that at the gelation point, the volume fraction occupied by all the clusters is constant, independent of the particle volume fraction, as shown in **Fig. 1**. This is strong evidence that for a given colloid, the same crowding condition has to be reached in order to start the percolation forming a gel. Interestingly, this crowding condition depends on the particle size. It is observed that the occupied volume fraction at the gelation point is substantially larger for a colloid with a smaller particle radius than with a larger radius (see **Fig. 1**).

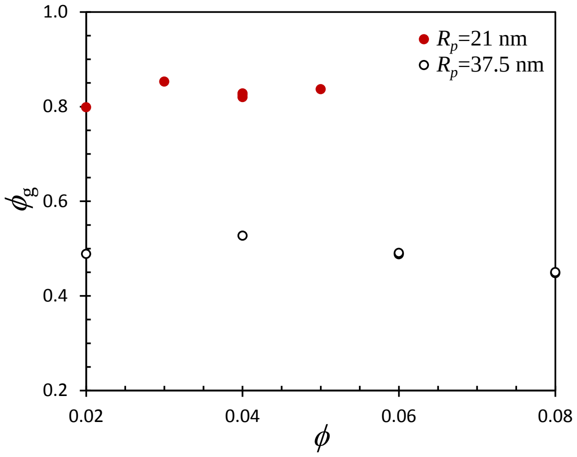

Fig. 1 The volume fraction occupied by all the clusters in the system (ϕ_g) at the gelation point as a function of the particle volume fraction (ϕ), in the cases of the primary particle radius, R_p=21 nm and 37.5 nm, respectively.

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Lipase Immobilized At The Interface Of Microemulsion-Based Organogels For The Epoxidation Of Fatty Acids

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Microemulsions have been considered as adequate media for carrying out bioconversions. They provide an aqueous phase to host hydrophilic enzymes, an interface for their surface-active moieties, and an organic phase for hydrophobic substrates or products [1]. However, the major problem on applying microemulsions in industrial processes is the difficulty in recovering the products and regenerating the enzyme. To overcome this problem, microemulsion-based gels (MBGs) are suggested as alternative media for enzyme immobilization. Lipases immobilized in such MBGs can catalyze interesting synthetic reactions with great biotechnological interest. The enzyme in such media maintains its catalytic activity and stability for long periods. MBGs contain a series of networked aqueous rods stabilized by a surfactant layer, and perhaps co-existing with a population of conventional w/o microemulsion droplets [2].

Epoxides are of great industrial interest because they are intermediate compounds for the production of polymers, adhesives, resins and other materials. Recently the chemo-enzymatic method has been applied therefore progress was made towards reducing the limitations of industrial scale syntheses by making the procedure a more environmentally acceptable alternative for vegetable oil transformations [3].

In the present work *C. antarctica* lipase was immobilized in hydroxyl-propyl-methyl cellulose (HPMC)-based organogels, and used for the catalysis of oleic acid epoxidation with H_2O_2. The optimization of several reaction conditions such as temperature, substrates' concentration and the enzyme content in the microemulsion, has been examined using the central composite design 2^3. Under optimum reaction conditions, the kinetics of the reaction has been studied. Moreover, the epoxidation of linoleic acid has also been tested. Additionally, the agreement of GC and LC/MS methods for obtaining interchangeably the conversion rate of the epoxidation reaction in HPMC/lecithin organogel, has also been confirmed.

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Synthesis and characterization of core-shell particles with low refractive index

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Using copolymerization we have successfully synthesized core-shell particles for which the core consists mainly of fluorinated polymer and the shell of polyethylene glycol (PEG). The system is expected to be well suited for studying interactions between the particles using optical and light scattering techniques. Due to the low refractive index (n_p=1.38) of the particles it is possible to refractive index match the particles in water by adding a co-solvent such as dimethyl sulfoxide (DMSO). The advantage of refractive index matching is that it enables use of light scattering techniques also on highly concentrated dispersions. The surface orientation of the PEG is confirmed using measurement of the zeta potential and cryo-TEM. The particle size, size distribution, aggregation behaviour and stability in salt solutions have been determined.

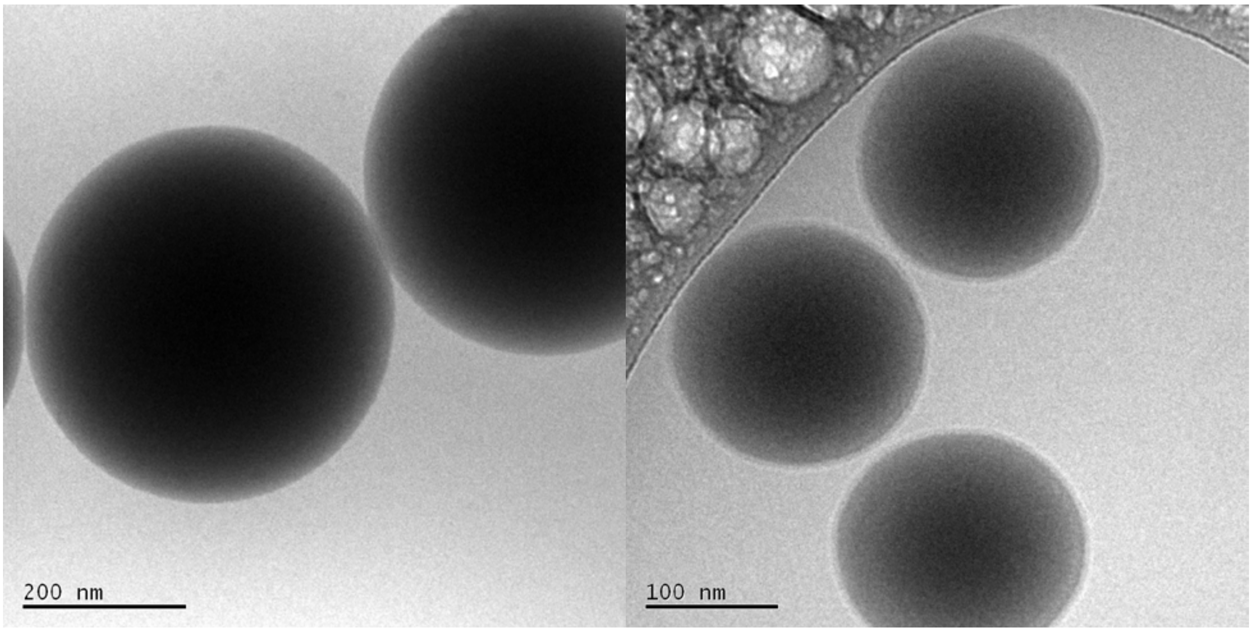

Fig. 1 On the left: Cryo-TEM image of particles without PEG. On the right: Core-shell particle where the surface-grafted PEG layer is visible.

Mechanical features of alginate hydrogel designed as a thin membrane

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We present an experimental study on the mechanical properties of a hydrogel that composes the shell of liquid core capsules. The spherical core-shell structures result from the gelification of an alginate solution surrounding a liquid drop (either oil or water solution) made by co-extrusion in a dripping or in a jetting regime. The fluidic devices enable to produce monodisperse millimetric and sub-millimetric capsules and to tune the hydrogel membrane thickness from 300 micrometers to less than 40 micrometers.

We investigate the mechanical features of a single capsule having an aqueous core under osmotic pressure. The osmotic pressure, and therefore the mechanical stress applied to the thin membrane, can be tuned by varying the concentration of polymer inside the core. In that way, different regimes of deformation are observed: from a viscoelastic behavior to a plastic one. The inflation of the capsule can even lead to its rupture. Consequently, the release of its content into the surrounding medium is allowing a stress relaxation characterization. We also report a study on the mechanical properties of a stack of capsules under compression. A concentrated dispersion of capsules in water is compressed by a semi-permeable piston of variable weight. The stack of capsules is thus in contact with a reservoir into which water can flow. This configuration gives us access to the evolution of the osmotic pressure Π, linked to the piston weight, and the volume fraction Φ of capsules. Therefore, the equation of state $\Pi = f(\Phi)$ of these material can be assessed together with an elastic modulus of the hydrogel membrane. The various behaviors, from a viscoelastic one to a plastic one, are also recovered.

The bonds that built up the hydrogel made of alginate come from electrostatic interaction. The composition of the surrounding medium, like the presence of small monovalent ions, directly impacts on the activation energy needed for unzipping non-covalent cross-link zones. The modifications of the hydrogel properties as a function of the continuous phase composition are evaluated with the two tests previously described. In addition, the geometrical parameter h/R (where R is the capsule radius and h the membrane thickness) is tuned since it is correlated to an amplification of the stress transmitted to the membrane.

To conclude, the understanding of the mechanical behavior of hydrogel shaped as thin membrane is a challenge regarding the large spectrum of applications that these novel materials find. These capsules can be used either in cosmetics to encapsulate active principles or in biotechnologies as 3-D reservoir for the culture of cells and micro-organisms.

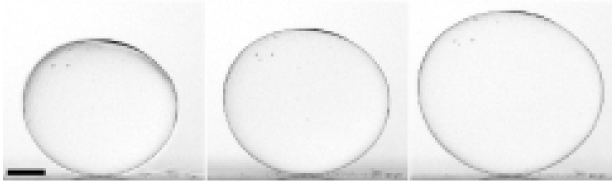

Fig. 1 Osmotic swelling of a capsule made of thin alginate membrane and liquid core containing concentrated polymer. Scale bar = 0.86 cm.

Probing the Adsorption of Dendronized Polymers on Different Surfaces at Single Molecule Level

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Dendronized polymers have attracted considerable scientific interest in recent years. They consist of a central linear polymeric core with appendent dendrons and attain a rod-like, cylindrical shape. Because of their dendritic structure, they provide the possibility of studying scaling behavior with respect to the number of monomers in the side chain [1].
Interactions between individual polymethacrylate-based dendronized polymers of different generations (PGn) and three different surfaces were investigated using atomic force microscopy (AFM) by imaging and then manipulating single polymer chains in solution. The force measurement was performed directly after imaging on the precise position on the molecule [2].
AFM-based single molecule force spectroscopy provided a detailed insight into material properties at the molecular level. As a result of the generation dependence investigation, one can conclude that particular polymer conformation of PG5 (pearl-necklace structure) induces different adsorption properties in comparison with the lower generations. The unique behavior of PG5 can be demonstrated even further. While PG1-PG4 show single force events (peeling and pulling), PG5 presents multiple pulling events and two peeling forces.

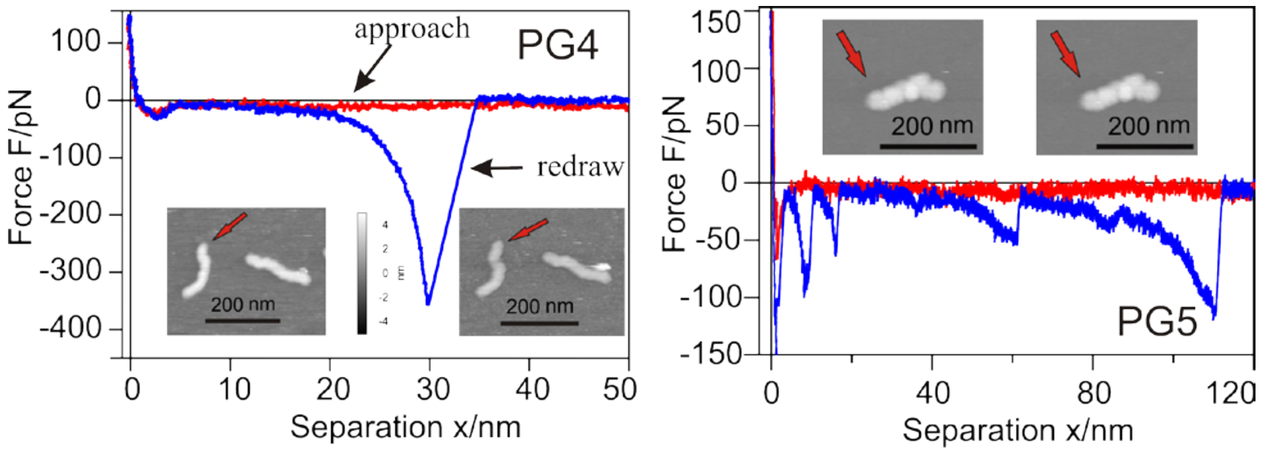

Fig. 1 AFM height images and force curves of PG4 and PG5 on mica in solution at pH 4.

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Hydrogel Templating Technique to Fabricate Lightweight Meso-porous Composites

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Porosity adds a new dimension of functionality to a variety of materials. Porous materials have applications in electronics, chemical filtration, biomedicine and pharmaceutics. Moreover, porous materials have lower mass density and usually higher thermal insulation properties which makes them attractive as building materials. Improvement of the properties and reduction in the cost of production of the composite materials is beneficial, which calls for new routes for their fabrication. Lightweight building materials have always been appealing for their lower transportation costs and better thermal and sound insulation.

We explore a non-conventional way of preparation of lightweight mesoporous materials by templating hydrogels with a range of hydrophilic and hydrophobic scaffolding materials.[1] Blended sub-millimetre hydrogel slurries of polyacrylamide and gellan gum were templated with aqueous slurries of cement, gypsum and clay-cement mixtures or alternatively, dispersed in curable polydimethylsiloxane (PDMS). After solidification of the scaffolding material, the evaporation of the structured hydrogel produced porous composite material, whose pores mimic the hydrogel meso-structure. We studied the density, volume contraction, compression strength and sound absorption of the formed porous materials as a function of the hydrogel initial volume fraction. This versatile hydrogel templating method can be applied very inexpensively to a range of scaffolding materials to yield lightweight porous materials with a great potential for use in the building industry in heat and sound insulation panels, an alternative to aerated concretes, lightweight building blocks, porous rubber substitutes and foam shock absorbers.

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Acknowledgements:

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Calcium mediated polyelectrolyte adsorption on like-charged surfaces: stabilization effects in nanoplatelet suspensions

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One of the most widespread example of a polymerically stabilized colloidal system is fresh cement paste. In this context, anionic comb polymers with a charged backbone (mostly polycarboxylate esters) adsorb on the highly negatively charged cement nanoplatelets (calcium silicate hydrate) at conditions of high pH and high calcium concentration. Grafted to the backbones are hydrophilic side chains (PEG) which are thought to provide the required entropy (steric hindrance) to overcome ion correlation forces which otherwise cause the cement to aggregate[1]. The result is a high performance concrete with enhanced workability, durability and mechanical properties. In this contribution, our aim is to rationalize the mechanisms of the polymer adsorption and the resulting stabilization.

By means of Monte Carlo simulations at the level of the primitive model, the polymer model parameters and the ion-pairing between calcium ions and charged monomers were determined by fitting experimental titration data[2,3] of polyacrylic acid in various salt solutions. The adsorption behavior of model polyelectrolytes (linear and branched) in contact with like-charged surfaces and divalent counterions, was then studied as a function of the calcium and polymer concentration. Under similar conditions, a model dispersion of many negatively charged platelets, was studied in the presence of three different types of anionic polyions. For this purpose, molecular dynamics simulations were employed to calculate potentials of mean force of 2-platelet systems as well as monitoring the time evolution of the corresponding many-platelet systems.

The polymer adsorption is found to occur as a result of surface overcharging by the calcium ions and ion pairing between charged monomers and calcium[4]. The ion pairing interactions are shown to strongly enhance the adsorption. Finally our calculated potentials of mean force, together with the many-platelet simulations, show that our simple model very well capture the stabilization mechanism originating from steric repulsion between adsorbed comb polyanions onto overcharged nanoplatelet surfaces.

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Structural Investigation of Aqueous Systems of Nonionic Polysaccharide Levan by SAXS, SLS and DLS

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Non-ionic polysaccharide Levan exhibits rather peculiar non-gelling behavior in pure aqueous systems up to high polymer concentrations (60 wt. %) [1]. On the other hand only up to 8 wt. % of this polysaccharide in some bacterial biofilms already forms a weak hydrogel (e.g. biofilms of *Bacillus subtilis* subsp. *Subtilis* str. NCIB 3610, where Levan was found as the major polymeric component). Our long-term goal is to explore these differences in behavior of polysaccharide Levan isolated from biofilm of *Bacillus subtilis* in various aqueous systems from the structural point of view in order to recognize and address the possible causes for such discrepancies. On the first stage the structural features of pure aqueous systems of polysaccharide Levan of the bacteria *Bacillus subtilis, Zymomonas mobilis,* and *Erwinia herbicola* were investigated by the small angle x-ray scattering method (SAXS) utilizing the data evaluation based on the string-of-beads model [2]. This model has already been proven to be useful for such type of structural investigations yielding the detailed information about the values of molecular parameters such as molecular flexibility, persistence and correlation lengths on different length-scales, and information on effective interparticle interactions. Basic information on the size of polymer molecules in the system that is needed to set up such model can be obtained utilizing the static light scattering (SLS) technique. Similarly the dynamic light scattering (DLS) method can provide complementary dynamic and structural results.

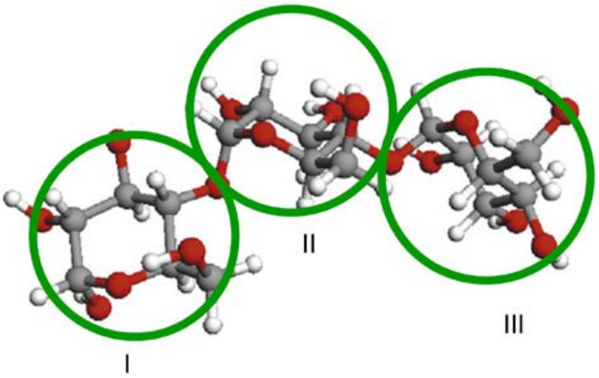

Fig. 1. Monomer units of polymer are approximated by spheres that are connected into a string in the string-of-beads model. Adapted from ref. [2].

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Interfacial Layers from the Protein HFBII Hydrophobin: Dynamic Surface Tension, Dilatational Elasticity and Relaxation Times

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The pendant-drop method (with drop-shape analysis) and Langmuir trough are applied to investigate the characteristic relaxation times and elasticity of interfacial layers from the protein HFBII hydrophobin. Such layers undergo a transition from fluid to elastic solid films. The transition is detected as an increase in the error of the fit of the pendant-drop profile by means of the Laplace equation of capillarity. The relaxation of surface tension after interfacial expansion follows an exponential-decay law, which indicates a barrier mechanism of adsorption. The experimental data for the relaxation time suggest that the adsorption rate is determined by the balance of two opposing factors: (i) the barrier to detachment of protein molecules from bulk aggregates and (ii) the attraction of the detached molecules by the adsorption layer due to the hydrophobic surface force. The hydrophobic attraction can explain why a greater surface coverage leads to a faster adsorption. The relaxation of surface tension after interfacial compression follows a different, square-root law. Such behavior can be attributed to surface diffusion of adsorbed protein molecules that are condensing at the periphery of interfacial protein aggregates.

The surface dilatational elasticity, *E*, is determined in experiments on quick expansion or compression of the interfacial protein layers. At lower surface pressures (< 11 mN/m) the experiments on expansion, compression and oscillations give close values of E that are increasing with the rise of surface pressure. At higher surface pressures, E exhibits the opposite tendency and the data are scattered. The latter behavior can be explained with a two-dimensional condensation of adsorbed protein molecules at higher surface pressures. The results could be important for the understanding and control of dynamic processes in foams and emulsions stabilized by hydrophobins, as well as for the modification of solid surfaces by the adsorption of such proteins.

Effect of Different Parameters Over the Dispersion Stability of Silica

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Silica dispersion has a number of applications in our daily life and needs detail investigation to establish the effect of various parameters over the size, size distribution and its stability. Therefore, the silica was dispersed and the size and size distribution and surface charge have been investigated as a function of ultrasonication time, added polymer (Polyvinylpyrrolidone) concentration and molecular mass. It has been concluded that though the size distribution remains almost unaffected by the ultrasonication time but the surface charge was increased with the increase in ultrasonication time up to 20 minutes and then it leveled off. Further the polymers added were adsorbed over the surface of the particles and increased the surface charge (Zeta potential) and the increase proportional to the molecular mass of the polymer. Due to the reason the added polymers introduced the steric as well as electrostatic stabilization and the dispersions became stable. However, if the particles were not properly dispersed before the addition of polymer then the available agglomerates did not break by ultrasonication and hence the distribution of the particles size was widened.

Keywords: Silica dispersion; Zeta potential; Poly (vinylpyrrolidone); pH; ultrasonication; stability of dispersion.

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Acknowledgements:

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The Synergism between Hydrophobically Modified Inulin and Cationic Surfactant

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As petroleum feedstock decreases, the development of new renewable bio-based and efficient chemicals has attracted more and more interest. Recently, a natural polydisperse polysaccharide named inulin has gained considerable attention. This polysaccharide extracted from chicory roots consists mainly of ß(2-1)-fructosyl furanose units, and has unique properties due to its linear structure and its rather low molecular weight range in comparison to other polysaccharides such as cellulose and starch.

This relatively small polymer has focused special interest when several hydrophobic chains are attached on its backbone [1]. This hydrophobically modified inulin (HMI) is able to stabilize many dipersed systems such as o/w emulsions, solid dispersions or films by steric stabilization mechanisms [1]. Additionally, it possesses other important properties like surface activity comparable to those of molecular surfactants or thermo-reversible associative behaviour in aqueous solutions. Also, the hydrophobic groups grafted onto the polyfructose backbone tend to aggregate in order to limit their contact with the solvent leading to the formation of stable core-shell soft nanoparticles [2].

In the present work, we explore the interaction of these macromolecular structures with a well-known vesicle forming cationic surfactant, didodecyldimethylammonium bromide (DDAB). Initially, one could expect that HMI would stabilize vesicles by the already described steric stabilization mechanisms, but surprisingly this is not the case. Helped by characterization techniques, we have elucidated the nature of these polymer-surfactant interactions by proposing interaction models for surface tension, zero-shear viscosity and SAXS profiles. Here, we present our results with several synthesized HMIs [3] together with pristine inulin (without hydrophobic modifications) and Inutec®SP1 (commercial HMI) for comparative reasons, and we propose some possible applications for these interesting mixed micelles formed by DDAB and HMI.

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Non-equilibrium nature of two-dimensional isotropic and nematic coexistence in amyloid fibrils at liquid interfaces

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Two-dimensional alignment of shape-anisotropic colloids is ubiquitous in nature, ranging from interfacial virus assembly to amyloid plaque formation. The principles governing two-dimensional self-assembly have therefore long been studied, both theoretically and experimentally, leading, however, to diverging fundamental interpretations on the nature of the two-dimensional isotropic–nematic phase transition. Here we employ single-molecule atomic force microscopy, freeze-fracture shadow-casting cryogenic scanning electron microscopy and passive probe particle tracking to study the adsorption and liquid crystalline ordering of semiflexible β-lactoglobulin fibrils at liquid interfaces. Fibrillar rigidity changes on increasing interfacial density, with a maximum caused by alignment and a subsequent decrease stemming from crowding and domain bending. Coexistence of nematic and isotropic regions is resolved and quantified by a length scale-dependent order parameter $S_{2D}(d)$. The nematic surface fraction increases with interfacial fibril density, but depends, for a fixed interfacial density, on the initial bulk concentration, ascribing the observed two-dimensional isotropic–nematic coexistence to non-equilibrium phenomena.

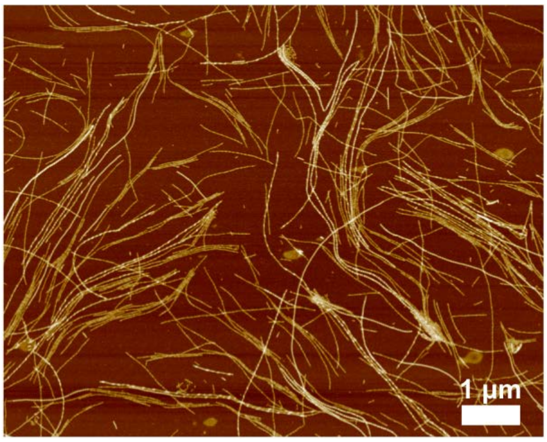

Fig. 1 *Atomic Force Microscopy image of semiflexible β-lactoglobulin amyloid fibrils that have aligned into two-dimensional liquid crystalline domains by passive adsorption to an air-water interface.*

Literature:

Sophia Jordens[1], Lucio Isa[2], Ivan Usov[1], Raffaele Mezzenga[1]. 2013. Non-equilibrium nature of two-dimensional isotropic and nematic coexistence in amyloid fibrils at liquid interfaces. Nature Communications. doi:10.1038/ncomms2911

A Density Functional Study of End-Grafted Chain Layers: Temperature Effects

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The properties of end-grafted chain layers have been intensively studied in recent years. These systems are important for numerous technological processes, including stabilization of colloidal suspensions, chromatographic separation, lubrication, adhesion, drug delivery and production of protective coatings. The structure of the chain interphase result from a complex interplay between entropic and enthalpic effects in the system. A lot of theoretical approaches have been applied to describe polymer-tethered surfaces. One of them is the density functional theory proposed by Yu and Wu [1] and extended in our previous papers [2-4].

In this work we present the density functional study of the structure of end-grafted chain layers immersed into explicit solvents. We introduce the following model. The chains are freely jointed tangent spheres. The grafted chains are inert with respect to the substrate. The fluid molecules interact with the solid surface via Lennard-Jones (9-3) potential. All segments interact via Lennard-Jones (12-6) potential. We have calculated the density profiles of all components and the thickness of the brush. The calculations have been carried out for selected model systems.

First, we investigate an influence of temperature on the structure of the grafted chain layer. We study the brushes in solvents with different affinities to the grafted chains. We discuss how the fluid density, grafting density and fluid-brush interactions affect the brush thickness at selected temperatures. We consider the brush thickness as a function of temperature. It is shown that a shape of such a function depends on the fluid density. For low fluid densities the brush height monotonically increases with increasing temperature. On contrary, at high fluid densities the brush thickness decreases. We show that at a certain fluid density the brush height is almost independent of temperature. Moreover, it is shown that an increase of fluid density causes an increase or a decrease of the brush height depending on temperature.

Second, we calculate the force acting on a selected segment of a tethered chain that leads to pulling the chain off the wall. The effects due the presence of other chains and fluid molecules, as well as temperature, are considered.

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Adsorption Of Short Block Copolymers On Solid Surfaces. A Monte Carlo Study

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Adsorption of diblock copolymers on flat surfaces is studied using lattice Monte Carlo simulations. The model consists of fully flexible diblock copolymer adsorbed on a square lattice. We determine full topology of the phase diagrams for a series of symmetric copolymer models starting from chain lengths M=4 up to 16. For the shortest chains the order-disorder phase transition is of the first order while for the longer chains we find a critical end-point. The chemical potential and density for the gas-disordered liquid increases non-monotonically, whereas the critical temperature increases monotonically with chain length. We also determine Minkowski measures in order to better characterize the structure of the adsorbed phases.

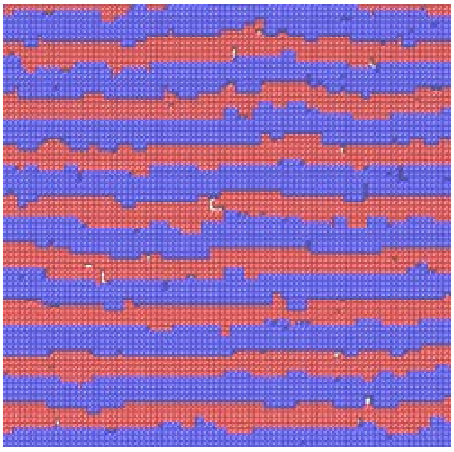

Fig. 1 Snapshot for an ordered phase of the adsorbed diblock copolymer. Chain length M=8.

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Behaviour of Thermo-sensitive Copolymer Microgels at the Oil/Water Interface

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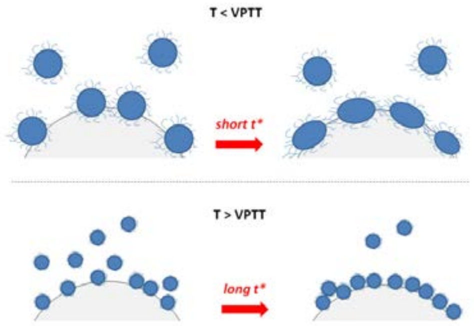
Microgels are soft particles consisting of physically or chemically cross-linked polymer network. A novel application of microgels has been developed recently, in which they are employed in the formation of particle-stabilized emulsions, similar to Pickering emulsion.[1] However, microgels have the behavior that falls between hard spheres and ultra-soft systems.[2] The assembly laws deduced from the interfacial behavior of hard particles at the oil/water interface seem to be not completely suitable for microgels, since soft microgel particles are highly deformed at the oil/water interface.[3]

Herein, copolymer microgels based on N-vinylcaprolactam (VCL) and two acrylamides, N-isopropylacrylamide (NIPAm) and N-isopropylmethacrylamide (NIPMAm), with various copolymer compositions were synthesized, and investigated in the aspect of interfacial tension. A statistical distribution of the monomer units in the both microgel networks[4] gives a straightforward possibility to study systematically the influence of the chemical structure on the interfacial behavior of microgels. The equilibrium interfacial tension and the time for reaching the equilibrium status, which can be considered as thermodynamic aspect and kinetic aspect, respectively, vary with temperature and chemical compositions of microgels. It is also indicated that the chemical environment itself, rather than through microgel size has a governing influence on the interfacial behaviour of microgels at the toluene/water interface.



Scheme 1. The adsorption of microgels below and above VPTT.

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Effect of PEM Coated PDMS on Freshwater Biofouling

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Biofouling is one of the biggest problems of water-borne systems.[1] Since not only marine but also freshwater-based structures are affected,[2] the results of a study of biofouling in this environment are presented in the poster. The focus of the study are the antifouling properties of polyelectrolyte multilayers (PEM)[3] compared with currently used silicon rubber (PDMS)[4] based fouling release coatings. The poster contains the results of a systematical screening of the mechanical, surface charge and surface nano- heterogeneous properties of the investigated PEM and PDMS systems. It can be shown that negatively charged non crosslinked and crosslinked PEM coated PDMS succeds the antifouling properties of purely PDMS based fouling release coatings. The PEM films are not only able to reduce the biofouling, but are additionally able to control the type of settled bacteria (gram positive or negative). The negative terminated surfaces inhibit the settlement of gram positive bacteria, probably due to repulsion of negatively charges, whereby the positive terminated surfaces inhibit the settlement of gram negative bacteria, due to the liquification of the bacteria cell wall[5] due to interaction of positively charged hydrophobic PEM and the cell wall[5].

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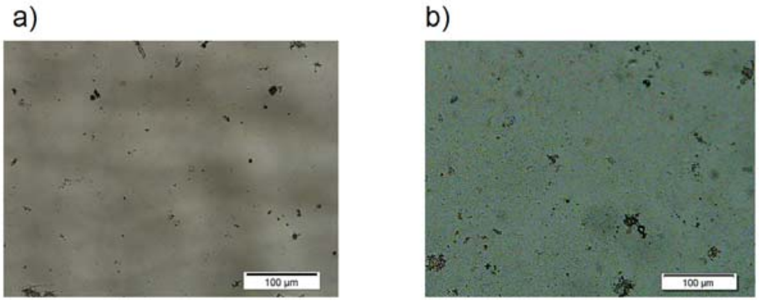

Fig. 1: Biofouled surfaces after 21 days a) negatively charged PEM, b) PDMS reference sample

Acknowledgements:

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Temperature-induced Phase Transition in Aqueous Polymer Solutions and Gels Studied by NMR and Other Methods

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It is well known that thermoresponsive polymers show in aqueous solutions a lower critical solution temperature (LCST). They are soluble at lower temperatures but heating above the LCST results in phase separation. For dilute solutions a coil-globule transition was revealed by light scattering at the LCST while for semidilute and concentrated solutions aggregation results in formation of larger globular-like structures called mesoglobules. When these polymers are chemically crosslinked their hydrogels undergo around this temperature a volume phase transition (collapse). Their thermosensitivity makes thermoresponsive polymers interesting for miscellaneous biomedical and technological applications. Of various methods, NMR spectroscopy was also used in investigations of these systems[1]. Three types of thermoresponsive polymer systems studied by us recently will be discussed here:

(*i*) From comparison of the values of the enthalpy change ΔH based on data obtained by ^{1}H NMR spectroscopy with ΔH values obtained by DSC we confirmed for D_2O solutions of several thermoresponsive homopolymers (poly(*N*-isopropylmethacrylamide) (PNIPMAm), poly(vinyl methyl ether), poly(*N*-vinylcaprolactam)) in broad range of concentrations that cooperative unit is the whole macromolecule and that also in semidilute and concentrated solutions their chains undergo coil-globule transition during phase separation.

(*ii*) Using ^{1}H NMR spectroscopy we studied temperature-induced phase transition in D_2O solutions of diblock and triblock copolymers poly(ethylene glycol) (PEG)-poly(*N*-isopropylacrylamide) (PNIPAm) of the AB and $A(B)_2$ type, respectively. We have found that presence of the PEG block significantly affects phase transition and globular structures of PNIPAm component, as well as behaviour of water molecules.

(*iii*) Combination of NMR, DSC and dynamic mechanical measurements was used to study collapse phase transition in hydrogels of interpenetrating networks (IPN) PNIPAm/ PNIPMAm. A single transition at temperatures between transition temperatures of neat components was revealed in most IPN samples by NMR and DSC, indicating enhanced mutual intertwining of PNIPAm and PNIPMAm chains. In all samples the collapse transition results in substantial increase of both components of the shear modulus.

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Acknowledgments:

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Translational Dynamics of Molecules in Synthetic and Natural Polymers as Studied by NMR

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This work is dedicated to the examination of those contemporary NMR- methods, which are used in the study of molecular translational dynamics in the systems of different level of complexity (solutions of polymers, emulsions, gels, polymer films, biopolymers and the porous heterogeneous systems of natural origin or construction materials) [1-4]. Contemporary possibilities of the methods of NMR- relaxation (spin-spin, spin-lattice and cross relaxation), NMR diffusometry (pulse field gradient NMR) and methods of double-quantum-filter (DQF) NMR in a study of diffusion properties and molecular dynamics in the systems with the anisotropic properties are considered [1, 3, 4]. The work shows how the study results in an information about molecular dimensions / form of limitations, structure of fluid medium in the heterogeneous systems, character of limitation and the structure of the surrounding matrix [1, 3]. DQF NMR is applied for investigating the systems, in which there is an order (on the macro- or the micro-levels), in particular for fibres and porous systems or the systems with anisotropic motion of molecules [1, 4]. The results obtained reveal also the special feature of the approaches of one-dimensional and two-dimensional NMR [1, 5] and show examples of the work of these methods [5] in addition to the traditional methods of single- quantum NMR-spectroscopy. The work presents the data of two-dimensional correlation NMR-spectroscopy (DD COSY) as the distributions of diffusion coefficients in two orthogonal directions on the systems with anisotropic mobility [5]. Simulations of two-dimensional NMR-experiments have been done showing how it leads to the explanation of experimental data on the anisotropy of diffusion coefficients. These NMR- methods reveal the correlation of the diffusion motion of molecules along either collinear or orthogonal directions of applied pulse gradients of magnetic field. The results on some materials with anisotropic structure demonstrated how these methods reveal microscopic local anisotropy in the presence of global isotropy.

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Surface Charge Effects on the Hydration of Polyelectrolyte Multilayers under Confinement

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A polyelectrolyte multilayer (PEM) is formed from alternate layer by layer deposition of cationic and anionic polymers. Potential applications of PEMs range from biomedical uses[1], to optics[2], to drug delivery[3]. For all applications the amount of hydration, and therefore the swelling of the layer, is vital to the designed effectiveness of the PEM.

Using neutron reflectivity we examine how the hydration of PEM stacks with 11, 23 and 47 bi-layers responds to a mechanical compression between 0 and 5 bar with a surface force type apparatus utilising a flexible Melinex® membrane[4], fig. 1. We also consider the odd-even effect under confinement where the final layer is either the cationic polymer poly(allyl amine hydrochloride), PAH, or the anionic polymer poly(styrene sulfonic acid), PSSA.

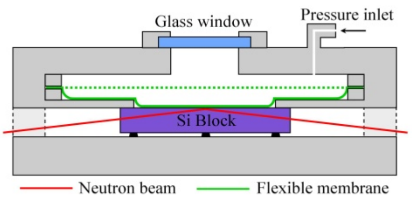

Fig. 1: Schematic of the compression cell.

To assist our analysis, 3 selected layers in each sample are fabricated using deuterated PSSA to split the sample into 4 equal cells. This allows us to analyse the distribution of the water within the PEM stack and to determine the role and importance of the terminating layer, the number of bi-layers and the confining pressure. In addition, we also consider a special case where we compress a PAH terminated PEM on the silicon with a PSSA terminated PEM on the Melinex® membrane, so that there is no net surface charge.

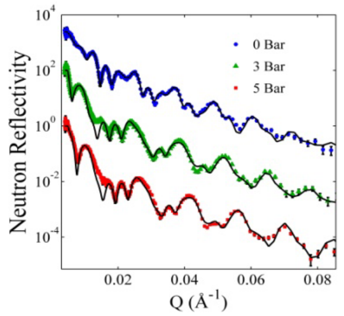

Fig. 2: Neutron reflectivity curves and fits for a PSSA terminated sample with 47 bi-layers at 0, 3 and 5 bar. Data sets offset for clarity.

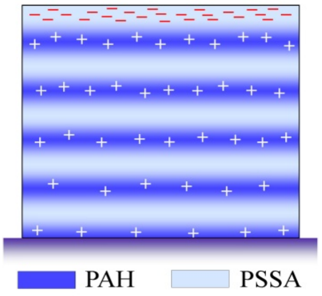

Fig. 3: Charge distribution in a PSSA terminated sample.

Our results demonstrate that the PSSA terminated PEM stacks are more hydrated than PAH terminated stacks and that with a 5 bar confining pressure the hydration is dependent on the number of bi-layers. The hydration is also observed to be uniformly distributed in PSSA terminated samples, whereas the layers closest to the Si preferentially dehydrate for PAH terminated samples. In the case where two PEMs are compressed together, the PEM dehydrates more in the layers nearest to the contact interface.

To explain our observations, we use a qualitative model whereby the surface charge of the PEM, which is determined by the final adsorbed layer, influences the charge distribution within the rest of the PEM, fig. 3. The amount of charge is then directly linked to the hydration of the PEM when confined. This model describes all the observed behaviour of PEMs under confinement.

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New Surface Tension Prediction of Complex Mixtures

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While the surface tension of complex mixtures determines the fate of important natural processes like the stability of aerosol droplets in clouds and the biological function of lung surfactants, the property is notoriously difficult to interpret and model. It was established over a decade ago that some strongly interacting polyelectrolyte/surfactant (P/S) mixtures exhibit a striking cliff edge peak in their surface tension isotherms while others merely have a plateau [1]. More recently we have systematically linked the surface tension peak of a strongly interacting P/S mixture to slow dynamic changes in its bulk phase behavior [2] and have demonstrated the non-equilibrium nature of the system [3]. Here we announce a simple new unifying approach that successfully predicts the surface tension of two synthetic (Pdadmac/SDS and PSS/DTAB) and one biologically-relevant (DNA/DTAB) mixtures. The approach is based on the non-equilibrium framework of comprehensive precipitation and importantly does not need any measurements of the surface properties of the mixtures; only knowledge of the surface tension isotherm of the pure surfactant and some bulk measurements of the mixtures are required. This simplification in our understanding of the surface properties of strongly interacting macromolecular mixtures may lead to the optimization of a broad range of applications involving commercial synthetic polymers, DNA and proteins at surfaces in areas such as targeted drug and gene delivery.

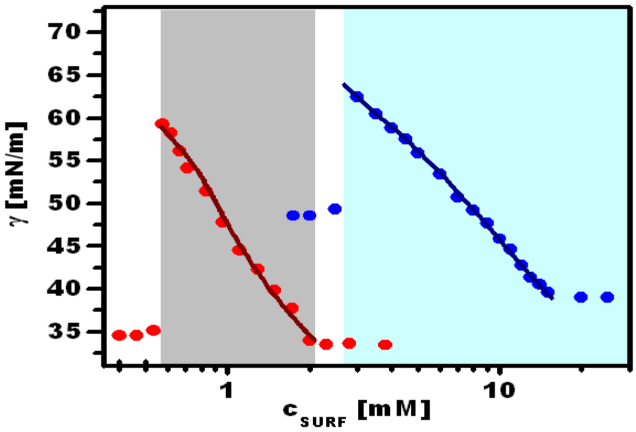

Fig. 1. Surface tension of aged Pdadmac/SDS (red) and PSS/DTAB (blue) solutions with predictions of their surface tension not based on any surface measurements of the mixtures.

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Non-equilibrium Morphological Transition Kinetics in Block Copolymer Micelles Observed by Millisecond Time-Resolved SAS

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The kinetics of block copolymer micelles is still not fully understood [1]. Such processes include both equilibrium kinetics, e.g. molecular exchange, and non-equilibrium kinetics associated with morphological transitions and the formation of micelles. Earlier we have focussed on the formation kinetics where we showed that the kinetic pathway is characterised by a nucleation & growth type mechanism where unimer (single) chain exchange is the dominating fundamental elemental step [2]. Here we focus on the structural and kinetic aspects of a cylinder-to-sphere structural transition occurring in a model amphiphilic block copolymer system upon variation of the interfacial tension. We demonstrate that the transition is governed by entropic chain stretching in the core, which is more prominent at high interfacial tensions. We further show that we can directly follow these transitions in the real time by small angle scattering methods using both neutrons (TR-SANS, D11, ILL) and X-rays (TR-SAXS, ID02, ESRF) and by employing a stopped-flow apparatus for rapid mixing. The results show that the cylinders typically rapidly dissociates into spherical micelles within some few hundreds of milliseconds and thereafter reorganize to the final equilibrium spherical micelles within seconds. Interestingly, the transition seems to be driven by instabilities over the whole cylinder leading to fragmentation, which is followed by reorganization and growth of these entities into final spherical micelles. This contrasts earlier studies where the cylinders were suggested to decompose from the (more) unstable ends [3]. The opposite transition is not possible where the system rather ends up in another spherical micellar structure. We will discuss this behaviour in connection with some recent results on the respective “equilibrium” exchange kinetics that can be accessed using time resolved SANS [1]. We will try to interrelate and discuss kinetic pathways in block copolymer micelles and how this insight might be used to create cost-effective nano-particles.

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Cononsolvency of PNiPAM at the Transition between Solvation Mechanisms

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Poly-N-isopropyl acrylamide (PNiPAM) is a thermo-responsive polymer, which exhibits the rather rare phenomenon of cononsolvency [1]. An example of this cononsolvency phenomenon is the behaviour of PNiPAM in water / methanol mixtures. At a fixed temperature of T = 20°C PNiPAM is perfectly soluble in both pure water and pure methanol, but it is insoluble in certain mixtures of the two solvents, as shown in Fig.1a. Directly correlating with the reentrant transition of soluble-to-insoluble-to-soluble, the PNiPAM dimensions change as a function of solvent composition, describing a reentrant coil-to-globule-to-coil transition [2], as schematically shown in Fig.1b.

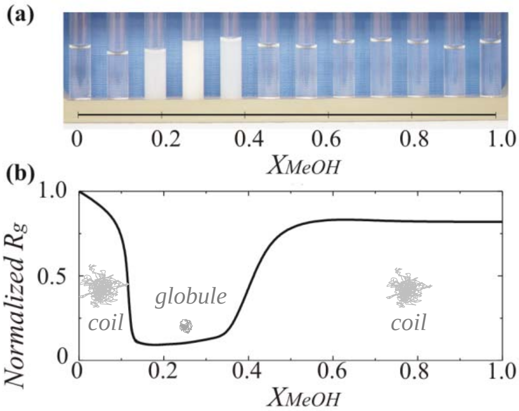

Figure 1: *(a) Phase behaviour of PNiPAM in water/methanol mixtures as a function of the methanol molar fraction X_{MeOH} at a fixed temperature T=20°C. (b) Schematic of the dependence of the radius of gyration R_g on methanol content obtained at a fixed temperature T=20°C (drawn from [2]).*

We show that such phenomena can be understood as the result of a transition between solvation mechanisms. In water-rich environments, the solvation of PNiPAM is primarily determined by the enthalpic gain of water, solvating the polymer via hydrophobic hydration. In alcohol-rich environments it is instead the gain in the mixing-entropy that determines solubility. Cononsolvency is observed in the transitional range between these two solvation mechanisms, where neither the gain in solvent enthalpy nor the gain in solution entropy is prevailing.

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Acknowledgements:

We gratefully acknowledge financial support from the Swiss National Science Foundation Grants (200020_140908) and (200020_130056) and the Adolphe Merkle Foundation.

DNA hybrids structure formation

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Relying on the achievement of a general mechanism to eventually solve critical biological and medical issues through the observation and manipulation of biochemical mechanisms, we are investigating the structure formation and modes of interaction of DNA hybrids, in particular copolymer self-assembly and crystallization (Figure 1) as well as interpolyelectrolyte complex formation. We are predominantly focusing on reaching a comprehensive understanding of the organization of these peculiar macromolecules which can undergo specific interactions such as biological recognition to ultimately establish a general process of their association.

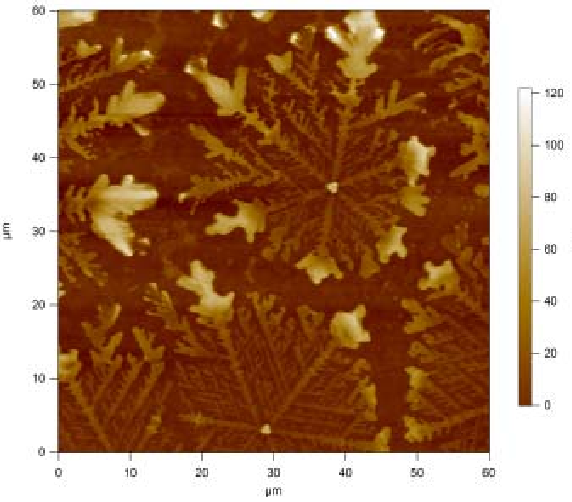

Fig. 1 Crystallization of chitosan-DNA hybrids on a gold surface as observed by atomic force microscopy

Acknowledgements: The University of Geneva and the Swiss National Science Foundation for Research are greatly acknowledged for financial support

Smart PNIPAM-g-PEO Nanoparticles for Delivery of NSAIDs

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Biocompatible and nontoxic PNIPAM-PEO graft copolymers pertain to the group of thermoresponsive smart materials. In aqueous solutions and at temperatures higher than the lower critical solution temperature (LCST) the polymer molecules undergo coil-to-mesoglobule transition. Core-shell nanoparticles are obtained with predominantly hydrophobic core and hydrophilic corona. Surfactant-type drugs (e.g. nonsteroidal anti-inflammatory drugs) are incorporated in these particles (in vitro, at lower temperatures) and released under controlled conditions at body temperature (mimicking conditions in vivo). These processes are finely tuned by temperature and the presence of specific additives. Combined investigations of bulk and interfacial properties of the polymer-drug-additive systems are performed. The studies address static and dynamic adsorption properties, surface dilational rheology, the drainage kinetics and stability of microscopic thin liquid films. HRTEM, DLS and bulk rheology chacterizations of the complex aqueous solution have also been carried out.

New data about the mutual relationship between the structure and composition of the polymer/drug solutions, the adsorption layer properties at the air/solution interface and the foam film stability are obtained. It is established that higher degree of copolymer grafting results in a remarkable frequency dependence of the surface rheological properties at room temperature and in more pronounced thermal responsivity of the copolymer-drug formulation. The higher grafting density benefits the formation of smaller core-shell nanoparticles. This enhances both the efficiency of encapsulation at 22oC and of the drug release at 37oC.

Important input is added in view of optimal composition of the copolymer/drug formulation aimed at possible pharmaceutical applications. It was found that ethanol quantity of 10% (v/v) is the lowest limit of pharmaceutical interest and the range of 15-20% ethanol quantity is the optimal composition for this specific polymer-drug system

The obtained results add new knowledge about the mechanisms of the drug entrapment and release events. The basic outcome is the possibility to elaborate an efficient protocol for the procedure of fine-tuning the incorporation and the discharge of hydrophobic drugs by the polymer nanoparticles.

Acknowledgements:

The financial support of NSF of the Ministry of Education, Youth and Science (Bulgaria) by Projects MU03/137 and BG 051PO001–3.3.06–0038 are gratefully acknowledged.

Doubly Crosslinked Microgel/Polyelectrolyte Complexes: Three Simple Methods to Tune and Improve Gel Mechanical Properties for Regenerative Medicine Applications

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Doubly crosslinked microgels (DX MGs) are hydrogels composed of covalently-interlinked microgels. They are injectable and have potential application in soft tissue repair. Here, we investigate the effect of added polyelectrolyte and NaCl on the mechanical properties of the gels[1]. The method is depicted in Fig. 1. Addition of polycations improved ductility and decreased the storage modulus (*G'*) of the DX MG / polyelectrolyte complex (DX MG / PECs) gels. The best DX MG / PEC gel had a yield strain (γ_c) of 109%, which is the highest reported to date for any DX MG. Our DX MG / PEC gels maintained high *G'* values (up to 300 kPa) as well as good ductility when swollen at pH = 7.5. We investigated the effect of addition of NaCl during DX MG and DX MG / PEC preparation. This caused remarkable increases in both *G'* and ductility. Addition of linear polyacrylic acid also increased *G'* values.

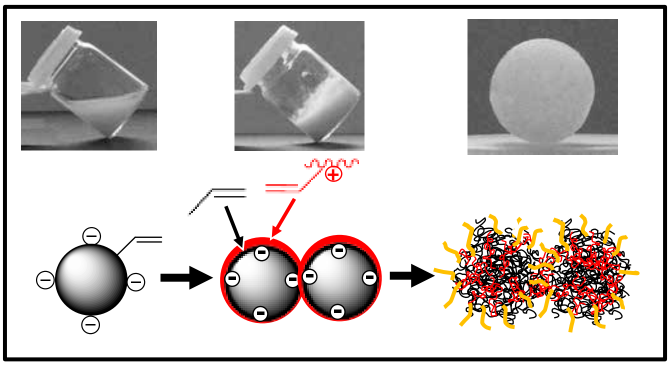

Fig. 1 From injectable fluid to doubly crosslinked microgel

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Characterization of Oil-free and Oil-loaded Liquid Crystalline Particles Stabilized by the Negatively Charged Stabilizer Citrem

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Purpose: The present study was designed to evaluate the effect of the negatively charged food-grade emulsifier citrem as a new nontoxic and sufficient stabilizing agent for oil-free and oil-loaded aqueous dispersions (hexosomes) of phytantriol (PHYT) and glyceryl monooleate (GMO). Hexosomes have highly ordered internal nanostructure that permits loading of different drugs and imaging agent types, and holds potential for controlling the release of a high variety of agents. These nanostructures have further gained a lot of interest due to their close resemblance with structures found in biologically relevant systems as well as their biodegradability and biocompatibility.

Methods: Synchrotron small angle X-ray scattering (SAXS) and cryogenic transmission electron microscopy (cryo-TEM) were used to characterize the dispersed and the corresponding non-dispersed phases of inverted-type non-lamellar liquid crystalline phases and microemulsions based on the citrem-stabilized PHYT- and GMO-based aqueous dispersions.

Results: The results suggest a drastic effect of the stabilizer citrem on the internal nanostructures of the aqueous dispersions. In addition to the main function of citrem as stabilizer that adheres to the surface of the dispersed particles, it has a significant impact on the internal nanostructures that is governed by the following factors: (1) the penetration of citrem between the hydrophobic tails of the lipid molecules, and (2) the degree of the incorporation of citrem into the lipid-water interfacial area. In **Figure 1** a schematic description of the stabilization mechanism of citrem on a PHYT-based hexosomal dispersion is illustrated.

Conclusion: The present study described the structural characteristics of a series of oil-free and oil-loaded lipid-based nanoparticulate formulations that were stabilized by the small-molecule emulsifier citrem. Citrem has been shown to provide stabilization for the milky dispersions by adhering to the surface of the dispersed particles. This anionic stabilizer has in addition shown a potential for the functionalization of hydrophilic domains by the enlargement of the hydrophilic nanochannels of the internal H_2 phase in hexosomes and the hydrophilic core of the L_2 phase in emulsified microemulsions. This is particularly attractive for solubilizing and controlling the release of positively charged drugs.

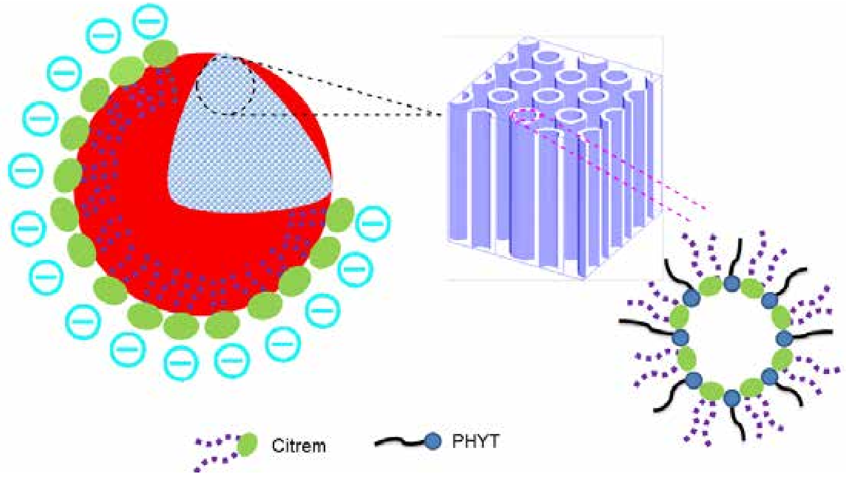

Figure 1. A schematic description of the stabilization mechanism of citrem

SPECT/CT Imaging of Radiolabeled Phytantriol-based Cubosomes and Hexosomes: Potential Medical Applications

Christa Nilsson[1,*], Brianda Barrios-Lopez[2], Anukka Kallinen[2], Pasi Laurinmäki [2], Sarah J. Butcher[2], Mari Raki[2], Jouko Vepsäläinen[3], Kim Bergström[2], Susan W. Larsen[1], Jesper Østergaard[1], Claus Larsen[1], Arto Urtti[2], Anu J. Airaksinen[2], and Anan Yaghmur[1]

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Purpose: Cubosomes and hexosomes are aqueous dispersions consisting of particles enveloping internal nanostructures of inverted type bicontinuous cubic (Q_2) and hexagonal (H_2) phases. These nanostructured dispersions have recently gained increasing interest due to their unique properties. Our major goal was to ensure a successful radiolabeling of biodegradable cubosomal and hexosomal nanocarriers for biomedical applications. It was also our main attention to investigate the utilization of these nanocarriers as imaging probes using NanoSPECT/CT. Herein, the molecular imaging involves the administration of compounds or delivery vehicles labeled with a radionuclide to patients for diagnostic and therapeutic purposes.

Methods: Two different radiolabeling techniques were used to investigate the possibility of radiolabeling the dispersions in question; the remote loading and surface chelation methods. The experiments include the evaluation of radiolabeling efficiency and radiolabeling yield as well as stability of the radiolabeled cubosomes and hexosomes in plasma using thin layer chromatography. Further, the effect of radiolabeling on their internal nanostructures and overall size was investigated by either SAXS, cryo-TEM or DLS.

Results: The results show that the developed surface chelation method is a powerful tool for the radiolabeling of phytantriol-based hexosomes. The radiolabeled hexosomal dispersion is > 90% radiochemically pure and demonstrates 83% labeling efficiency as well as good stability in human plasma, 83% of the labeled hexosomes was still intact after 24 hours. However, the remote loading method used to label cubosomes proved to be insufficient. Our NanoSPECT/CT experiments of subcutaneously administered radiolabeled hexosomes to the flank of mice showed remarkably a high targeting to the subcutaneous adipose tissue (~ 343%ID/g) with low uptake in other organs/tissues (**Figure 1**).

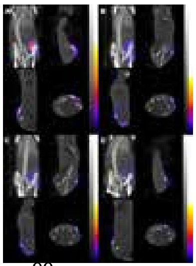

Figure 1. NanoSPECT/CT imaging of ^{99m}Tc-SpmTrien-hexosomes at 0-24h

Conclusion: In the present study, we report on the preparation and the structural characterization of OA containing PHYT-based hexosomes and also their *in vivo* evaluation. For the imaging purpose, a ^{99m}Tc-radiolabeling method based on the surface chelation method using the new bifunctional chelating agent SpmTrien was developed. The NanoSPECT/CT results suggest the formation of a radiolabeled hexosomal depot in the subcutaneous adipose tissue. It could be possible in the future to develop drug-loaded radiolabeled hexosomes for the detection and treatment of obesity and obesity related cancers. Finally, it may be concluded that a promising non-invasive visualization tool applicable for SPECT/CT is introduced. It could serve as a useful tool for the development and further investigation of the *in vivo* performance of theranostic cubosomal and hexosomal nanocarriers.

Relative Humidity Influence on Spreading, Pattern Formation and Adhesion of a Drying Drop of Whole Human Blood

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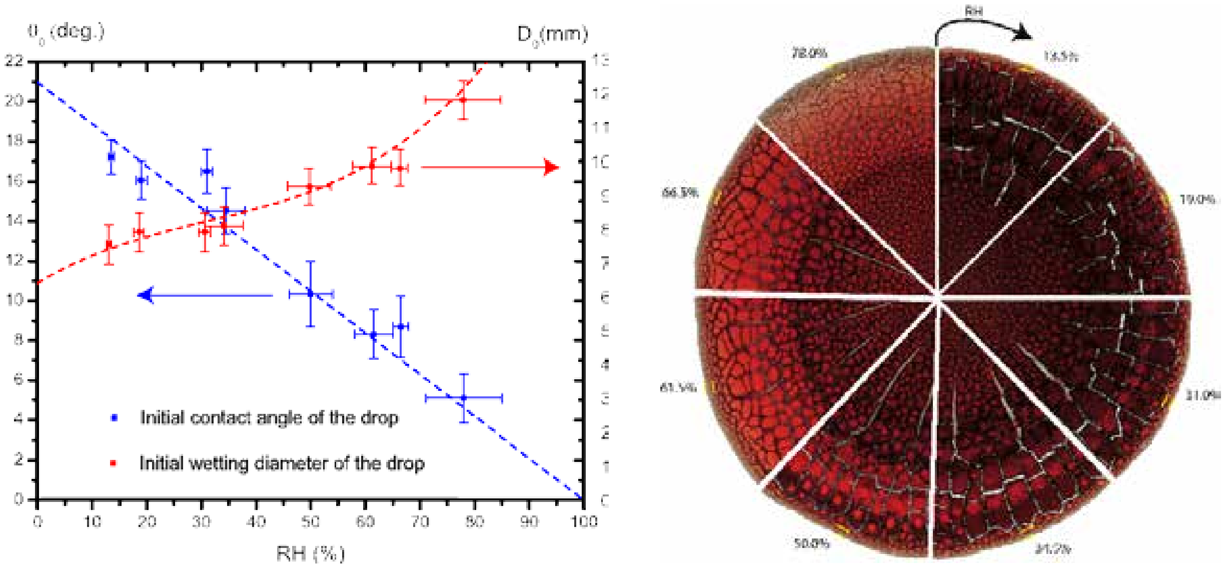
The drying of a drop deposited on a solid substrate has been the subject of numerous investigations. Some of these studies focus on the complex final drop pattern observed at the end of the evaporation process. Our experimental work aims to investigate the effect of relative humidity (RH) on the spreading behavior and on the pattern formation of a dried drop of whole human blood at the end of the evaporation process. A range of RH between 13.5% to 78.0% is studied.



Figs. 1 Left graph - Variation of the initial contact angle θ_0 and the wetting diameter of the drop of blood D_0 function of the RH values. The dashed lines are the linear fit for θ_0 and the cubic fit for D_0 passing by the measurement points. Right picture - Final deposition morphology for a various RH values (RH varying between 13.5% and 78.0%). Area between dashes (-) represents the fine periphery corona.

We will present the results of this study that evidence the increase of spreading for increasing RH. The fracturation modification due to the change in RH will also be presented using morphological analysis recently published or submitted for publication [1,2].

Refereces:

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Enantioselective Adsorption of Ibuprofen Enantiomers on a Chiral Adsorbent with Grafted Eremomycin Antibiotic

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Ibuprofen is a non-steroidal anti-inflammatory drug with analgesic and pyretic properties. It is known that only the (S)(+)-form of ibuprofen is biologically active, while the (R)(−)-form is therapeutically inactive or partially converted to the (S)(+)-form. R-isomer is supposed to have anti-cancer activity.

To measure the adsorption isotherms of ibuprofen enantiomers commercially inavalable R-isomer of ibuprofen was obtained by the diastereomeric crystallization method.

Adsorption isotherms of the ibuprofen enantiomers was measured on a chiral stationary phase Diaspher-Chiralsel-E with a grafted eremomycin antibiotic in a wide range of analyte concentrations. The mobile phase was a solution of the acetate buffer - ethanol (40:60, 50:50, 60:40), the temperature range was 15–40 °C, concentration of the sample was 4 and 40 $g \cdot L^{-1}$. Injection sample volume was 5–80 μL. Experimental data were processed with the help of modified Glueckauf method. The adsorption isotherm obtained from the values of the equilibrium concentration of the adsorbate on the stationary phase surface and in a liquid phase.

It was shown, that reproportioning of mobile phase from 40:60 to 60:40 results in considerable alteration of the shape of elution curves and R- and S-enantiomers adsorption isotherms as well as the increase of the absorbed ibuprofen optical antipodes amount. The largest nonlinearity is exhibited by adsorption isotherms measured for both enantiomers in a mobile phase acetic buffer-ethanol 40:60 (they have a bent in shape).

This work was supported by the Russian Foundation for Basic Research, project no. 13-03-00464-a, by the grant of the president of RF no. MK-675.2013.3.

Adsorption Thermodynamics of Phenylcarboxylic Acids Enantiomers on a Chiral Adsorbent with Grafted Eremomycin Antibiotic

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Many synthetic drugs are produced as achiral mixtures containing only one spatial isomer as a pharmacologically active component. Therefore, eduction of individual enantiomers becomes of current importance. Chiral chromatography is most often used to analyze pharmaceuticals and intermediates of their synthesis. Chiral stationary phases (CSP) with grafted macrocyclic glycopeptide antibiotics have high enantioselectivity towards various classes of chiral compounds.

Separation was performed on the CSP Nautilus-E (250×4 mm, sorbent particles diameter 5 μm) with a grafted eremomycin antibiotic. Mandelic, 2-phenylbutyric, 2-phenylpropionic, and α-methoxyphenylacetic acids were chosen as experimental specimens. Mobile phases prepared from 0.1 M CH_3COONH_4 and 1 %vol. of CH_3COOH in solvents of different water–ethanol compositions were used for enantiometric separation. The experiment was conducted in temperature range 22-50˚C.

The influence of mobile phase composition on the retention of phenylcarboxylic acid enantiomers, separation selectivity, and thermodynamic properties of adsorption (enthalpy, entropy, Gibbs energy) were studied. It is shown that an increase in temperature and in ethanol concentration of the mobile phase causes a decrease in retention factor values of S- and R-enantiomers of all compounds under investigation, with no decrease in selectivity over the entire temperature range. This phenomenon helps reduce the amount of eluent during enantiometric separation. It is uncovered that the adsorption heat value for the enantiomers of all compounds under investigation decreases as the ethanol concentration in the mobile phase increases, thus indicating a weaker bond between adsorbate and adsorption centers.

This work was supported by the Russian Foundation for Basic Research, grant no.13-03-00464-A), by the grant of the president of RF no.MK-675.2013.3.

Electron and X-ray Diffraction Study on the Intercellular Lipid Organization in Human Skin Stratum Corneum

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The primary role of the stratum corneum (SC), the outermost thin layer of the human skin, is to serve as a physicochemical interface between the inner body and the outer external environment. The SC has been attracting our interest because of its highly sophisticated barrier function encompassed in a layer of a few ㎛ thick. It is thought that the molecular organization in corneocytes and intercellular lipids, which are main components of the SC, has a key role for the skin barrier properties [1-3].

Notwithstanding the extensive studies on the structure of intercellular lipid layers, which plays a crucial role for the skin barrier properties, a lot of problems are left open owing to lack of in situ direct evidence for the structure-function relationship. Using low-flux electron diffraction and synchrotron X-ray diffraction methods we deepened understanding of the healthy or diseased skin state and the percutaneous drug delivery.

Both synchrotron X-ray diffraction (XD) and low-flux electron diffraction (LFED) methods are very powerful tools to analyze the intercellular lipid organization in SC. The XD has higher resolution than the LFED, but requires invasive operation because a large amount of skin sample is necessary to obtain reliable data. On the other hand, the LFED makes it possible to analyze the structures of the SC noninvasively, but radiation damage by electron beam must be suppressed [4].

By best use of these methods we examined fundamental structural changes of SC accompanied by permeation of isopropyl myristate, the effect of temperature on the permeation process. We will present these results and discuss future perspectives in the SC structural study.

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Acknowledgements:

This work was supported by Adaptable and Seamless Technology Transfer Program through target-driven R&D Exploratory Research (AS242Z01639P) to HN and JSPS Grant-in-Aid for Young Scientists (B) Grant Number (25870955) to HN.

Investigation of Drug Loading and Release Behaviour of Layer-by-Layer Polyelectrolyte Blend Films

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One of major challenge in drug delivery is to produce controlled, sustained or triggered release systems for bioactive materials. In the last decade, some reports were published on the drug loading, release and biomedical applications of lbl assembled multilayers by famous research groups [1-3]. In this study, it is aimed to investigate the drug loading and release behaviour of the blend films as a function of blend composition, lbl deposition conditions and type of drug. Also, the formation of multilayers was followed using quartz crystal microbalance-dissipation (QCM-D), UV-Vis analysis and scanning electron microscopy (SEM). For this purpose, 10 bilayered polyelectrolyte blend and films were prepared upon alternating electrostatic adsorption of polyvinylamine hydrochloride (PVA) and polystyrene sulfonate sodium salt (PSS), or mixtures of PSS and polyacrylic acid (PAA) in different ratio. Ibuprofen (IBF) was used as a model drug compound. It was found out that pure PVA/PAA films exhibit a faster release of IBF than those of pure PVA/PSS and blends probably due to a rougher surface and a more porous structure. Interestingly, the IBF release characteristics of blend films differed from pure systems. A two-step release behavior was observed. In the first step, after a strong release within the first 16 hours a plateau was reached. In step two, after about 86 h, the release again increased and was complete after 160 h (Fig.1). High loading of drugs inside the lbl films and rapid pH-induced decomposition of the films can be desirable for future applications in drug delivery devices.

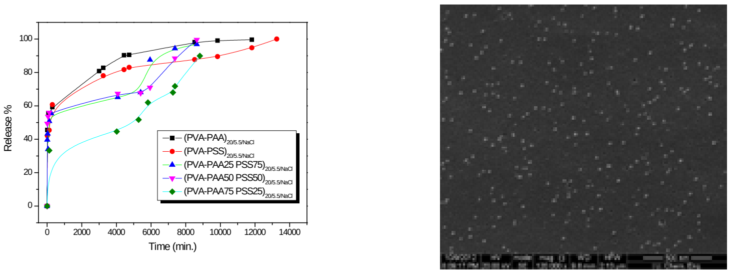

Fig. 1: IBF release % through self assembled membranes as a function time in PBS solution (pH:6.8) and SEM image of IBF-Na released membrane.

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Acknowledgements: One of the authors, Hüseyin Deligöz, thanks TUBITAK-BIDEB 2219 programme for financial support.

Chondroitin-sulfate-A-coated Magnetite Nanoparticles in Biocompatible Magnetic Fluids

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Superparamagnetic iron oxide nanoparticles (SPIONs) have been widely studied because of their potential biomedical application (MRI contrast agents, drug delivery, magnetic hyperthermia). These require the SPIONs to be non-toxic, chemically stable, uniform in size, and well-dispersed in aqueous media. Polysaccharide-coated magnetite nanoparticles (MNPs), such as the dextran-coated MNPs are known biocompatible magnetic products. Chondroitin-sulfate (CS) is a polysaccharide of natural origin with different types (A, C, D, and E). The CS iron colloids (CSIC) have been used in the treatment of anaemia in Japan, and the synthesis of magnetite nanoparticles in the presence of CS has been patented.

The main goal of this study is to characterize systematically the surface modification of MNP with CSA, and the preparation of stable magnetic fluid (MF) for biomedical application. MNPs were prepared by the co-precipitation of Fe(II) and Fe(III) salts. The pH- and ionic strength-dependent charge state of MNPs and CSA were characterized by potentiometric acid-base titration. The adsorption isotherm of CSA was determined at pH~6.5 and 0.01 M NaCl. ATR-FTIR spectra were recorded to characterize the bond formation on ^{o}Fe-OH sites. The average particle diameters and the electrophoretic mobilities of the pure and the CSA-coated MNPs (CSA@MNP) dispersions were measured. The effect of CSA on the colloidal stability of MNPs was tested in coagulation kinetic experiments at pH~6.5. The CSA@MNP synthesized under special conditions was tested in blood sedimentation and cell proliferation experiments [1].

The results of potentiometric acid-base titration proved that a special pretreatment of CSA is required. CSA adsorption on MNPs has a high-affinity isotherm reaching a plateau at ~0.1 mmol/g, however well-stabilized MF can be synthesized only under special conditions. ATR-FTIR spectra show the different roles of -COO^- and -OSO_3^- groups in adsorption. Electrophoretic mobility was measured at increasing CSA loadings at pH~6.5, isoelectric point was at ~0.035 mmol/g CSA. Small amounts of CSA induce the aggregation of MNPs, while its larger amounts can stabilize dispersions over the range of pH~3-10. The salt tolerance of MNPs characterized by critical coagulation concentrations increases up to ~0.5 M with increasing CSA loading. The results of blood sedimentation and cell proliferation experiments suggest that CSA@MNP synthesized under special conditions is promising candidate for biomedical application.

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Acknowledgements:

This work was supported by OTKA (NK 84014) and TÁMOP-4.2.2.A-11/1/KONV-2012-0047.

Development of Particle Characterization Methods (Dynamic Image Analysis and Dynamic Light Scattering) for pharmaceutical products.

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Development of nano-technology based products, colloids and polymers for therapeutic applications is a rapidly growing field. Bringing these products into market, however, presents a huge regulatory challenge, especially because many of those therapeutics are administrated as injectable solutions. Physicochemical properties (size, shape, surface potential and extent of particle-particle interaction, etc) of such products have to be well understood and monitored through manufacturing and stability. First and foremost, their particle size distribution (PSD) has to be well characterized. Two methods to access PSD of two therapeutical products have been developed, and will be presented. I) Dynamic Image Analysis (DIA) comprises optical imaging of a flowing liquid and allows to access PSD and to count any present particles in the range of 1-500 micron. We have developed a DIA method to access the quality of a therapeutic polypeptide solution. II) Dynamic Light Scattering, DLS, is a dark-field optical technique, allowing PSD evaluation at a much smaller range, down to 1nm. We employed DLS to access aggregation state in the range 1nm-200nm of an antisense DNA oligonucleotide therapeutical product. For both methods accuracy, precision, robustness and specificity have been demonstrated.

Biogenic Gold Nanoparticles Enhance Methylene Blue-induced Phototoxic Effect on *Staphylococcus Epidermidis*

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Antibiotic-resistant bacterial infections, particularly those caused by *Staphylococcus epidermidis* strains, are a growing problem nowadays in many healthcare facilities [1, 2]. Therefore, much effort is being undertaken to develop new non-antibiotic antimicrobial strategies such as antimicrobial photodynamic therapy (APDT) [3]. The APDT approach is based on the photodynamic therapy concept that comprises the action of three components: a photosensitizing agent, a light source of an appropriate wavelength (artificial light or sunlight) and oxygen. This therapy represents a potential alternative methodology to inactivate microbial cells and has already been shown to be effective *in vitro* against bacteria, fungi, viruses and protozoa. However, a great number of variable influences the number of microorganisms affected by this technique including type and concentration of the photosensitizer, microorganism's physiologic stage, photosensitizer incubation period before the irradiation, exposure period and density of laser energy etc. No cases of microbial viability recovery or any resistance mechanisms against APDT are yet known.

In the present work we demonstrate an antimicrobial photodynamic therapy approach using methylene blue-biogenic gold nanoparticles (MB-Au NPs) conjugates and different light sources allowing rapid eradication of *S. epidermidis in vitro*. The gold nanoparticles (AuNPs) were formed by the cell-free filtrate of *Trichoderma koningii* as a reducing and stabilizing agent. The Fourier transform infrared (FTIR) spectrum suggests that proteins are mainly responsible for reduction of chloroauric acid. Various techniques such as UV-Vis spectroscopy, scanning electron microscopy with an energy-dispersive elemental analyzer (SEM-EDS) and transmission electron microscopy (TEM) were employed to characterize the nanoparticles. Bacterial suspensions were incubated with MB, Au NPs and MB-Au NPs conjugate for 30 min and then irradiated with different light sources for varying time spans. Following irradiation, samples were serially diluted and analysed by the spread plate method. Significant reduction of plate counts was observed for the samples treated with MB-Au NPs conjugate compared with controls and samples incubated with MB or Au NPs alone. The method is highly effective against *S. epidermidis*.

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Equilibrium and Dynamic Osmotic Behavior of Aqueous Solutions at Constant and Varied Volume

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Osmosis is of prime importance for living organisms. In biological systems the process usually occurs in confined volumes and may express specific features. The osmotic pressure in aqueous solutions was studied here experimentally as a function of solute concentration (0.05 – 0.5 M) in two different regimes: of constant and variable solution volume. Sucrose, a biologically active substance, was chosen as a reference solute for the complex tests. A custom made osmotic cell was used. A novel operative experimental approach, employing limited variation of the solution volume was developed and applied for the purpose. The established equilibrium values of the osmotic pressure are in agreement with the theoretical expectations, and do not exhibit any evident differences for both regimes. In contrast, the obtained kinetic dependences reveal striking divergence in the rates of the process at constant and varied solution volume for the respective solute concentrations. The rise of pressure is much faster at constant solution volume, while the solvent influx is manifold greater in the regime of variable volume. The results obtained suggest a feasible mechanism for the way in which the living cells rapidly achieve osmotic equilibrium upon changes in the environment.

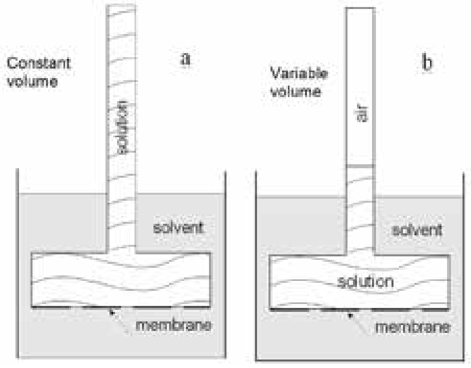

Fig. 1 Schematic of the two experimental osmotic regimes:
(a) open cell (variable volume); (b) closed cell (constant volume).

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Acknowledgement:

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Gibbs Layers of *Quillaja* Bark Saponin at Water Surface

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Saponins are natural glycosides produced mainly by plants, where they play an important role in the defence system. They are found in large quantities in the tissues most susceptible to attack by fungi, bacteria and insecticides (root, tuber, bark, leaves, seeds and fruits) [1]. For their surface-active properties saponins have been used traditionally as detergents (Latin *sapo*≡"soap"), but nowadays their field of application has much broadened and spreads from foaming agents, emuslifiers, nutraceuticals, through cholesterol-lowering agents, to immunological adjuvants [2].

Despite a growing number of present and prospective applications of saponin-rich extracts from the bark of *Quillaja* saponaria Molina tree (Quillaja Bark Saponin, QBS), their surface properties are still not well characterised, partly because of their huge variability. Consequently, many details of their structure, surface activity, and especially biological interactions are missing. In this paper we address the issue of the structure of spontaneously adsorbed layers (Gibbs monolayers at air/water interface) of QBS obtained from Sigma probed by surface pressure (Π) and neutron reflectivity (NR).

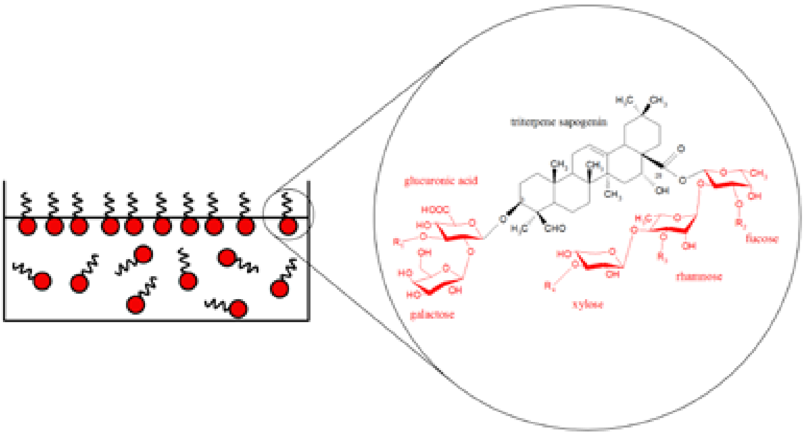

Fig. 1 Schematic illustration of a Gibbs monolayer of QBS at the water-air interface

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Acknowledgements: This work was financially supported by the Polish National Science Centre, grant no. DEC-2011/03/B/ST4/00780 and COST CM1101 Action

Interaction of Polyhedral Oligomeric Silsesquioxanes with Model Biological Membranes

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Polyhedral oligomeric silsesquioxanes (POSS) have attracted considerable attention over the last years because of their unique hybrid properties. POSS compounds have found numerous applications in various fields ranging from medicine to chemistry [1]. While numerous reports have presented properties of POSS in blends with polymers [2], very little is known about interaction of these compound with biological membrane. In this study we investigated model biological membranes containing phospholipids and cholesterol using Langmuir trough. The closed- cage silsesquioxanes were mixed with dipalmitoylphosphatidylcholine (DPPC) or cholesterol (CHOL) and spread at the air/water interface. The surface pressure-area isotherms, Brewster angle microscopy and surface potential were used to determine the interfacial properties of the films. Moreover, the dilational viscoelasticity of the monolayers was investigated by oscillating barriers method measuring the surface pressure response to harmonic oscillatory perturbations of the interfacial area at controlled amplitude and frequency.

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Acknowledgements:

The research was financially supported by Polish National Science Centre by grant No. UMO-2012/05/B/ST5/02200

Protein Aptasensor Built on Graphene Oxide Surface Fixed on Solid Support: Basic Mechanism Study and On-chip Device Application

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Graphene oxide (GO) is attracting considerable interest in many basic and applied research fields. One such application is biosensing using a GO surface modified with an aptamer (GO aptasensor). As GO is readily dispersed in water, most GO aptasensors were operated in an aqueous medium. By contrast, we recently reported a GO aptasensor fixed on a solid support [1]. Our GO aptasensor has several advantages.

One is that we can directly observe phenomena that occur on the GO surface during protein recognition using surface science analytical tools (**Fig. 1**). With thrombin as a target, the GO surface was modified with a receptor composed of pyrene (linker)–thrombin aptamer–probe dye. The dye fluorescence was quenched at the initial stage, and recovered after the thrombin had been added (**Fig. 1 top**). The shape of the green fluorescence area corresponds to that of the topography. The GO thickness had increased by about 2.9 nm after the recognition, which agrees well with the thrombin adsorption on the surface (**Fig. 1 bottom**).

Another advantage is that we can combine the sensor with microfluidics to realize an on-chip GO aptasensor. We examined the versatility and selectivity of the GO aptasensor for prostate specific antigen (PSA) using an on-chip device with three microchannels (**Fig. 2**). Fluorescence was observed only from the microchannel filled with PSA solution, which demonstrated the good selectivity of the GO aptasensor.

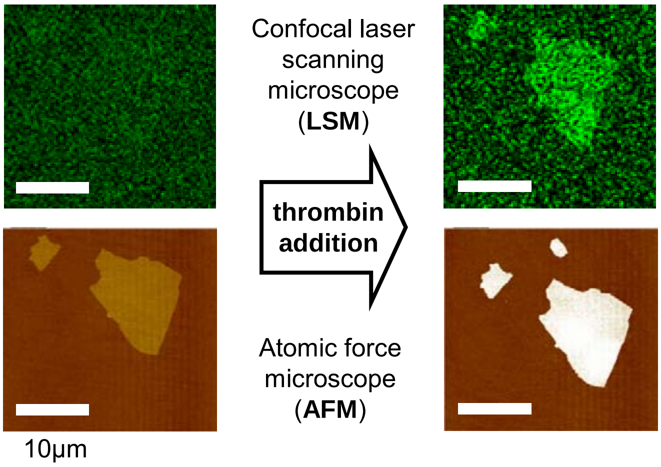

Fig. 1. Confocal microscope (fluorescence, top) and atomic force microscope (topography, bottom) images of an identical single piece of GO before and after protein recognition. The target protein is thrombin.

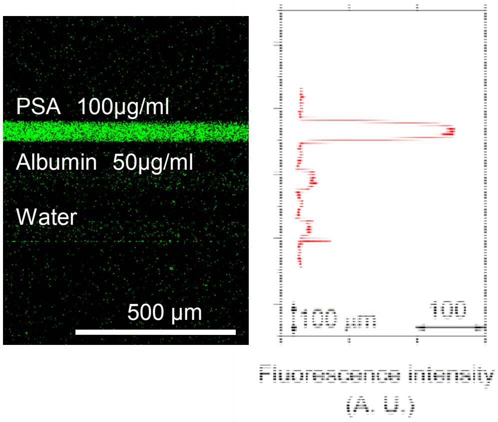

Fig. 2. Confocal microscope image of on-chip GO aptasensor for PSA with three microchannels (left) and the average fluorescence profile (right). The microchannels are filled with PSA (top), albumin (middle) and water (bottom).

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Novel Fabrication Method of Biocompatible Nanoparticles for Theranostic Applications

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Nanoparticles are useful for transporting drugs across biological barriers and for medical imaging with X-ray computed tomography. Previous studies have demonstrated that albumin nanoparticles, which are produced by chemical fixations, are implemented as theranostic tools for delivering drugs to the cancers. We have recently developed that theranostic application of tunable plasma lipoproteins, composed of a nanoparticle core, self-assembled lipid, protein and fluorescent probe, to research on the therapies for neurodegenerative diseases and cerebral atherosclerosis (1). Such biocompatible nanoparticles will begin to be used in the clinical trials. Moreover, this suggests that biocompatible nanoparticles have potential promise to connect physiological functions with disease processes. However, since it is difficult to control nano-structured self-assembly of proteins and phospholipids which possess amphoteric colloidal behavior, application of traditional techniques (desolvation and chemical synthesis) have great limitation to create biocompatible nanoparticles. Moreover, methods for the adjustment of particle size and shape or tuning of protein and phospholipid species remain unknown. In addition, biological information on nano-structured proteins is not understood.

In the present study, we established a novel method of fabrication of biocompatible nanoparticles based on the isoelectric point of each intramolecular domain or fragment peptide of protein. We investigated the endothelial dysfunction involved in the pathogenesis of cerebral atherosclerosis in the mouse. Subsequently, our techniques enabled us to identify the incident regions of endothelial function and dysfunction. Therefore, our method of constructing biocompatible nanoparticles may lead to key advances in the development of theranostic applications to cerebral atherosclerosis.

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Properties of β-carotene and Retinoic Acid in Mixed Monolayers with DPPC and Solutol

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Encapsulation constitutes a promising approach to preserve the nature properties over time of liposoluble vitamins and carotenoids. They are sensitive molecules and their antioxidant properties can be dramatically affected when included in membrane environment or in encapsulated carriers as liposomes or lipid nanocapsules (LNCs).

The formation, the state and rheological properties of mixed monolayers of b-carotene (bC) or retinoic acid (RA) with dipalmitoylphosphatidylcholin (DPPC) as simples membrane model or Solutol (Sol) forming the soft layer covering the LNCs were studied by measuring the surface pressure (p), surface potential (DV) and surface elasticity (E). The miscibility and the interfacial properties of the mixed monolayers depend on the nature and the composition of the studied surface monolayers. The obtained results are in agreement with the observed by means of AFM structures.

Diffusion of anti-TB Drug from Calcium Alginate Hydrogels

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Long-term treatment with high doses of several TB drugs often causes patients with toxic-allergic complications. In this regard, it is important to find a way to reduce the dosage of antituberculosis drugs. One way of solving this problem is the application of polymeric anti-TB drugs with prolonged action. Such products may be prepared including the known antituberculosis drugs in the structure of polymeric carrier. This work presents the results of immobilization of anti-TB drugs rifampicin in hydrogels based on calcium alginate. Hydrogels are prepared by reacting of the sodium alginate aqueous solution with calcium chloride. To optimize the process of obtaining a hydrogel, the effect of calcium ion concentration on the swelling of the hydrogel in the physiological solution was studied (fig.1). The optimal concentration of calcium chloride for obtaining the hydrogel is 0.1M. Fast swellable and mechanically unstable microparticles obtained at low concentrations of calcium ions formed into the slowly swellable microparticles when the concentration of calcium ions was higher than 0.1M.

To obtain prolonged forms of rifampicin, the diffusion of the drug from the swollen and dried microparticles studied (Fig. 2). The release of rifampicin from the swollen microparticles(1 line) is faster than from the dried microparticles(2.3 lines).

Also the release of rifampicin from alginate microparticles coated with chitosan layer was studied (fig.3). We investigated that the thicker the layer of chitosan is, the slower drug releases.

Thus, it is shown that anti TB drug with prolonged action can be obtained by immobilizing rifampicin into the alginate hydrogels modified with surface layer of chitosan.

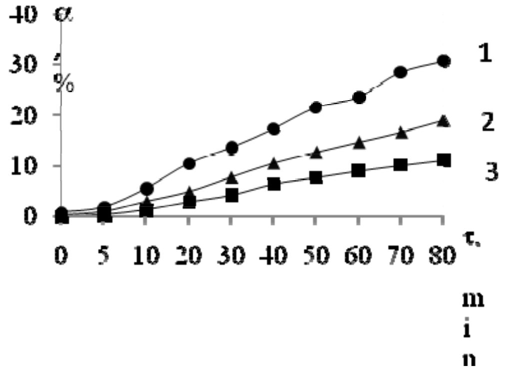

Fig. 1 Swelling kinetics of hydrogels obtained at different concentrations of calcium chloride in physiological solution. (1)-0.05M, (2)-0.1M, (3)-0.2M.

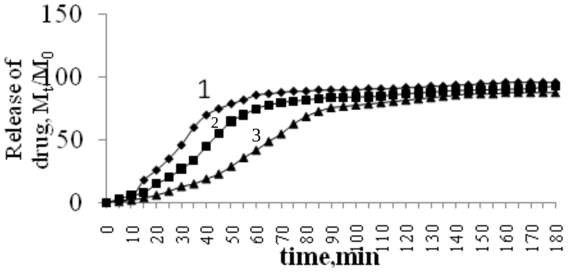

Fig. 2 Desorption kinetics of drug from swollen (1) and dried (2, 3) hydrogels.

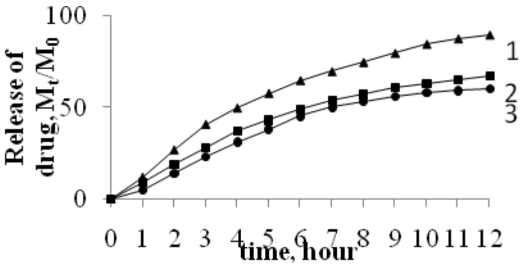

Fig. 3 Desorption kinetics of drug from microparticles coated with chitosan layer at different thickness of layer. (1)-25 mkm, (2)-65 mkm, (3)-125 mkm.

Polysorbate and the Adsorption of monoclonal antibodies – a common strategy under evaluation

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Introduction: Polysorbates are frequently added to stabilize protein pharmaceuticals in solution. Below the critical micelle concentration (CMC) stabilization is thought to originate from increased conformational stability due to protein-surfactant interaction. Above the CMC stabilization is attributed to saturation of surfaces and hence, reduced adsorption. Available information on the interaction of monoclonal antibodies with polysorbates is rather limited.

Aim: To evaluate the mechanism of polysorbate 80 (PS80) in modifying adsorption behavior of two pharmaceutical monoclonal antibody products to hydrophobic and hydrophilic model surfaces.

Method: Total internal refection fluorescence enables real time measurements and quantitation of protein adsorption. Proteins are loaded in concentration ranges reflecting hospital dosing protocols. Polysorbate is added at concentrations of 50% and 200% CMC in different schemes.

Preliminary results: Antibodies introduced to the flow chamber without the presence of PS80 adsorb readily to hydrophilic and hydrophobic surfaces. Loading protein after exposing a hydrophobic surface to PS80 below and above CMC does not lead to measurable adsorption within the time frame of 15min. This indicates that under these conditions the hydrophobic surface is sufficiently saturated with polysorbate 80 to reject proteins from the surface. However, if protein and PS80 are introduced simultaneously, adsorption occurs.

Perspective: Long term adsorption experiments are planned to evaluate the influence of size and affinity of the competing species after the system reached equilibrium.

Wetting Behavior of Pulmonary Surfactant Aqueous Solutions

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The wetting properties of pulmonary surfactant aqueous solutions with respect to solid surfaces with different degree of hydrophobicity have been studied. A special procedure for hydrophobization of the SiO_2-glass hydrophilic surface allows the preparation of hydrophobic glass surfaces with different degree of hydrophobicity. As a measure for the degree of hydrophobicity of a solid surface we have used the contact angle θ_w□□of a drop of pure (tri-distilled) water on this surface. The contact angles θ of drops from a pulmonary surfactant solution onto SiO_2-glass surfaces have been measured as a function of their degree of hydrophobicity θ_w. The completely hydrophilic SiO_2-glass surface is essentially hydrophobized by the animal-derived pulmonary surfactant *Curosurf*. The hydrophobization depends on the surfactant concentration - the contact angles increase with increasing the *Curosurf* concentration C_s in the low concentration range, but they remain almost constant in a wide range of $C_s > 90$ µg/ml. Additions like NaCl and bovine serum albumine (BSA) influence the θ-values. The contact angles θ□□naturally□increase with increasing θ_w but this dependence is not linear - the curve steepens at larger θ_w-values. Similar are the $\theta(\theta_w)$ curves for aqueous solutions of the synthetic pulmonary surfactant *CHF 5633*. Practically no significant difference in the wetting behaviour of the aqueous solutions of the natural surfactant *Curosurf* and the synthetic surfactant *CHF 5633* has been established, however about 25% less *Curosurf* than *CHF 5633* was needed to achieve almost the same wetting behaviour.The thickness h of the wetting thin liquid films from aqueous solutions of *Curosurf* as well as of *CHF 5633* on SiO_2-glass surfaces depends on the degree of hydrophobicity θ_w of the solid surface. The $h(\theta_w)$ curves always pass a minimum. The h-values, as well as the $h(\theta_w)$ curve, are mainly determined by the balance of the positive (repulsive) steric and negative (attractive) hydrophobic disjoining pressures, which depend on the orientations and conformations of the molecules adsorbed on the solid surface from the very complicated multi-component aqueous solutions.

Mechanism of Cholesterol Lowering by Calcium, as Studied in Vitro

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In the human digestive tract, the pancreatic lipase is an enzyme which catalyzes the hydrolysis of water insoluble triglycerides into partially soluble fatty acids (FAc) and 2-monoglycerides (MG). In vivo these reaction products should be solubilized in the molecular aggregates of the bile salts (so called “bile micelles”) in order to be transferred to the walls of the small intestine and absorbed by the human body. In the current study we used a relatively simple in vitro model for triglyceride (TG) lipolysis which mimics closely the conditions in the human stomach and small intestine. The main model advantages are: (1) As in vivo, sodium bicarbonate is used for buffering the reaction mixture; (2) The pH-profile in small intestine is closely matched; (3) The experimental procedure does not include complex equipment. This model was applied to quantify the effects of Ca^{2+} concentration, C_{Ca}, on the degree of TG lipolysis and the solubilization of lipolysis products and cholesterol, for fats and oils with different saturated/unsaturated FAc content. We found that complete TG lipolysis is achieved for all studied fats and oils, and at all C_{Ca} studied. Filtration and centrifugation were used to separate the aqueous phase from the heterogeneous reaction mixture and to study the solubilization of the various lipophilic components in the bile micelles. We found that Ca^{2+} significantly decreases the solubilization of cholesterol, FA and unsaturated MG. Furthermore, we found that the unsaturated FA and MG promote cholesterol solubilization in the bile micelles, while the saturated ones do not affect it. We thus conclude that Ca^{2+} decreases the solubilization of the unsaturated FA and MG in the bile micelles which, in turn, reduces the cholesterol solubilization in these micelles.

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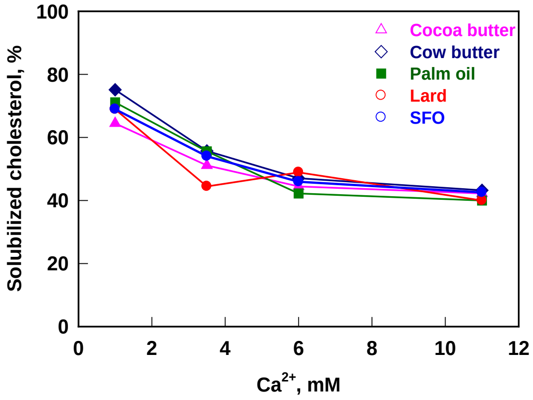

Fig. 1. Percentage of solubilized cholesterol in the aqueous phase after filtration, as a function of Ca^{2+} concentration in the reaction mixture.

Kinetic Mechanism of Monoclonal Antibody Aggregation

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The stability of biocolloids has received great attention during the last years due to its numerous implications in various research fields such as biology, biomedicine, pharmacy, food science and nanotechnology. Here, we focus on the stability of therapeutic proteins, and in particular monoclonal antibodies (mAbs), which represent a growing part of the pharmaceutical market. The presence of protein aggregates may compromise biological drug activity or induce an immunogenic response of the organism, and must therefore be avoided. The goal of this work is to understand and quantify the mechanisms and kinetics of monoclonal antibody aggregation, which is the consequence of a series of microscopic events, including the formation of an aggregation prone intermediate in a non-native conformation, nucleation of oligomers, monomer addition to preformed aggregates and cluster-cluster aggregation. By applying a combination of several biophysical techniques we characterize the monomer depletion, the oligomer formation, the average hydrodynamic radius and the average molecular weight of the aggregates. It is found that the aggregates exhibit effective fractal geometry and that the aggregation kinetics can be well rationalized based on modified Smoluchowski's Population Balance Equations, which describe in a coarse-grained approach both the protein 'structure stability', represented by the kinetics of protein unfolding, and the protein 'colloidal stability', which depends on the type and strength of intermolecular interactions between two aggregating units. By combining model simulations to experimental data, we show that it is possible to extract information on the contribution of the single microscopic steps on the global aggregation rate. In particular, we aim at gaining a comprehensive picture of the role of co-solutes such as polyol sugars, salt or surfactant on mAb stability. We discriminate the effect of co-solutes on the single microscopic steps, i.e. protein unfolding and aggregation rates, and quantify their impact on effective interaction potentials.

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Novel Formulations Based on Colloidal Systems for Transdermal Drug Delivery

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Colloidal systems consisting of vesicles entrapped in gels were prepared as novel transdermal drug delivery systems. AOT or Pluronic L64 aqueous systems were prepared to obtain lamellar, L_α, phases. The same surfactants were used to obtain the vesicular systems (niosomes) that were added to the corresponding gel. Simple AOT and L64-based niosomal formulations and L_α phases were then prepared and used as control. The percutaneous permeation profiles of Sulfadiazine Sodium Salt, Propranolol Hydrochloride and Tyrosol from novel liquid crystal-niosomes formulations as multicomponent systems, were investigated. The obtained multicomponent drug carrier was characterized by Deuterium Nuclear Magnetic Resonance spectroscopy, in order to understand if the introduction of the drug or drug-loaded niosomal suspension, as third component in the formulations, could influence the microstructure of the system and then the drug delivery across the skin. Different drugs percutaneous availability was achieved, and the results revealed that the obtained gel-niosomes carriers were affected by the chemical structure of the drugs and by their affinity for the components. As a consequence these systems could be proposed, since they were found able to control the percutaneous permeation of small drugs across the skin.

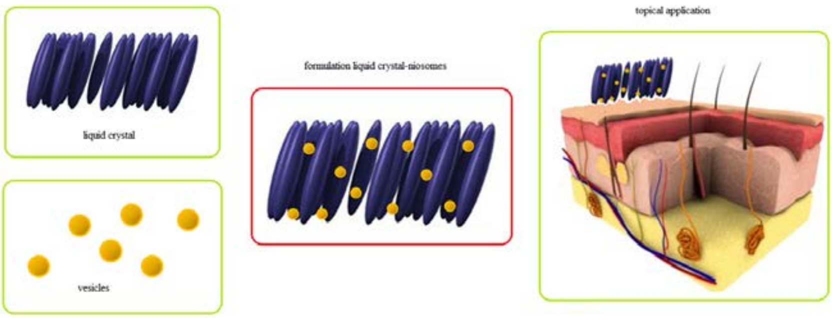

Fig. 1 Schematic illustration of colloidal transdermal drug delivery system.

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Self-Assembling Kinetics and Mechanism of the Amphiphilic Peptide RADA 16-I

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In the last decades the rational control of the self-assembling of single molecular building blocks into highly organized structures led to the design of many functional materials. RADARADARADARADA (RADA 16-I) is a small amphiphilic peptide designed to self-assemble into fibrils and higher ordered structures depending on environmental conditions. Biocompatible RADA hydrogels found several applications in 3D cell culture, tissue engineering and drug delivery. Despite the large number of applications, the physico-chemical basis of the self-assembling process, crucial for controlling material properties and functions, is still not completely understood.

In this work, using a combination of microscopy, chromatography, light scattering, rheology and spectroscopic techniques we investigated the aggregation state of the peptide as a function of peptide concentration, pH and ionic strength. We characterized different self-assembling levels from fibrils at the nano and micron scale to hydrogels at the macro scale. In particular, we elucidated the mechanism of fibril network formation of RADA 16-I nanofibril dispersions at low pH. We identified a two-steps gelation process consisting of irreversible end-to-end fibril-fibril elongation followed by reversible gel network formation. The phase transition occurs directly from the isotropic liquid phase to the gel phase, and no nematic phase is observed. By applying population balance equations model of aggregation kinetics we quantified the effect of buffer composition on the effective fibril-fibril interactions governing the fibril dispersion stability.

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1. Dr. Alessandro Butte' and Dr. Francesca Quattrini, Lonza Ltd., LES R&D-DSP, Technologies, Visp, Switzerland
2. Anna Carola Motta, ETH Zurich, Switzerland
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Importance of Lipopolysaccharide Aggregate Disruption for the Anti-endotoxic Effects of Host Defense Peptides

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Lipid membrane and lipopolysaccharide (LPS) interactions were investigated for a series of amphiphilic and cationic peptides derived from human heparin cofactor II (HCII), using dual polarization interferometry, ellipsometry, circular dichroism (CD), cryoTEM, and z-potential measurements. Antimicrobial effects of these peptides were compared to their ability to disorder bacterial lipid membranes, while their capacity to block endotoxic effects of LPS was correlated to the binding of these peptides to LPS and its lipid A moiety, and to charge, secondary structure, and morphology of peptide/LPS complexes. While the peptide KYE28 (KYEITTIHNLFRKLTHRLFRRNFGYTLR) displayed potent antimicrobial and anti-endotoxic effects, its truncated variants KYE21 (KYEITTIHNLFRKLTHRLFRR) and NLF20 (NLFRKLTHRLFRRNFGYTLR) displayed partially retained and substantially reduced anti-endotoxic effects, respectively, hence locating the anti-endotoxic effects of KYE28 to its N-terminus. The antimicrobial effect, on the other hand, is primarily located at the C-terminus of KYE28. While displaying quite different endotoxic effects, these peptides bind to a similar extent to both LPS and lipid A, and also induce comparable LPS scavenging on eucaryotic membranes. In contrast, fragmentation and densification of LPS aggregates, in turn dependent on the secondary structure in the peptide/LPS aggregates, correlate to the anti-endotoxic effect of these peptides, thus identifying peptide-induced packing transitions in LPS aggregates as key for anti-endotoxic functionality.

Micromechanical Characterization of Hydrogel Beads for Single Cell Analysis

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In order to best possibly simulate *in vivo* conditions cell studies are increasingly extended to three-dimensional environments mimicking the extracellular matrix [1]. Thereto materials - typically hydrogels - have to be chosen fulfilling several prerequisites: suitable pore size and mechanical properties, biocompatibility and –degradability, cell-adhesion sites [2]. Relying on a microfluidics approach well defined, monodisperse collagen/gelatin beads were produced offering the potential to serve as single cell 3D microcompartments.

Here, we focus on their micromechanical characterization. By means of AFM force spectroscopy, in particular with a colloidal probe technique, we have a versatile and high-precision tool at hand to investigate soft matter particle systems. We show that the mechanical properties of gelatin beads can be tuned both by a mild crosslinking procedure and by variation of concentration. The determined moduli are in a biologically favorable range of some kPa. In addition, we find that the degree of cell spreading can be correlated to the stiffness of the surrounding material.

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Toward a Better Understanding of the Interfacial Growth Mechanism of Dairy Fouling at a Stainless Steel Surface: A Multiscale Approach

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Fouling is generally defined as the unwanted formation of thermally insulating materials or deposits from process fluids onto heat transfer surfaces, leading to severe sanitary risks in food-processing industries[1] and forcing them to take drastic and expensive cleaning measures[2]. Research teams are actually intensively working on antifouling coatings development, which is an issue, as many parameters are involved; however no fundamental study on the fouling growth mechanism at the interface after only a few seconds fouling has been carried out yet.

In this study, the interfacial behaviour of two different model dairy foulings at a stainless steel surface after different times of exposure to dairy solutions in a heat exchanger were investigated using Electron-Probe Micro Analysis (EPMA), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Atomic Force Microscopy (AFM). Deposits were formed using two model fouling solutions respectively containing 30 ppm (sol.1) and 120 ppm Calcium (sol.2). After two hours fouling, characterisations show that when sol.1 is used, the fouling layer is thin, smooth and homogeneous, whereas it is very thick, rough, and shows a growth mechanism in arborescence when sol.2 is used. This evidences the role of Calcium in the fouling growth. To better understand the early stages of the fouling growth, samples were submitted to only one minute fouling in both solutions. Using AFM, XPS and ToF-SIMS 3D image reconstructions (**Fig.1 a,b**), the fouling was proven to be initiated by unfolded proteins (size of 60 nm) in the first seconds of exposure to both fouling solutions. Unstable amorphous calcium carbonate nuclei (size 150-400 nm) formed in the sol.2 at 90°C are stabilized by the protein and are preferentially trapped in the steel roughnesses. The unfolded protein covers again these calcium particles, etc. This explains the arborescence growth structure observed by EPMA (**Fig. 1,c**). When sol.1 is used, calcium (Ca^{2+}) is chelated or trapped in the protein layer, without creating the same roughness effect.

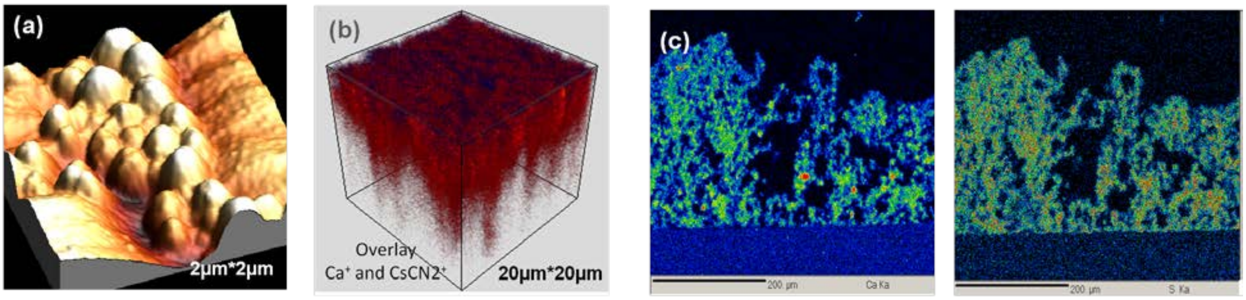

Fig.1: (a) AFM and (b) 3D Tof-SIMS image reconstruction after 1 minute fouling with sol.2 and (c) EPMA X-Ray mappings in Ca and S (protein) after 2 hours fouling.

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The Influence of Simulated Biological Fluids on the Wettability and Composition of Selected Mucoadhesive Polymers

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Mucoadhesion involves the attachment of a polymer to a biological substrate. It is a practical route of drug immobilization or localization and an important new aspect of controlled drug delivery [1,2]. The surface tension of the mucus and the mucoadhesive polymer in the wetting theory correlates with its ability to spread on the mucus layer [3,4]. Adsorption process is preceded by the wetting process on the surface, therefore the wetting process needs to be taken into account in considerations of surface properties of polymers.

The aim of our study was to analyze the effect of simulated biological fluids e.g. saliva, gastric and vaginal on the wetting properties of selected mucoadhesive polymers and their mixtures in the forms of discs and powders. The polymers selected: Kollidon VA 64 (poly [1-(2-oxo-1-pyrrolidinyl)ethylene]), Hydroxyethylcellulose, Polycarbophil AA–1 (acrylic acid polymer crosslinked with divinyl glycol) and Carbopol 974P NF (carboxy polymethylene) are widely used in many pharmaceutical formulations based on the mucoadhesion phenomenon [1,3,5].

Measurements of advancing contact angle of simulated biological fluids on the polymer's surfaces compressed and their mixtures were carried out using the sessile drop method with the instrument Tracker I.T.Concept. Powder wettability of polymers was measure by KSV Sigma 701 instrument. The confocal microscope was used in order to a qualitative evaluation of polymeric surfaces. Additionally, the swelling index of the polymers tested in biological fluids was determined. Our research indicate the wettability of examined polymers depends on the type of polymers, their structure and the biological fluids.

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Fabrication of Functional Artificial Free-Standing Yeast Biofilms

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The fabrication of hybrid structures based on biological cells might be achieved in different ways. Cells modified with polyelectrolyte nanocoatings doped with fluorescent silica nanoparticles [1] and magnetic nanoparticles [2,3] prepared via the layer-by-layer (LbL) assembly have been used in imaging, detection and characterization of cells, and for fabrication of biosensors and integrated microfluidic devices. In addition, the LbL method has been utilised in development of artificial multicellular structures, where the individual cells were controllably assembled by colloid interactions in complex biomimetic live clusters. Such multicellular "man-made" assemblies are believed to have potential applications in tissue engineering, microfluidic devices and cell-based microreactors. Here, fabrication of artificial free-standing yeast biofilms built using sacrificial calcium carbonate-coated templates and layer-by-layer assembly of extracellular matrix-mimicking polyelectrolyte multilayers have been studied. Such biofilms were initially formed on glass substrates of circular and ribbon-like shapes coated with thin layers of calcium carbonate microparticles. The templates were then coated with cationic and anionic polyelectrolytes to produce a supporting multilayered thin film. Then the yeast alone or mixed with various micro- and nanoparticle inclusions was deposited onto the multilayer composite films and further coated with outer polyelectrolyte multilayers. To detach the biofilms from the glass substrates the calcium carbonate layer was chemically dissolved yielding free-standing composite biofilms.

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Tuning Conformations and Stability of Fibrinogen Monolayers on Latex Particles

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The conformation and orientation of proteins on solid surfaces have been of interest for both theoretical and practical point of view [1]. In the past year, several hundred published papers tackled problems ranging from fundamental aspects of protein surface interactions to applied problems of surface blood compatibility and protein surface immobilization.

Platelet activation by polymer surfaces is thought to require preliminary adsorption of fibrinogen and changes in fibrinogen conformation. We measured fibrinogen adsorption on negatively charged latex particles for a broad pH range and high ionic strength of 0.15M. In our studies we investigated changes in electrophoretic mobility of latex particles covered by different amount of fibrinogen in pH cyclings starting either from pH 3.5 or 7.4 [2] . These experimental data were consistent with charge distributions and conformations of the fibrinogen molecule characterized by the expanded conformations of fibrinogen at pH 3.5 and semi-collapsed conformations at pH=7.4 [3]. It was also confirmed that variations in the zeta potentials could be described in terms of 3D elektrokinetic model using the effective cross-section areas of the molecule. These measurements revealed that fibrinogen adsorption on latex particles was irreversible. Results obtained in this work enabled one to develop an efficient procedure for preparing fibrinogen monolayers on latex particles having controlled conformation and coverages.

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Curli Expression Genes Influence on Spatial Distribution of Forces of Adhesion on the Cell Surfaces of *E. Coli*

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Bacterial adhesion is a complex process that concerns both the bacteria in question as well as the surface properties that bacteria adhere leading to the formation of complex 3D microbial structures known as biofilms. These properties of the surface allow the bacteria to adhere in two ways; primarily direct adhesion may occur to the surface via non-specific interactions; secondly through indirect binding to the surrounding materials adsorbed on the material. Certain forces are at large during the phases of attachment; for example, at the initial stages of biofilm formation, reversible adhesion is governed by weak van der Waals forces, with molecules approaching the surface through Brownian motion forming a conditioning layer. Maturation can only take place with further attachment in regards to the conditioning film, whereby the bacteria uses, depending of the species, nanofibres such as pili and curli or produce exopolymeric substances and bridges the cell to the surface irreversibly [1].

Two strains of *Escherichia coli*, a well known and widely studied bacterium, were used MG1655, its corresponding *ompR234* mutant and *E. coli* MG1655 containing a plasmid expressing *csgD*. *ompR* gene regulates the production of the *csgD* gene which itself is responsible for the expression of curli upon attachment. Curli are similar to pili and flagella of a number of bacteria and act as anchoring systems to allow adhesion at the interface. Moreover, PHL628 has an *ompR* mutation, known as *ompR234,* which governs the over-expression of the *omp* gene; hence, as a direct consequence, the *csgD* gene is also over-expressed resulting in curli overexpression; *E. coli csgD* overexpressed curli directly [2].

It was observed that the adhesion forces for all cell lines (MG1655, MG1655 *csgD* and PHL628) were normally distributed with standard deviation about a tenth of the mean. Furthermore, PHL628 and MG1655 *csgD* demonstrated higher forces of adhesion at around with a mean of 27nN compared to MG1655 which gave a mean adhesion force of around 4nN.

These results quantify for the first time the increase in forces of adhesion resulting from curli expression and demonstrate that the same outcome is achieved when *csgD* is directly expressed or it is overexpressed as consequence of the increased expression of its regulatory gene *ompR*. Therefore, the mechanism of enhanced adhesion appeared covered by physical-chemical phenomena due to the composition of the curli and not by mechanical trapping of the cell.

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Evaluation of Therapeutic Pulmonary Surfactant Preparations by Thin Liquid Films

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Exogenous surfactant substitution represents the standard therapy of respiratory distress syndrome (RDS). Naturally derived surfactants are most often used clinically and consist mainly of lipid extracts from bovine or porcine lungs with a varying amount of lipophilic surfactant proteins. Commercially available surfactant preparations have been investigated repeatedly with regard to their in vitro properties, and conclusions have been drawn from these in vitro data to their in vivo physiologic effects. These in vitro properties are usually assessed with reference to static surface adsorption and dynamic changes in surface tension during cyclic film compression. The results for behaviour and properties of thin liquid films from pulmonary surfactant or its components, represent these films as an adequate structure-functional experimental model. The horizontal microscopic black foam film (BFF), formed under the ambient conditions of the lung alveoli (capillary pressure, film radius, electrolyte concentration, and etc.) are used to characterize the therapeutic exogenous surfactants (TES). The purpose is to carry out an evaluation of the four widely used preparations: Curosur, Infasurf, Survanta and Alveofact by black foam film method. The effect of TES composition on black film properties by means of experimental measurements of the probability (W) for black film formation versus surfactant concentration (CS), thickness (h) of the obtained films as a function of electrolyte concentration and direct measurements of disjoining pressure/film thickness isotherms ($\Pi(h)$) was investigated. The introduced parameters from BFF method, reflecting surface behaviour of the preparations at air/water interface, can be used in the process of TES manufacture to verify and improve the quality as well as in the development of a new generation of fully synthetic exogenous surfactant.

Kinetics of reorganization of lipid nanocapsules at model membrane monolayers

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The lipid nanocapsules (LNCs) spread at air-water interface (A-W) interface undergo a destabilization and disaggregation leading to the formation of triglyceride (TG) surface film. The kinetics of the reorganization and formation of TG surface film was followed by measuring the change of the surface pressure at constant area and the surface area at constant surface pressure. From the experimental data the effectiveness of TG spreading and the rate of LNC disaggregation at A-W interface covered with preformed model membrane monolayers of DPPC, Curosurf and mucus were determined. A partial LNC stabilization due to their interaction with the model membrane monolayers was observed and characterized by atomic force microscopy. The obtained results show that the LNCs spread on mucus surface layer (model of the epithelial surface) are more stable than on DPPC and Curosurf surface layer (model of the alveolar surface).

Complex Structures of “Sand” and “Chalk”

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In recent years, bio-inspired materials have aroused a great deal of interest due to their promising properties and potential relevance for various applications. Thereby, many studies were carried out in order to elucidate the influence of certain organic (macro)molecules and/or supramolecular matrices, as typically found in biomineralization processes, on the crystallization of naturally abundant minerals. By contrast, our current research is dedicated to explore such effects in purely inorganic environments, namely by using dissolved silica as an additive during mineralization of alkaline-earth carbonates. Under suitable conditions, these simple components can assemble into fascinating architectures, termed “silica biomorphs”, which display morphologies and structures very similar to those produced in biomineralization, such as periodically twisted filaments, flat sheets, or worm-like braids (see Fig. 1) [1-3]. Moreover, this methodology allows us to prepare elaborate core-shell-shell nanoparticles in a straightforward one-step process, by slightly changing precipitation parameters (Fig. 2) [4]. The formed particles were investigated in detail with HR-TEM and micro-EDX, in order to reveal compositional details.

On the other hand, silica-mediated self-organization mechanisms can also be observed in the absence of carbonate, simply by adding soluble metal salt crystals to alkaline silica sols. The resulting “silica gardens” also show stunning structures reminiscent of living forms such as trees or aquatic plants. Recently, we developed an experimental setup by which we could trace the evolution of relevant species in situ during growth of silica gardens prepared with iron- or cobalt salts [5]. Recently, we have extended this approach to study chemical gardens prepared with calcium salts (Fig. 3), as the mechanisms occurring in this system are very similar to those underlying Portland cement hydration. Therefore, calcium-based chemical gardens might serve as model system for detailed analysis of the temporal evolution of dissolution and precipitation processes that occur in the inside of the C-S-H membrane. To characterize these processes, we utilized scanning electron microscopy (SEM) in combination with EDX to investigate structural and compositional details of the formed structures as a function of time.

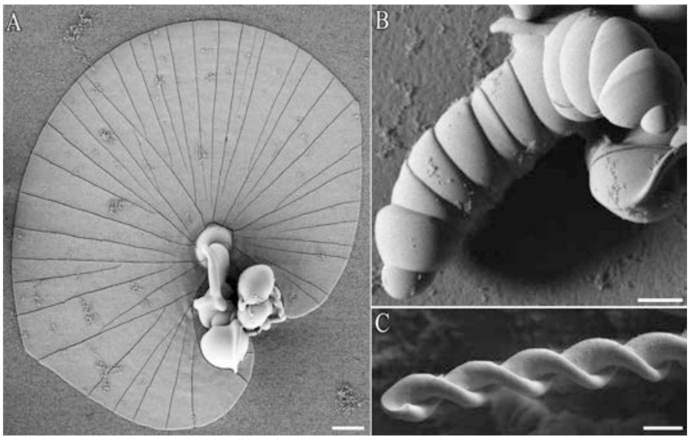

Fig. 1. Overview of typical morphologies displayed by silica biomorphs: (A) Flat sheet-like objects, (B) worm-like braids, and (C) complex helical filaments. Scale bar is 20 µm.

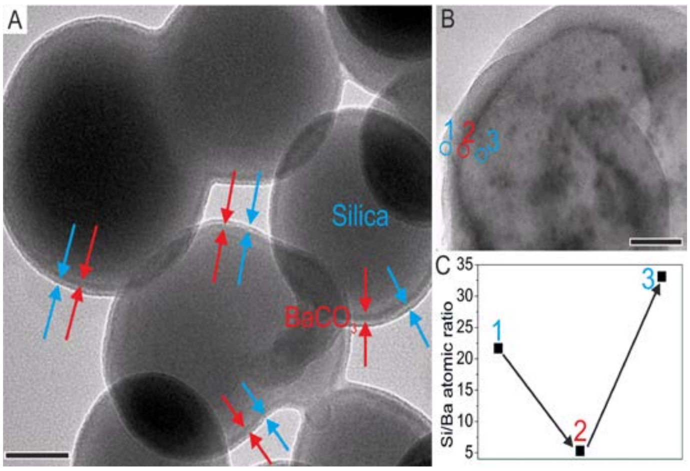

Fig. 2. (A-B) Bright field TEM images of core shell-shell particles formed by increasing both, the carbonate and silica supersaturation. Red and blue arrows in (A) mark the interstitial BaCO$_3$ layer and the outer silica skin, respectively (scale bars are 40 nm). (C) Si/Ba atomic ratios calculated from three selected points (as defined by circles in (B)) along an EDX line-scan analysis over the rim of the composite particles. The arrows shall be a guide for the eye.[4]

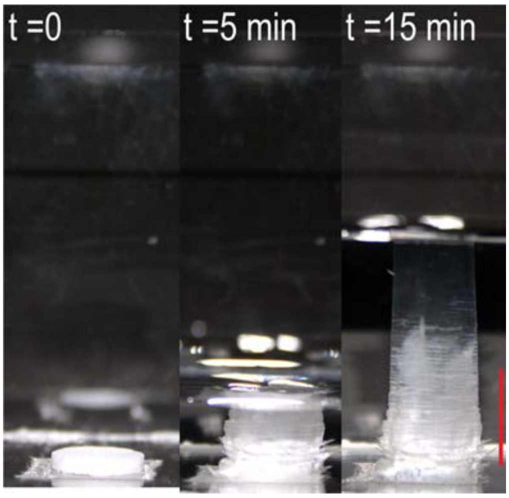

Fig. 3. Sequence of photographs illustrating the formation of a tubular membrane with defined dimensions upon addition of diluted silica solution to a tablet of CaCl$_2$. Scalebar is 10 mm.

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Extraction of Protein with Reverse Micelles Formed by Gemini Surfactant

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Reverse micelles have great potential for the separation, concentration and purification of bioactive proteins, including enzymes. Some of the advantages of reverse micellar extraction are no loss of native function/activity, high capacity, ease of scale-up, and potential for continuous operation. In the liquid–liquid reverse micellar extraction process, a target protein is selectively solubilised into the organic phase (forward extraction) and subsequently stripped into the aqueous phase (backward extraction) by the addition of fresh aqueous buffer. It should be noted that the surfactants used in protein extraction so far have been almost exclusively AOT and CTAB; as far as we know, there have been just a couple of reports where other surfactants were used, and research about the effect of surfactant structure (for example, the hydrophobic chain length, the size and structure of head group) on protein extraction efficiency has been limited. Therefore, to study whether and/or how the surfactant structure affects protein extraction efficiency should be meaningful for liquid–liquid reverse micellar extraction process. In the present paper, we extract ovalbumin (OVA) with gemini surfactant reverse micelles. We found that less amount of gemini surfactant than monomeric surfactant was needed for transferring almost complete protein into organic phase from aqueous phase. Moreover, OVA can go into gemini surfactant reverse micelles without inorganic salt, while an adequate amount of inorganic salt was essential for OVA extracted into single-chained reversed micelles. The maximum backward extraction efficiencies were above 80 % with $C_{12}C_5C_{12}$, $C_{16}C_5C_{16}$ and $C_{16}C_8C_{16}$ reverse micelles and ca. 70 % with $C_{12}C_2C_{12}$ reverse micelles. However, the backward extraction efficiencies of OVA with $C_{12}C_8C_{12}$ and $C_{12}C_{12}C_{12}$ reverse micelles were very low. CD spectra illustrated that the secondary structure of the extracted OVA was remained with $C_{12}C_5C_{12,}$ $C_{16}C_5C_{16}$ and $C_{16}C_8C_{16}$ reverse micelles. So far, the reports about the effect of surfactant structure on protein extraction have been limited. This study indicates the important role of the spacer of gemini surfactant in protein extraction process and may provide more knowledge on how to optimise surfactant structure.

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Acknowledgements:

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Development of Chitosan Derivative Carrier for Insulin Oral Delivery

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Insulin is a pharmaceutical peptide for treating diabetes. Because its regular injection gives mental and physical burdens to patients, development of oral administration technology for insulin has been expected. However, it has not been achieved yet due to its low chemical stability and low membrane permeability in gastrointestinal tract. Our research is aiming development of a carrier which improves the stability and membrane permeability of insulin.

β-Cyclodextrin-grafted chitosan (BCC, Fig. 1), which had chitosan main chain and cyclodextrin side chains, was synthesized as a carrier by four steps. Insulin made complexes with BCC or chitosan in acetate, citrate and phosphate buffer solution. Binding efficiency of BCC with insulin was higher than that of chitosan. ^{1}H-NMR and fluorescent measurements revealed that tyrosine residues were responsible for the electrostatic interaction between BCC and insulin, while both tyrosine and phenylalanine residues seemed to interact with the CyD side chains via hydrophobic interaction. The fluorescence study indicated that binding constant between CyD side chains in BCC and insulin was much stronger than molecular CyD due to multivalent interaction comprised of electrostatic and hydrophobic interactions. Complexes formed by insulin and BCC were visualized by optical and transmission electron microscopes. In the presence of insulin, BCC particles aggregated in citrate and phosphate buffer solution. On the other hand, in acetate buffer solution, the network structure formed by BCC and insulin was observed. These results indicated complexes between BCC and insulin were affected by buffer species. Stabilization effect of carriers was evaluated in acetate buffer solution contained pepsin. By adding BCC or chitosan, insulin was stabilized against the digestive enzyme (Fig. 2), and the stabilization effect corresponded well with the binding efficiency. It indicated the insulin was protected from the enzyme by making complexes with BCC or chitosan.

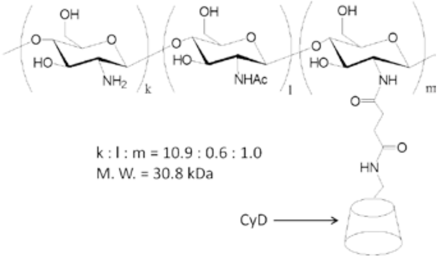

Fig. 1 Structure of BCC

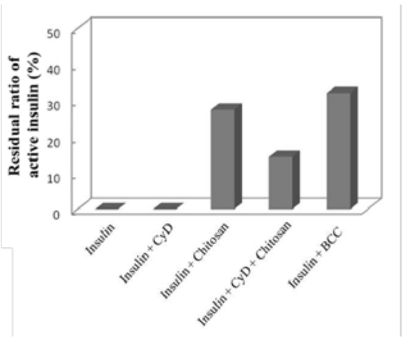

Fig. 2 Residual insulin after adding the pepsin solution

In summary, it is expected that BCC improves the insulin stability in gastrointestinal tract. Because the interaction between the carrier and insulin was not governed by the non-specific interactions, BCC may be used for various peptides.

Mechanism of Cholesterol and Saturated Fatty Acids Lowering by Quillaja Saponaria Extract, Studied by in-Vitro Digestion Model

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High concentration of cholesterol in the blood is a risk factor for the development of life-threatening cardiovascular diseases. It can be caused by the ingestion of foods rich in cholesterol and saturated fatty acids (SFA). As cholesterol and SFA are insoluble in water, they must be solubilized in order to be absorbed in the gastro-intestinal tract. In-vivo, this is accomplished by the so called “bile micelles”, which are colloidal aggregates of bile salts (biosurfactants with steroidal structure) and phospholipids.

Clinical study in humans [1] showed that saponin-containing extract of Quillaja saponaria can decrease blood cholesterol. However, the mechanism behind this effect is unclear. Two mechanisms are suggested in the literature: formation of large (100-1000 kDa) bile salts:saponin aggregates, or precipitation of cholesterol.

In the current study, we investigate the effect of the non-purified saponin extract Quillaja Dry (QD) on the solubilization of cholesterol and SFA in the bile micelles, during in-vitro digestion of cocoa butter emulsions. To quantify the cholesterol and SFA solubilization, we separated the aqueous phase by filtration and analysed it by gas chromatography. The concentration of bile salts in the aqueous phase was determined by high-pressure liquid chromatography (HPLC). We found that QD decreases significantly cholesterol and SFA solubilization, Figure 1. Centrifugation experiments showed that the latter are precipitated. In contrast, QD has no effect on the concentration of bile salts in the aqueous phase. In conclusion, the decrease of blood cholesterol by Quillaja saponaria extract is due to decreased intestinal solubilization of cholesterol and SFA, while the bile micelles are not affected by QD.

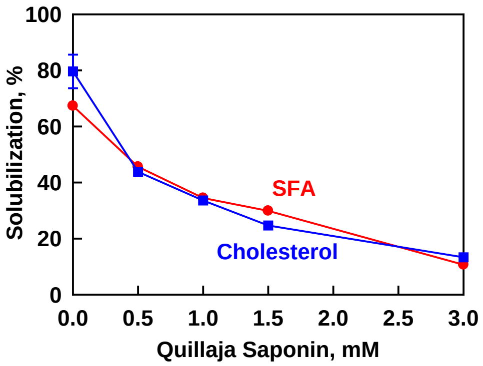

Figure 1. Percentage of solubilized cholesterol (blue squares) and SFA (red circles) in the aqueous phase, as a function of Quillaja saponin concentration, obtained after in-vitro digestion of emulsion of cocoa butter (with added cholesterol).

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Lung and Tear Surfactant Films: A Surface Chemistry Approach

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Lung and tear surfactants form films at the air/water interface at the pulmonary and ocular surface. The surfactants dysfunction results in the pathologies of respiratory distress syndrome and dry eye syndrome respectively. Both surfactants share common tasks: to lower the surface tension of the physiological surfaces; to assure stable film during compression/decompression cycling; to allow air diffusivity etc.

In our research we utilize model membranes and develop surface chemistry approach to understand the composition/structure/function relationship of the two surfactants.

The lung surfactant studies were performed at one isolated (planar and spherical monolayers) and two interacting air/water interfaces (foam films) respectively. The foam film model allows to combine original quantitative parameters with direct observation of film structure. Variety of lung surfactants were examined: from the natural tracheal and gastral aspirates to the clinically used exogenous preparations Exosurf, Survanta, Alveofact and Curosurf. Insights were obtained in the adsorption, surface structure and function of the lung surfactant films. The capability of plasma proteins to inhibite surfactant functions and of some hydrophilic polymers to recover the surfactant activity was evaluated. The specific action of the hydrophilic polymers to exogenous preparations is demonstrated.

The tear surfactant films were studied by Langmuir surface balance and Brewster angle microscopy. The studies revealed that tear lipids form continuous viscoelastic multilayer at the air/tear surface, capable to rapidly reorganize at blinking and to efficiently suppress the evaporation of tear fluid. Hydrophilic surface active molecules impair the integrity and properties of tear film. In contrast pharmaceutical agents well miscible with the lipid layer or capable to form hydrogen bonds with the polar lipid headgroups improved the spreading and the surface properties of the tear surfactant films.

PEG/Surfacted Magnetite Core-Shell Nanoparticles for Biomedical Application

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Aqueous dispersions of magnetic nanoparticles (MNPs) designed for diagnostic or therapeutic applications are in the focus of scientific interest last decades. A protective layer is needed to prevent the aggregation of uncoated particles, to stabilize the dispersion and hinder the chemical and biological degradation of nanomagnets [1]. Recently the pegilation, i.e. the covering nanoparticles by polyethylene glycol (PEG) (called also as polyethylene oxide (PEO)), is the most favoured way to ensure their biocompatibility [2].

Based on our former experiences PEG molecules do not adsorb directly on the nanoparticle's surface, so the main goal of this paper is to prepare designed multi-layered core-shell magnetite nanoparticles in aqueous medium, which are stable under physiological conditions (in blood e.g. pH~7.4, 0.15 M NaCl) as well. First a surfacted shell, i.e. a double layer of oleic acid (OA) or oleate (OL) was built up on the nanomagnets' surface on two pathways, and then a PEG top coating was realized using PEO polymers with different molecular weights. The pegilated nanomagnets were characterized at different pHs (2-11) and at various PEG loadings (0-360 mmol EO/g magnetite) by dynamic light scattering (DLS) and electrophoresis measurements; the adsorption mechanism was studied by infrared spectroscopy (ATR FT-IR). The correct characterization of colloidal stability, i.e., the quantification of salt tolerance was performed at neutral pHs by DLS.

Comparing the two groups of PEG/surfacted magnetite nanoparticles, significant difference in the adsorption mechanism of the first OA or OL layer on nanomagnets was found using AT-FTIR measurements. However, the aqueous dispersions of magnetite nanoparticles modified by oleic acid/oleate double layer and PEG show similar colloidal behaviour studied by DLS and electrophoresis. Indirect evidence was obtained for PEG adsorption on the surfacted nanomagnets from the electrophoresis measurements and the IR spectra. PEG coating screens the negative charges around the particles and its macromolecular character leads to the nanomagnet's steric stabilization. Determining the free amount of oleate by tensiometric measurements, we found that the decrease in pH or addition of PEG at 5 mmol EO/g MNP loading influences the amount of oleate remaining on the surface. Magnetic relaxation measurements were performed to test some pegilated MNPs as possible contrast agents in MRI. Enhanced r_2 relaxation characteristics were experienced for PEG/surfacted magnetic nanoparticles at magnetic field strength of 1.5 T. In addition, hematology tests demonstrate that the pegilated MNPs with enhanced biocompatibility have strong theranostic potential in future.

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An Examination of the Formation and Stability of Programmed Biodegradable Polyplexes

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Nonviral gene delivery systems have become a safer and cheaper alternative to traditional viral vectors in gene therapy. However, some optimization is required before their use in clinical applications. Thorough physicochemical studies are needed to develop a most advantageous gene vector.

In this work, a choice of positively charged poly(β-amino esters) has been used to condense plasmid DNA. These biodegradable polymers undergo hydrolysis at physiological conditions, yielding shorter chains that could be more easily metabolized by cells thus reducing the toxicity. Additional functionalization with redox-sensitive linkers allows the carrier to release its cargo in a controlled manner, owing to the fact that disulfide bonds remain intact in the oxidizing extracellular space, while they break in the reducing intracellular environment.

The properties of the formed complexes, and consequently their biological usefulness, are affected by (a) polyplex-related factors such as polymer architecture, molar ratio, hydrophobicity, etc. and (b) bulk-related factors such as pH, salinity, dilution, etc.

We have analyzed a broad range of those variables and their influence in the formation of the so-called *polyplexes* and their subsequent stability. Our results show that particles with similar size and zeta potential, which are almost the only physical properties commonly studied in this field, present remarkable differences in their formation, structure and stability.

This means that a detailed understanding of the relevance and strength of the forces involved in the formation of DNA-polymer complexes and the interaction potentials controlling their stability is necessary and it might help to find a viable chemical alternative to viral transfection.

General Anaesthesia: Membrane Interaction & Pressure Reversal

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General anaesthetics (GAs) are widely used in medicine, however the precise mechanism of their action is still poorly understood. The ubiquity of the GA effect and the chemical diversity of the molecules that can lead to it (such as high pressure nitrogen and the generally unreactive halothanes) seem to suggest that the process must spring from a structural rather than a specific pharmacological antagonism effect. In a series of ground-breaking experiments in 1950, Johnson and Flagler were able to show that anaesthesia in tadpoles by 2-5% ethanol was reversed at a pressure of about 130 atm.[1] This has been demonstrated further in a number of other studies, all of which identify pressure reversal as a defining feature of the general anaesthesia process.[2] [3] [4]

However, the structural interaction of GAs with the membrane and the mechanism by which reversal occurs is still poorly understood. Here we present a detailed structural study using neutron reflection from model floating lipid bilayers to identify both the position of GAs and the resultant effect on the membranes. This is combined with molecular dynamics (MD) simulations[5] and reflectivity and microscopy from Langmuir monolayers to investigate the inclusion and exclusion of GAs through increasing surface pressure. The results offer new insight into the contribution of lipids in pressure reversal, independent of protein interactions, and present a new opportunity for studying complex biophysical systems via this multi-scale approach.

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Functional Coordination Polymer Nanoparticles for Theranostics Applications

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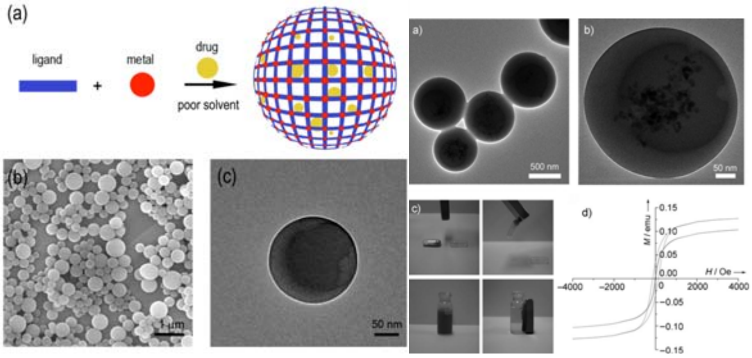
Many different materials have been used as matrices for drug delivery systems such as liposomes, cyclodextrins, chitosan, organic polymeric particles, dendrimers and carbon- or silicate-based hollow spheres. More recently, the development of nanoscale drug delivery metal-organic systems has also attracted great attention. The successful design of drugs adsorbed in porous metal-organic frameworks (NMOFs) and the good control on their release have opened an interesting research field in which metal-organic nanostructures can afford novel and revolutionary drug delivery systems whose design can be tailored at will by means of chemical synthesis.

Alternatively, our research group has developed the synthesis of coordination polymer nanoparticles [1] able to encapsulate a wide variety of substances and materials.[2] It has been proved that these amorphous nanostructures show the ability to encapsulate different drugs (doxorubicin (DOX), SN-38, camptothecin and daunomycin) while exhibiting drug release rates and notable in vitro citotoxicity effects.[3] In addition to drugs, the efficiency of the encapsulation process in metal–organic spheres allows for the simultaneous encapsulation of magnetic iron oxide particles (10 nm diameter). This represents the first example of a new family of coordination-based nanoparticles that may as magnetic nanocontainers for imaging applications and controlled drug release systems.



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Structure of Peptide-polymer Conjugates in Solution Studied by Small-angle X-ray Scattering: Polymer Conformation

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Hybrid biomaterials based on synthetic (polymer) and biological (proteins, peptides) building blocks, called protein-polymer conjugates, provide a wide range of opportunities for man-made materials to interface with biological system at the molecular level [1,2]. Encoded by the amino acid sequence, protein/peptide form rich intricate structures characterized by a high degree of order where local (secondary) structures (alpha-helices, beta sheets) self-assemble into tertiary structures such as coiled-coil bundles or beta-barrels in a hierarchical manner. For therapeutics, polymer functionalization, often by poly(ethylene glycol), PEG ("PEGylation"), is an effective method to improve the solubility, increase the life time and protect the proteins from the immune system[3]. However for such an approach, it is essential that the proteins maintain their structural integrity in solution- thus the role of the polymer and their interactions with proteins needs to be understood. In order to do so, characterization methods capable of assessing the structural details *in situ* on the nanoscale are needed. In this work we show how small-angle X-ray scattering (SAXS) can be used as a powerful technique to characterize detailed features in peptide-polymer conjugate systems in solution [4,5]. We specifically show that by applying geometrical modelling of the scattering data; very detailed structural features can be revealed, including the chain conformation of the polymers. In the presentation we will provide an overview of the methodology, specifically addressing model peptides that self-assemble into tertiary structures and relate their structure in solution to their crystallographic structure. Particular attention will be given to the effect of PEG and the modification of polymer conformation when attached to the peptides. We will also discuss modified peptides that form micellar structures.

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Organization and Compartmentalization of All-Aqueous Two-Phase Systems

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Aqueous two-phase systems (ATPS) consist of two immiscible (or partially) aqueous solutions, which display a relatively low interfacial tension, typically of the order of 0.1 mN/m. The combination of an all-aqueous environment and the low interfacial tension makes these systems a medium of choice for biomolecules, such as proteins and enzymes as well as living cells, since ATPS provide the mild conditions that do not denature or destabilize these biomaterials. Our research focuses on the structuration and compartmentalization of micro-emulsions based on ATPS. Different approaches have been envisioned, it encompasses production and stabilization via microfluidics of core-shell particles for delivery of biomolecules, patterning of substrates with ATPS for, for instance, growth of living cells on specific support, and the use of surfactants to organize micro-emulsions which can be further cross-linked to maintain the structure. Our strategy mostly relies on the use in-situ of photo-initiated polymers incorporated to ATPS.

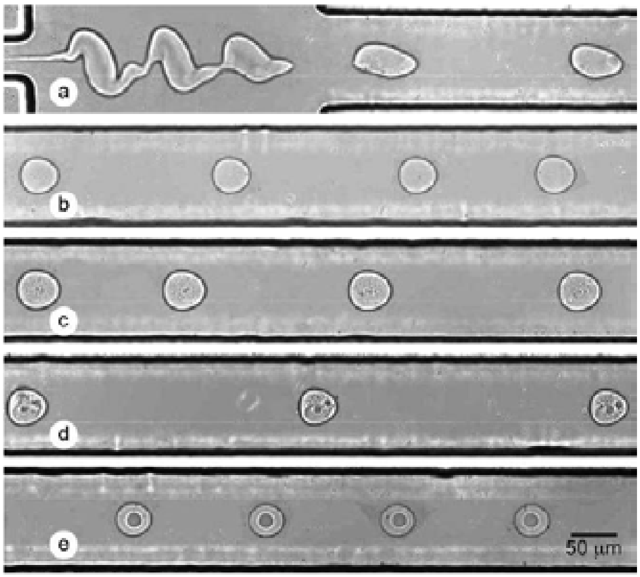

Fig. 1 Production and phase separation of core-shell emulsions made out of ATPS via microfluidics. Drops contain a solution of PEG and dextran that phase separates while the drops flow through the channel resulting in drops with a core of PEG and a shell of dextran. a) 0 mm, b) 0.5 cm, c) 2 cm, d) 3 cm, e) 4 cm from the drop maker.

Green bio-synthesis of Silver and Gold Nanopartciles Using Fungi

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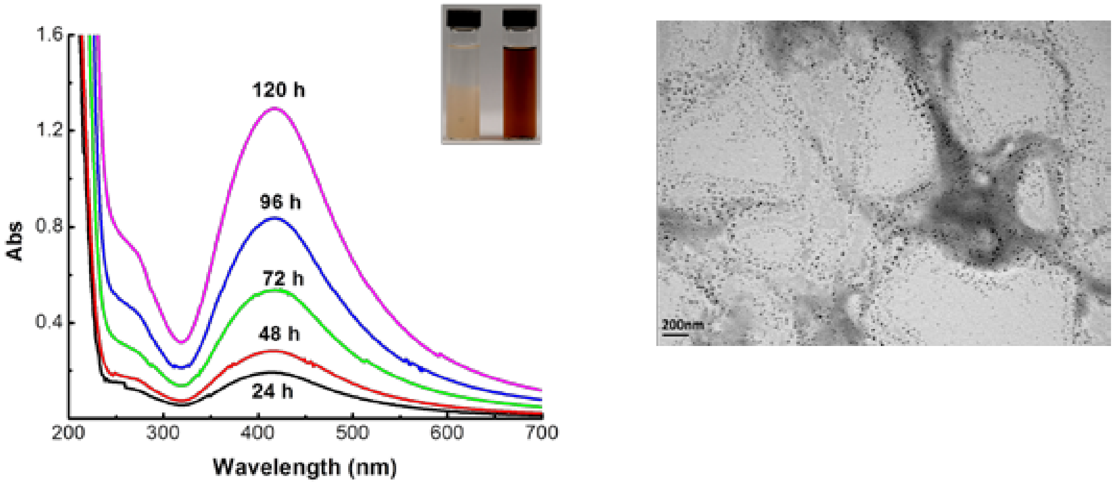
Colloidal nanoparticles, NPs, of Ag and Au are recognized for their electrocatalytic and medical applications. Performance of NPs is critically size/shape- dependent, hence, controlling factors that affect nucleation and growth of NPs is a challenge. Various techniques were developed to synthesize nanomaterials in which hazardous and pollutant organic passivators are used. Currently, synthetic approach based on natural biological systems provides a benign green alternative as many bio-organisms are known to produce inorganic materials and secrete proteins that serve as natural capping agents against NPs aggregation. In this work Ag and Au NPs were synthesized using two fungi (***Trichoderma harzianum*** and ***Ulocladium chartarum***) that were isolated from local soils of different areas in Kuwait and the physical/chemical bulk and surface properties of the NPs were extensively characterized using XRD, XPS, UV/Vis, and TEM. The results demonstrated the possibilty of using natural biological systems of Kuwait as green nanofactories for crystalline NPs production.



(a) (b)

Fig. 1. (a) UV-Vis Absorption spectra of 10^{-3} M solutions of Ag precursor (inset shows Ag suspension sample). (b) TEM images of greenly-synthesized Ag nanoparticles.

Acknowledgements:

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Parallel Adsorption of Colloid Particles and Proteins on mica

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Adsorption of bimodal colloid mixture on solid surface was studied experimentally and theoretically. In our experiments, the suspensions composed of two sized monodisperse latex particles mixed at two bulk concentration ratios were used. Furthermore, the preliminary studies on the parallel adsorption human serum albumin (HSA) and fibrinogen from aqueous solutions on mica were presented. The bulk particle properties were determined by dynamic light scattering (DLS) and electrophoresis. The hydrodynamic diameters of latexes, determined via the diffusion coefficients measurements, were equal to 774 (referred to as larger particles) and 145 nm (referred to as smaller ones), independently of ionic strength and pH. The electrophoretic mobility (*m*) increased from 4.5 to 5.7 [mmcm/Vs] for larger particles and from 3.3 to 4.1 [mmcm/Vs] for smaller ones, when the ionic strength varied between 10^{-4}- 10^{-2} M. On the other hand, *m*of smaller microspheres was fairly independent of pH, assuming almost constant value equal to 3.3 [mmcm/Vs]. However the electrophoretic mobility of larger particles decreased with pH, varying between 5.8 [mmcm/Vs] for pH 3, and 3 [mmcm/Vs] for pH 11. The deposition processes of suspensions composed of bimodal particles as well as HSA and fibrinogen were studied *ex situ* by using AFM and SEM techniques. The coverages of microspheres and proteins were determined by direct enumeration of particles. The theoretical analysis of these phenomena was carried out using the random sequential adsorption (RSA) model. It was concluded that small particles or proteins present in trace amounts may significantly reduce adsorption rates of larger ones.

Acknowledgements:

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Janus Particles for Tunable Autonomous Propulsion

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As atoms and molecules can be found in different electronic or vibrational states and macro-scale bulk materials can react to external stimulus, Janus microparticles offer a meso-scale ability to perform as multifunctional individual systems. These systems have gained an increasing attention in recent years due to their unique features originating from the symmetry break and used for new forms of self-assembly, sensing probes, switches and auto-propelled motors. Recently, we introduced a new method to synthesize Janus particles[1]. In this method SiO_2 microparticles are embedded in Parafilm, leaving the upper and unprotected hemisphere exposed to chemical reactions. Janus SiO_2-Ag particles are formed after Ag is reduced onto the exposed surface. The released Janus particles are then used for auto propulsion, exploiting the catalytic nature of the Ag.

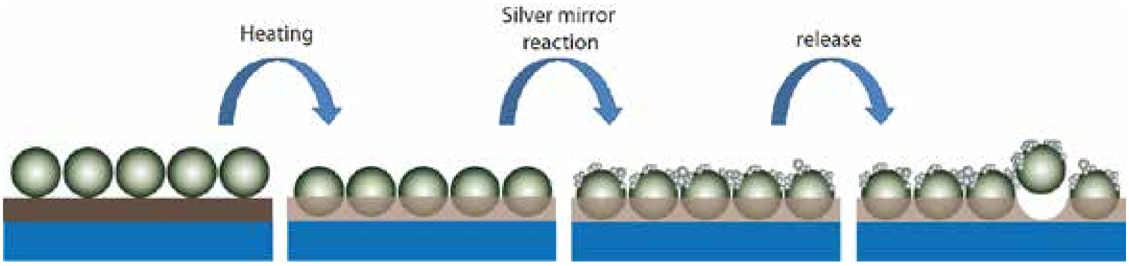

Figure 1. Janus particles synthesis via embedding in Parafilm.

Ag serves as a catalytic substrate for splitting hydrogen peroxide into water and oxygen. This reaction is being exploited to propel individual particles, acting as independent motors on the micro scale. The bubble on each particle is formed on the silver coated side and is growing bigger until buoyancy lifts the particle from the surface and promotes floating. Transition from 2D to 3D motion can be further manipulated by tuning the hydrophilic-hydrophobic interactions between the individual motors and the substrate on which they are positioned.

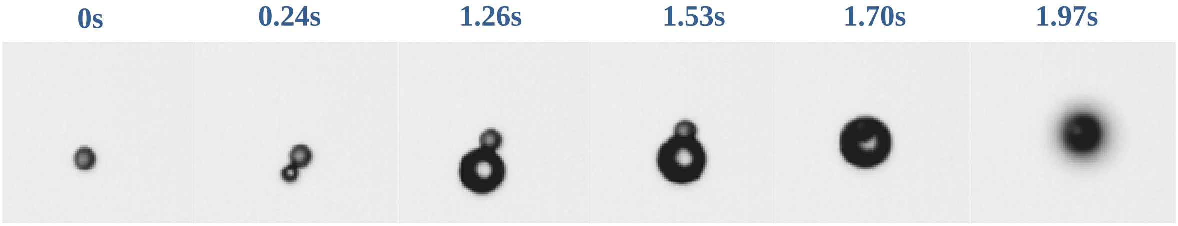

Figure 2. An auto propelled Janus SiO_2-Ag particle upon addition of H_2O_2. An oxygen bubble is formed on the Ag coated side and is expanding with time, until the particle starts to float. Exact times are indicated above each image.

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Removal of Metals From Aqueous Solution Using Functionalized Magnetic Nanoparticles

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The use of magnetic nanoparticles as a support material has drawn increased interest due to their rapidly and easy separation ability and recovery from the reaction medium using external magnetic field. A previous treatment of a silylating agent, containing the required functional groups is a method for the purpose of pendant organic chains covalently bonded to the support material. By applying such methodology the magnetic nanoparticles are progressively used in many activities such as biotechnology [1], cation removal [2], adsorption of organic compounds [3] and etc. Thioglycolic acid molecule embraces two basic centers, oxygen and sulfur, and can easily be grafted on Fe_3O_4 particle surface previously modified with the precursor silylating agent. Modification with thioglycolic acid gives to the nanoparticle, the ability to form stable complexes with several metals. In this study, thioglycolic acid was immobilized onto Fe_3O_4 nanoparticle surface using 3-aminopropyltriethoxysilane (APTES) as precursor silylating agent. This new surface displayed a chelating moiety containing nitrogen, sulfur, and oxygen basic centers which are potentially capable of extracting cations from water solution. Experimental conditions for effective sorption of metal ions were optimized with respect to different experimental parameters using batch method in detail.

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Synthesis, Characterization and Photocatalytic Activity of Pure and Mn Doped ZnO Nanowires

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The photodegradation of organic pollutants in air or aqueous medium, catalyzed by various semiconductors, is a promising remediation technology especially at lower concentration of the pollutant. Among the various semiconductors used, ZnO has been recognized as one of the attractive materials for its biological and chemical inertness, high catalytic efficiency, low cost and environmental sustainability. On the other hand, ZnO is used as a UV-blocker agent because it adsorbs light in the whole region of the UV-spectrum (UVA and UVB). Depending of the application, the photocatalytic properties of ZnO should be promoted or suppressed. This can be achieved by changing the particle size and/or by doping.

In the present study, the effect of manganese on the photocatalytic performance of ZnO is investigated. The ZnO and Mn/ZnO nanowires are prepared after annealing of zinc oxalate precursor, obtained via sol-gel method. The nominal ratio Zn:Mn in the doped sample is 99:1. The precursors and the obtained oxides are characterized by various methods: XRD, SEM-EDX, XPS and EPR. The photoluminescence and Uv-Vis spectra are recorded also and optical band gap is calculated.

The activity of ZnO and Mn/ZnO nanowires is tested in the reaction of photoassisted bleaching of the organic dye Malachite green (MG) under UV-light. The concentration of MG is determined by checking the absorbance at 616 nm using an UV–visible spectrophotometer. The degradation of MG follows the first order equation (Fig.1). From the slope of the curves the apparent rate constants are determined. The results show that doping with manganese quenches the UV-induced photocatalytic activity of ZnO nanowires. The photocatalytic tests to the degradation of MG under Vis-light are in progress.

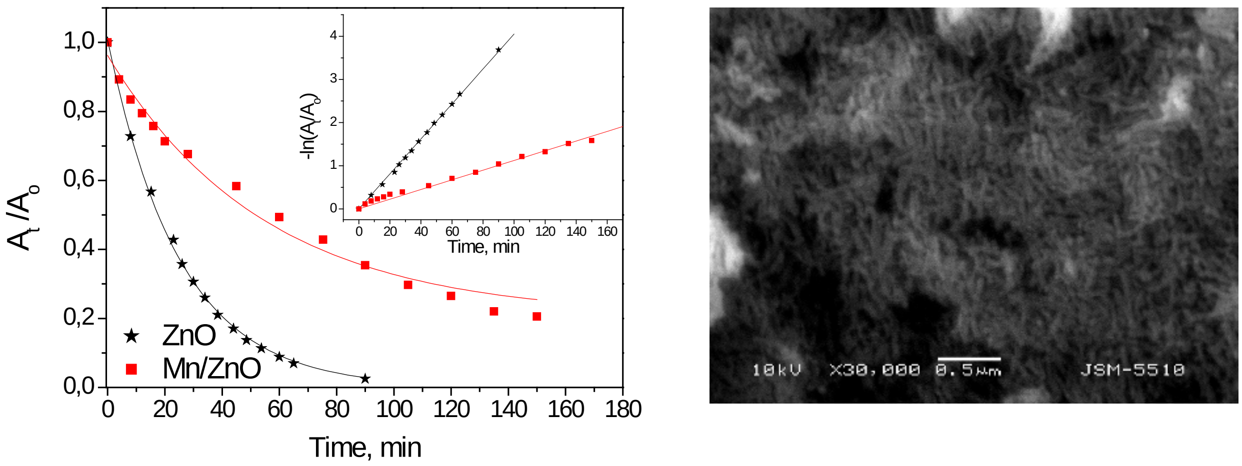

Fig. 1 Photobleaching of Malachite Green under UV-light (left);
SEM image of ZnO nanowires (right)

Iridescent Hollow Colloidosomes Prepared Using Accelerated Solvent Evaporation

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Colloidosomes are an important subgroup of microcapsules whose shells consist of coagulated or fused colloid particles. We demonstrate a new, scalable, simple and generally applicable two-step method to prepare hollow colloidosomes. Firstly, a high volume fraction oil-in-water emulsion was prepared. The oil phase consisted of CH_2Cl_2 containing a hydrophobic structural polymer, such as polycaprolactone (PCL) or polystyrene (PS), which was fed into the water phase. The water phase contained poly(vinylalcohol), poly(N-isopropylacrylamide) or a range of cationic graft copolymer surfactants. The emulsion was rotary evaporated to rapidly remove CH_2Cl_2. This caused precipitation of PCL or PS particles which became kinetically trapped at the periphery of the droplets and formed the shell of the hollow colloidosomes (Fig. 1(a)). Interestingly, the colloidosomes were iridescent (Fig. 1(b)). This implies a degree of nanostructuring of the particles that comprised the shells. The use of labelled particles and fluorescence microscopy revealed the shells had a thickness of about 1 μm (Fig. 1(c)). The colloidosome yield increased and the polydispersity decreased when the preparation scale was increased. One example colloidosome system consisted of PCL microcapsules stabilised by PVA. This system should have potential biomaterial applications due to the known biocompatibility of PCL and PVA.

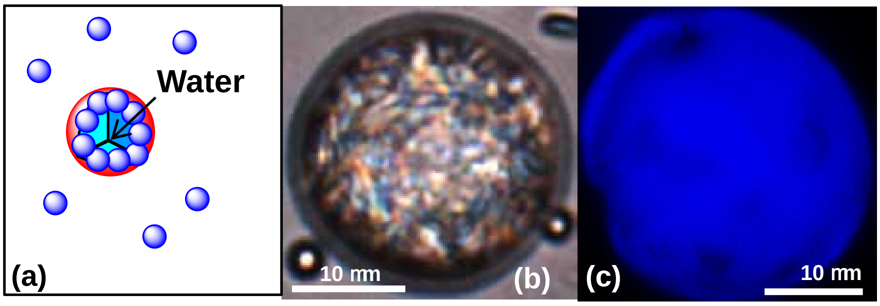

Fig. 1 Colloidsome structure (a), iridescence (b) and fluorescence micrograph (c).

Interaction and Organization of Boehmite Particles under Different Interaction Potentials

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Alumina obtained by the topotactic transformation of the aluminium oxyhydroxide called boehmite ($AlOOH \times nH_2O$) during calcination [1] is widely used as catalyst support for various refining processes. The textural and mechanical properties of alumina supports are closely related to the organization of boehmite nanoparticles dispersions which in turn depends on their concentrations, interactions and shear rates used in the shaping processes. The mesoporous volume, which is of interest for further catalytic applications, originates from the stacking of crystallites aggregates. Hence, changing the aggregation state should modify the porous volume [2].

The present work aims at understanding the interactions and organizations of boehmite particles in different aggregation states in diluted systems, and the evolution of these organizations at higher concentrations obtained by solvent extraction (centrifugation) up to the final calcined material. The correlation between rheological behavior, structure of the dispersion (SAXS/USAXS-DLS) and the textural and mechanical properties of the dried product is investigated. In order to vary the aggregation kinetic, the interaction potential is adjusted by dispersing boehmite particles in various solvents ranging from acidic water to less protic and polar alcohols. The viscosity increases as a function of the volume fraction, the birefringent behavior under shearing and its relaxation highlight the different nature of the dispersions according to the solvent. Thanks to SAXS/USAXS experiments, we discuss the case of acidic water where the potential is highly repulsive, allowing particles to repel from one another [3]. While in less protic and polar terbutanol, boehmite particles seem to quickly aggregate by diffusion in an open structure of typical fractal dimension 1.8 (DLCA mechanism) thanks to the strongly attractive potential. In intermediate aggregation state delivered by moderate protic and polar ethanol, particles would slowly collide forming a denser structure whose fractal dimension is 2.1 (RLCA mechanism) [4]. Those different aggregation kinetics lead to a more or less open fractal structure of aggregates. As a consequence of those particular microstructures in dispersion, the properties of the final alumina solids can be controlled on a wide range of porosity (from V_p= 0.3 ml/g to 1.5 ml/g and from D_p= 6 nm to 35 nm), highlighting the relation between organizations prevailing in the diluted suspensions and the textures existing in the final porous solids.

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Synthesis of Calcium Alginate Nanoparticles via A Nonionic Microemulsion-Based Route

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Calcium alginate beads with particle size less than 100 nm were obtained in water-in-oil microemulsions. The microemulsions were prepared using n-octane, mixtures of non-ionic surfactant Brij30 and triblock copolymer Pluronic L64, and aqueous solution. The nanoparticles were synthesized upon mixing two microemulsions containing sodium alginate and calcium chloride. These precursor microemulsions were characterised by dynamic light scattering (DLS) experiments, the resulting calcium alginate nanoparticles were visualised by atomic force microscopy(AFM) and insight into the alginate conformation in the water-in-oil microemulsion was obtained by Monte Carlo simulations. The light scattering data indicated that the size of water droplets could be tuned between 10 and 60 nm by varying the ratio of the two amphiphiles, L64/Brij30, and, at fixed L64/Brij30 ratio, the two calcium alginate precursors had different effects. No significant change in the water droplet size occurred upon calcium chloride addition, whereas, due to the strong confinement of the polymeric chain into the water domains, a modest droplet increase in the presence of sodium alginate was suggested. AFM micrographs of the isolated calcium alginate nanoparticles revealed a polydisperse population (**Fig. 1**) and hinted at the templating role of the water droplets. The computational studies implied that the radial density profile of the alginate in water droplet was not homogeneously and its conformation could not shrink by addition of the calcium chloride. In addition, the calcium binding was not a specific interaction as carboxyl, hydroxyl and ether oxygens could have all favourable positions for cations binding.

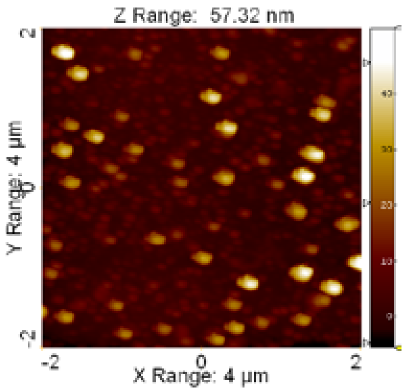

Fig. 1 AFM image of purified calcium alginate nanoparticles obtained in solute – n-octane – Brij30/L64 microemulsion.

Acknowledgements:

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PCL Based Degradable Structures: Nanogels and Nanogel/Polymer Composite Fibres

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Polycaprolactone is a well-known biocompatible and degradable polymer; therefore we believe it is interesting as a building block for different multifunctional structures. We prepared poly(*N*-vinylcaprolactam) (PVCL)nanogelscrosslinked by a star-shaped acrylate functionalised poly(ε-caprolactone) crosslinker via mini-emulsion polymerisation in the bulk material (we like to call “minibulk” emulsion). Thus, we achieved nanogels which are thermoresponsive, degradable and provide hydrophobic cavities for the uptake of substances like drugs or dyes. We were able to prove all these properties by experiments with dynamic light scattering, UV/Vis spectroscopy and electron microscopy.

Another approach is the one-step synthesis of hydrophilic modified nanogel/PCL composite fibres via electrospinning. Solutions of PCL in methanol/toluol mixtures as well as chloroform/dimethylformamide mixtures have been mixed with nanogels and spun into fibres of different morphologies. In these structures the PCL provides again the degradability; the PVCL nanogels provide the thermoresponsive behaviour as well as the modification of the hydrophilicity of the fibres. The latter as well as the degradability of these fibres can be tuned by the different fibre morphologies which we were able to achieve. We fabricated fibres with the nanogels only on the surface of the fibres or only in the interior. The thermoresponsive properties remain intact in the fibres, which can be proven by DSC measurements and both fibre types show a temperature dependant degree of swelling, as measured by TGA. Additional fibre properties have been studied by contact angle measurements, electron microscopy and dynamic light scattering, which can show the release of the nanogels into the surrounding media during the degradation. We believe that both structures can be very interesting for medical (drug release) or textile applications.

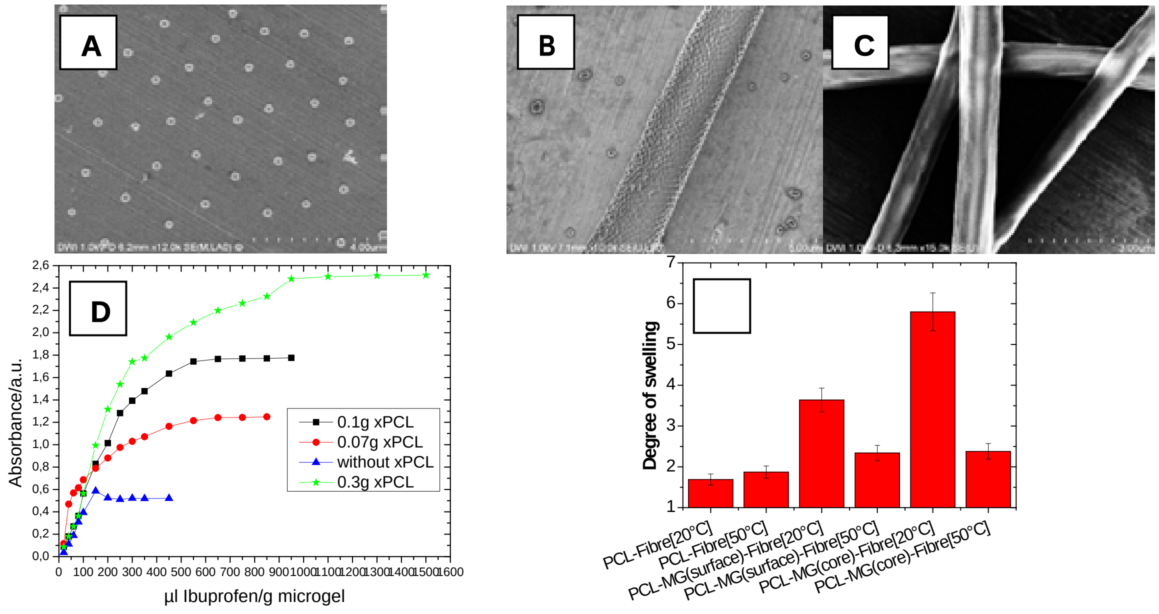

Fig. 1 Degradable nanogels by “minibulk” mini emulsion (A) and the uptake of Ibuprofen in the provided hydrophobic cavities (D); fibres spun from methanol/toluene (B) and chloroform/dimethylformamide (C) and their temperature dependant degree of swelling shown by TGA measurements (E).

NLC as a Potential Carrier System for Chemically Labile Active Compounds

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In the recent past, lipid nanoparticles have gained huge popularity as attractive carriers for the delivery of poorly soluble drugs. There are two types of lipid nanoparticles, solid lipid nanoparticles (SLN) and nanostructured lipid carriers (NLC). Both of them can be widely applied to deliver active ingredients through oral, parenteral and topical routes [1,2]. NLC were introduced to overcome the potential difficulties with SLN's structure. They are composed of the blend of solid and liquid lipids (oils) what cause a melting point depression compared to the pure solid lipid but the particles are still solid at room and body temperature. This results in significant differences in the particle matrix structure. NLC possess many imperfections which support to increase active loading capacity and decrease or avoid active substance expulsion during storage [3].

The aim of the study was to determine an optimal formulation, consist of biodegradable, physiological lipidic substances and stabilizers of GRAS status, as a potential carrier system for chemically labile compounds. Nanostructured lipid carriers (NLC), based on beeswax and caprilic/capric trigliceride mixture, were obtained by using hot high pressure homogenization technique. The influence of number of homogenization cycles on NLC properties was analyzed. Additionally, an effect of surfactant concentration (decyl glucoside) was studied. NLC particle size was characterized by means of dynamic light scattering (DLS) and optical microscopy. The systems stability was also assessed by light backscattering (Turbiscan Lab Expert) and macroscopic observation as well as by zeta potential measurements (Zetasizer Nano ZS). The most kinetically stabile formulations were obtained with 3 homogenization cycles, 4 % of surfactant concentration and particles diameters around 180 nm. These systems were selected for further experiments.

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Acknowledgements:

The research (work) was supported by the European Union through the European Social Fund within „Cracow University of Technology development program - top quality teaching for the prospective Polish engineers; University of the 21st century" project (contract no.UDA-POKL.04.01.01-00-029/10-00).

Structural Characteristics of Magnetic Nanowires: Effects of Polymer Type, Magnetic Field Strength and Charge Ratios

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Magnetic nanowires composed of polyelectrolytes and anionic maghemite nanoparticles were made by electrostatic desalting transition under magnetic field at two different magnetic field strengths. Three different polyelectrolytes, homopolymers PDADMAC(MW < 100,000) and PEI (MW 2000), and block copolymer of PTEA11K-b-PAM30K (MW 41,000), were used for the fabrication process using the same particles at the same particle concentration. For PDADMAC and PEI, two Z values are used, where Z defines the ratio of the charges on the particle divided by the charges on the polyelectrolyte. As the polyelectrolytes used are positively charged, Z=0.3 results in overall negatively charged nanowires and Z=7 gives positively charged nanowires.

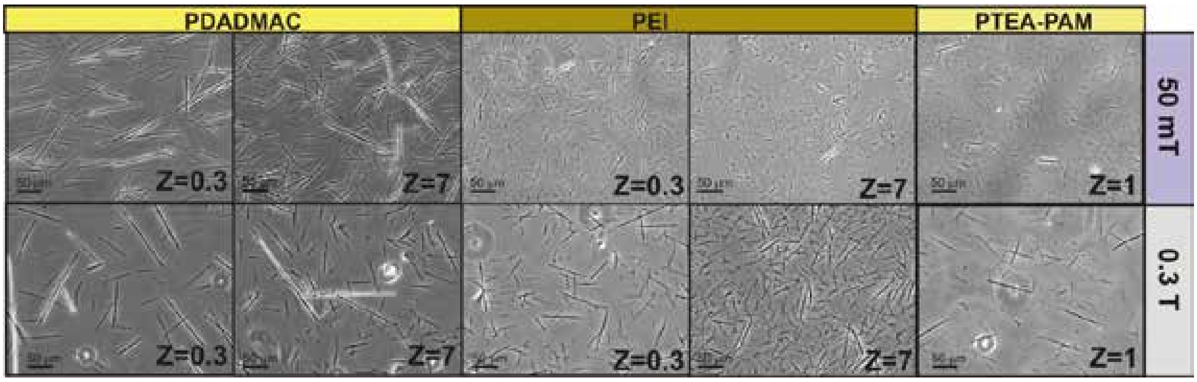

Fig. 1 Phase-contrast optical microscopy images (20×) of nanowires made from 8.3 nm □Fe$_2$O$_3$ particles using different polymers, at different charge ratios and at 50 mT and 0.3 T magnetic

It is observed that use of higher magnetic field strength for the synthesis results in longer nanowires. The effects of different Z values is less obvious, with PDADMAC showing longer nanowires for Z=0.3 at low magnetic field strength, while all others show a similar trend but less obvious. A more interesting finding was seen with the diameters of nanowires. Nanowires were observed to form "bundles", which were noticed to be different for different preparations. The diameter and length of the wires were measured by optical microscopy at higher magnification. The diameter does not necessarily imply the diameter of a single wire, but the total diameter of the bundles of nanowires. It was observed that nanowires made with PDADMAC and PEI were more readily forming bundles compared to the PTEA-PAM nanowires.

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Improved Mechanical Properties of Cement Nanohydrate/Polyelectrolyte Composite Material

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Due to its excellent mechanical strength and low cost, concrete is the most used building material in the world. However, its main drawback is its very low ductility.[1] The aim of project is to enhance the flexural strength of cement by increasing the cohesive force range between the nanoparticles of calcium silicate hydrates (C-S-H), i.e. the cementitious matrix, through the use of cationic polyelectrolytes.[2] The project consists of two complementary approaches, one numercial, based on molecular dynamics and Monte-Carlo simulations,[3] the other experimental, combining various characterizations techniques: adsorption isotherms, acoustophoresis, rheometry, atomic force microscopy and synchrotron U-SAXS.

The polyelectrolyte adsorption is found to decrease with the $Ca(OH)_2$ concentrations in qualitative agreement with our MC simulations which confirms the competition between Ca^{2+} and polycations as counterions to the negatively charged surface of C-S-H. In line with the adsorption measurements, the electrophretic mobility of C-S-H is found to increase and, eventually, at low $Ca(OH)_2$, to reverse its sign with increasing concentration of polycations. Two mechanisms, which increase the tensile strength of a C-S-H paste, have been put in evidence.

First, at low calcium and polymer concentration, linear and branched polycations strongly increase the critical strain (g_c) via a “wraparound bridging mechanism”, where polymer chains bridge individual particles or small aggregates of C-S-H wrapping them around. Accordingly, g_c is found to increase with the degree of polymerization. Upon increasing the polymer concentration g_c peaks near the charge neutralization and, upon further addition, decreases sharply in response to the C-S-H restabilization by overcharging the surface.

Second, at high Ca^{2+} concentration, the paste is formed by large and dense C-S-H aggregates where the branched copolymer is only found to increase g_c through a “surface bridging mechanism”. As a support to this result, simulated surface forces and AFM measurements, show an extended range of interaction with branched polycations. Rheological tests on cement paste using these branched polycations show increase ductility of the final cementitious material. The impact of polycations on the meso-structure of C-S-H gels were also investigated using synchrotron U-SAXS. These structural data help us in better understanding the resulting mechanical properties as they are intimately connected to the colloidal assembly and serve as good basis to validate our simulations.

We were thus able to elaborate a new ductile cement material using a branched polycation. Numerical models coupled with experiments on a model system allowed us to better understand the relationship between the nanoscale interactions and the mechanical properties of the final materials. Knowledge-based design of the polymer will be a huge help to further improved mechanical properties of cement/polycation hybrid materials.

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Nanocomposites based on Epoxy Resin. Simulation of Microindentation Process

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Microindentation process has been simulated by FEM for nanocomposites based on epoxy resin. Set of limiting conditions have been made

- Indentation process is quasi static.
- The material has elastic-plastic behaviour with linear hardening.
- When simulated microindentation, the penetration and the release of the indenter is assumed as a contact problem with 20 seconds total time.
- The indenter is simulated as a rigid body.
- The friction between the sample and the indenter is ignored.
- The task was simplified by replacing the geometry of the Vickers pyramid by a circular cone.

The shifting of the material on X axis in area of the indentation as well as the distribution of the equivalent stresses and deformations at maximum load and after unloading have been determined. Conclusions about influence of interphase interactions have been made by combining the results obtained from microindentation and PALS methods.

Acknowledgements: The study was financially supported by Transport University "T. Kableshkov" (N^o 1509/25.05.2013)

Host-guest-interactions in a Polyelectrolyte Multilayer Film: Molecular Recognition of a Guest Molecule by a Nanocontainer

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In terms of designing a new surface molecular imprinting system, the macrocycle Cucurbit[8]uril (CB[8]) was recently assembled to the functionalized polycation PMVC$_4$H$_9$ and then embedded as a nanocontainer into a polyelectrolyte multilayer film. After this, it was demonstrated that the cavity of the nanocontainer is able to distinguish between a linear guest molecule (AnPy) and its branched isomer (9-AnPy), revealing selectivity due to both a specific ion-dipole-interaction and sterical hindrance [1]. Here, we employed ultraviolet spectroscopy (UV) and dissipative quartz crystal microbalance (QCM-D) to extend the knowledge about the new imprinting system, particularly addressing the quantitative guest molecule uptake and its kinetics. From UV measurements in solution, the formation of a trimolecular inclusion complex between the nanocontainer, associated to the polyelectrolyte, and the linear guest molecule AnPy was confirmed. On the other hand, the branched guest 9-AnPy was excluded from the cavity, although the charge of the molecule might interact weakly with the nanocontainer. Subsequent reference experiments exhibited that the presence of the polyelectrolyte chain lowers the number of accessible nanocontainers slightly; however, the majority of the cavities (70 %) remain available for the inclusion. The oppositely charged building blocks PMVC$_4$H$_9$-CB[8] and PAA-N$_3$ were then utilized to assemble the polyelectrolyte multilayer PEI/(PAA-N$_3$/PMVC$_4$H$_9$-CB[8])$_8$/PAA-N$_3$ by alternating deposition on a quartz substrate. The surface coverage of the nanocontainer per cationic layer was calculated from the multilayer absorption signal to be $\Gamma_{CB[8]}$ = 1,26 nmol/cm^2. This indicates a dense packing of the nanocontainer within the cationic layers. When AnPy was provided to the multilayer, an effective inclusion ratio of 36 % was determined. An identical polyelectrolyte multilayer was then assembled in situ to obtain mechanistic information from QCM-D studies. The Δf development, caused by AnPy, indicated two kinetic processes: The first one is interpreted as a multilayer swelling generated by the additionally incorporated masses of the included guest and hydration water; the second process was exposed to be a multilayer rearrangement induced by the locally fixed positive charges of the guest molecule. Both kinetic processes were significantly minimized when the sterical hindered guest molecule 9-AnPy was provided to the multilayer, leading to the conclusion that the inclusion of the guest molecule into the nanocontainer is the driving force of the swelling.

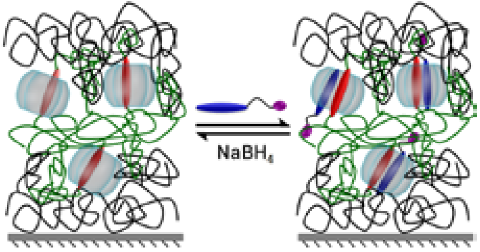

Fig. 1 Nanocontainer in polyelectrolyte multilayer film

Literature:

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Microscopic Mass Transport and Material Patterning with Reaction-diffusion Chemistry

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Competition between chemical reaction and mass diffusion (reaction-diffusion, RD) sometimes offers well-defined temporal and/or spatial periodic structures, which can be seen in many biological systems such as stripe patterns on a zebra known as Turing pattern. Understanding on RD phenomena enables to gain insight not only how nature utilizes such spatiotemporal periodic functionality, but also how we can manipulate artificial materials based on RD chemistry. In the present paper, we demonstrated two independent RD-driven material manipulations. The first one is mass transport driven by RD chemical-wave that is induced and propagated by chemical reactions. Different from conventional microfluidic mass transport devices driven by physical energy that require electric power supplier or syringe pump, completely free standing and chemical-reaction-driven mass transport devices was constructed. The second experiments enabled to construct RD-driven micropatterned materials based on Liesegang mechsnism but with non-precipitation reaction. General Liesegang rings are fabricated by precipitation reaction of insoluble salts. This is an essential limitation of Liesegang mechanism. However, it would be of scientific and technological significance if we could fabricate micropatterns consisted of materials other than insoluble salts such as molecule, polymer, nanomaterials by Liesegang mechanism. We proposed a model system that made possible to yield Liesegang patterns modified with other than insoluble salts.

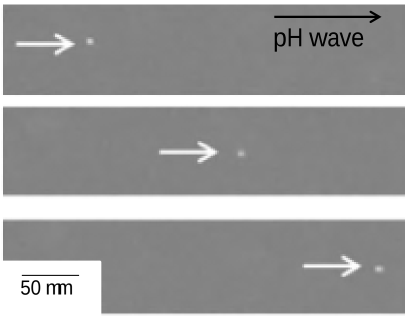

Figure 1. Successive microscope images of microsphere that is transported in the microchannel with pH-wave propagation.

First experiments concerning RD-driven mass transport were done with microchannels filled with $Na_2S_2O_3$, $KBrO_3$, and NaOH mixed solution as pH wave propagation medium. When microspheres (SDS-modified PS sphere, a few hundred mm) are doped in the solution, they were found to be transported to the same direction with the pH wave propagation without any physical biases such as electric field or water flow (Fig. 1). Control experiments revealed that pH wave propagation are essential to induce PS sphere transportation. The present system could have potential application to chemical-energy-driven microfluidic transport of microscopic materials including cells.

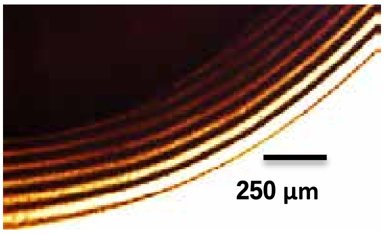

Figure 2. Microscope image of Liesegang rings consisted of silver nanoparticles.

Liesegang micro-patterns with non-precipitation reaction were achieved with citrate-contained gelatine thin film and $AgNO_3$-contained agar stamp gel. Once agar is put on the gelatine, Ag^+ ion diffuses into the gelatine film. When Ag^+ ion accumulates in the gelatine medium over a critical concentration, reduction of Ag^+ ion and nanoparticle growth occurs quite rapidly with the consumption of neighbouring Ag^+ and citrate ions. Spatial repetition of Ag^+ ion accumulation, rapid reduction, and rapid nanoparticle growth reaction resulted in the formation of Liesegang ring consisted of silver nanoparticle (Fig. 2), which is supported from TEM observation and plasmonic colour of rings. Since the reaction involved in the present system is redox reaction, not precipitation reaction, our system would be a model experiment to fabricate Liesegang rings with various functional materials other than insoluble salts, such as molecule, polymer, and nanomaterials.

Printable Nanodispersions for Gas Sensing

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This work describes a fully printable hydrogen sulfide (H_2S) gas sensor on a flexible paper substrate. Different sensor materials were tested including polyaniline composites with metal salt, metal salts of organic acids and metal nanoparticle composites. The rheological properties and stability of the dispersions and solutions were optimized for the printing or coating process and also for the sensitivity towards H_2S. The sensing device consists of flexographically printed or inkjet-printed silver electrodes. A sensing layer on top of the silver electrodes was deposited by drop casting, screen printing, inkjet printing or spray coating. The sensor yielded a several orders of magnitude change of resistance upon exposure to as low as 1ppm H_2S. The sensing layer was characterized by atomic force microscope (AFM), transmission electron microscopy (TEM), Time-of-Flight Secondary Ion Mass Spectroscopy (ToF - SIMS), conductometery and X-ray photoelectron spectroscopy (XPS).The large response of the sensor can be explained by the relatively large roughness and porosity of the paper substrate. Furthermore, the smallest obtained resistances are low enough to allow a LED lamp to be switched on using a low-voltage battery, thus serving as a proof of concept for mass - producible low cost H_2S sensors for, for example, the food packaging industry.

Acknowledgements:

Tekes (grant 3134/31/08), the European Regional Development Fund (ERDF) of the European Union, project A32103 and the Academy of Finland through the National Center of Excellence program are acknowledged for the financial support.

Bimodality of Mesoporous Silica Materials Induced by the Mixture of Pluronic P123 and Nonionic Fluorinated Surfactant

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The development of hierarchically ordered structures at multiple length scales has attracted much interest over the past few years. Indeed, such materials are of interest as potential catalysts and sorbents. In the literature many papers are focused on the synthesis of meso-macro, micro-macro or micro-mesoporous materials. However, only few of them deal with bimodal systems having two types of mesopores. In addition, the recovered materials either adopt disordered bimodal mesopore arrangements or ordered mono-modal mesopore with small size template molecular systems embedded in larger entities. Due to the difference in polarities between the fluorocarbon and hydrocarbon chains, nonideal net repulsive interactions can occur. Therefore, these surfactant mixtures appear to be excellent candidates to design bimodal mesostructures. In this study, a simple and effective route has been developed for the synthesis of bimodal (3.6 and 9.4 nm) mesoporous silica materials that have two ordered interconnected pore networks. Mesostructures have been prepared through the self assembly mechanism[1] by using a mixture of polyoxyethylene fluoroalkyl ether [$R^F_8(EO)_9$] and triblock copolymer [P123] as building block. The investigation of the $R^F_8(EO)_9$/P123/water phase diagram evidences that in the considered surfactant range of concentrations, the system is micellar (L_1). DLS measurements indicate that this micellar phase is composed of two types of micelles, the size of the first one at around 7.6 nm corresponds unambiguously to the pure fluorinated micelles. The second type of micelles at higher diameter consists of fluorinated micelles which have accommodated a weak fraction of P123 molecules. It should also be noted that both the fluorinated and the P123 surfactants, when used separately only lead to the formation of mono-modal mesoporous materials. Thus, the results reported here clearly show that the bimodality is due to the template. As long as the two networks are present, no significant variation of either mesopore size is detected with the variation of the P123 content in the surfactant mixture[2].

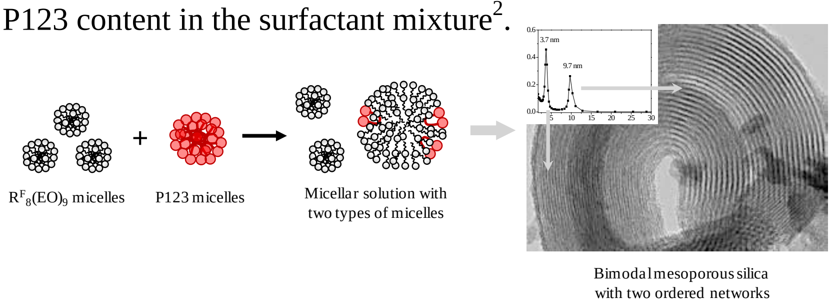

Fig. 1 : Scheme illustrating the formation of the bimodal mesoporous materials having two ordered mesopore networks

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The Influence of Physicochemical Characteristics of Zinc Oxide Particles on Their Antimicrobial Activity

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Inorganic antimicrobial agents are raising increasing interest for the control of microbial contamination and for their use as antimicrobial preservatives (1). Zinc oxide (ZnO) appears of major importance, thanks to its high antimicrobial activity, low toxicity and biodegradability (2). The knowledge of relationships between physicochemical properties of such particles and their antimicrobial properties gives new insights on the mechanisms of antimicrobial action of such particles; moreover it is required for a correct choice of a ZnO grade for a cosmetic application. The present work aims at investigating such relationships using several ZnO grades of different characteristics and various microbial strains (gram+ and gram- bacteria, molds, yeasts).

The physicochemical properties of three different grades of ZnO were investigated. X-ray diffraction and BET measurements provided information on the crystallinity, crystallite size, surface area and the porosity of ZnO powders. Size and shape of the elementary particles were studied by transmission electron microscopy (TEM) and light scattering provided the sizes of agglomerates in aqueous suspensions after their dispersion in water by means of ultrasounds. The various characteristics have been critically analyzed in order to select an independent set of physicochemical parameters. The antimicrobial activities against three bacteria and two fungal strains were measured, giving Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) as mains parameters for a systematic assessment of structure-activity relationships. The microbiology experiments have been adapted to the articulate nature of ZnO that caused specific troubles of dispersion, mixing and sedimentation during experiments.

Higher antibacterial activity is observed for smaller crystallite size and high porosity as most relevant parameters (Fig. 1). Agglomerate size, specific area and particle shape are parameters of lesser relevance. The positive charge of ZnO revealed by zeta-potential measurements is responsible of close adsorption of ZnO particles at the surface of bacteria. Direct contact between ZnO particles is not the unique mechanism of antimicrobial activity however; soluble Zn^{2+} ions and reactive oxygen species (ROS) generated by ZnO also contribute. Physicochemical properties of ZnO particles allow the control of the antimicrobial efficiency.

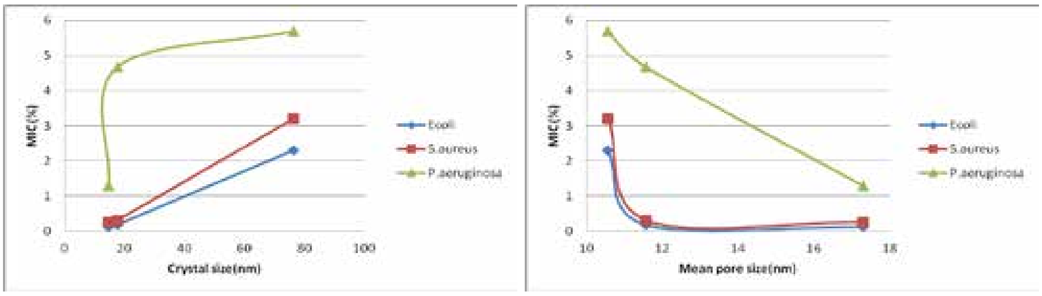

Fig. 1: Influence of crystallite and pore sizes on the antibacterial efficiency on various bacteria strains.

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PMMA-Grafted α-Fe_2O_3 Fine Particles with Anisotropic Shapes Controlled in the Graft Chain Length by ATRP

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Formation of particle-based self-organization structure has attracted a great deal of attention in material science. In the present study, we focused on introduction of self-organization property into morphology-controlled inorganic fine particles by surface dense modification of chain length-controlled polymers. Such polymer shells on the particle are expected to provide flexibility and self-standing ability into particles. Surface initiated atom transfer radical polymerization (ATRP) has been recently developed[1)] and applied to polymer-nanoparticle hybrids[2,3)]. In this study, we have prepared poly(methyl methacrylate) (PMMA)-grafted α-Fe_2O_3 monodispersed fine particles with anisotropic shapes as follows: Initially, spindle-type α-Fe_2O_3 particles **F1** and **F2**[4)] and cuboidal particle **F3**[5)] were prepared as shown in **Fig. 1** so that the mean length of long axis of **F1** and **F2** were calculated as 105 and 190 nm, respectively, with 4.8 in the aspect ratio. The cuboidal particle **F3** has 85 nm in the length of the side. Next, amino-groups were modified on the surface of **F1**-**F3** by a silane coupling reaction using *N*-[3-(trimethoxysilyl)propyl]aniline. ATRP initiator moieties were introduced on the surface of **F1-F3** by benzylation of the amine groups. The number of the ATRP initiator moieties on the surface of **F1**, **F2**, and **F3** was assigned as 0.88, 0.64, and 0.55 molecules/nm^2 using thermogravimetry. Finally, graft polymerization was carried out to obtain PMMA-grafted α-Fe_2O_3 particles **F1P-F3P** by CuBr-catalyzed ATRP of MMA on the surface of **F1**-**F3** in *N*,*N*-dimethylacetamide (DMAc) at 60 ºC. The graft chain length of **F1P-F3P** was changed with change the ATRP reaction periods and amount of free-initiator. Here, free-initiator was co-existed in the ATRP media to assign the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the grafted-PMMA on the surface of **F1-F3**. **Fig. 2** shows TEM images of **F1P**, **F2P**, and **F3P** prepared by the ATRP reaction. In each cases, all particles are well-isolated by the dense-grafted PMMA. The resulting M_ns of the grafted-PMMA on **F1**, **F2**, and **F3** were 169 x 10^3, 120 x 10^3, and 230 x 10^3, respectively. Further, M_w/M_n of **F1P**, **F2P**, and **F3P** were 1.3, 1.4, and 1.2, respectively. This means the grafted-PMMA chains of **F1P-F3P** were formed through living polymerization. We have also been investigating the self-organized structures of **F1P-F3P** by TEM observation.

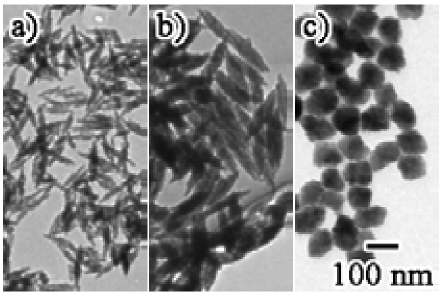

Fig. 1 TEM images of α-Fe_2O_3 particles a) **F1**; b) **F2**; c) **F3**.

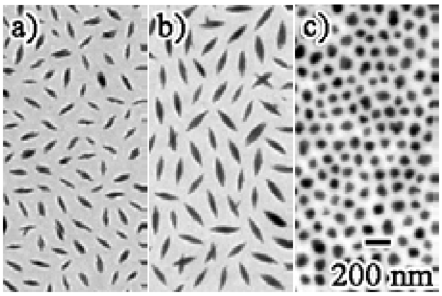

Fig. 2 TEM images of PMMA-grafted α-Fe_2O_3 particles a) **F1P**; b) **F2P**; c) **F3P**.

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Encapsulation and Characterization of Hematite Nano-particles Coated with Polyelectrolyte Multilayers

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The goal of the present study is to obtain stable suspension of hematite (a-Fe_2O_3) nano-particles, encapsulated by polyelectrolyte multilayer films, which can be loaded of corrosion inhibitor for metallic substrates – benzotriazol. It is well known as a corrosion inhibitor for copper and stainless steel. We prepare multilayer film by sequential adsorption of two oppositely charged polyelectrolytes onto hematite particles in aqueous solution. Since the process of layer-by-layer assembly is mainly driven by the electrostatic attractions between opposite charges on the polymer chains, the concentration of both polymers is chosen high enough to ensure overcompensation of the particle charge and stabilization of the suspension against flocculation.

Poly(acrylic acid) (PAA) and poly(diallyldimethyl ammonium chloride) (PDADMAC) were selected for encapsulation of the hematite particles. The optimal conditions concerning concentration of the polymers were determined by means of electro-optics and electrophoresis. We obtained stable suspensions of particles, coated with 10-12 layers of polymers at different pH conditions, and determined the thickness and electrical characteristics of the obtained coatings. The thickness of the films was found to increase linearly with the number of deposited layer, in close correlation with electrical polarizability of the coated particles. The experimental results will be used for controlled release of benzotriazol in alkaline and acid conditions.

Acknowledgements: The authors acknowledge the financial support of the project BG 051PO001-3.3.06-0038

Titania Coating of Gold Nanorods for Photocatalysis under Visible Light

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Coating of metal nanoparticles (NPs) can provide not only enhanced stability at harsh conditions (e.g., extreme pH, high temperature) but also novel optical and catalytic properties. Extensive studies have been reported on silica-coated metal NP systems, but titania-coated ones are much less developed, despite their potential importance in the photocatalysis under visible light. We present herein a facile method for titania coating of gold nanorods by tuning hydrolysis rate of a titania precursor in water / organic mixed solvent and their photocatalytic properties under visible light illumination.

The gold nanorods were prepared by the seed-mediated growth method[1]. As-prepared nanorods are stabilized with a bilayer of cationic surfactant cetyltrimethylammonium bromide (CTAB). Since these CTAB molecules readily desorb when the nanorods were put in organic solvents, they were substituted with 3-mercaptopropyltrimethylammonium chloride (MPTAC) which strongly adsorbs on the gold surfaces. After the removal of CTAB and excess MPTAC by repeated centrifugation, the gold nanorods were resuspended in water. Separately, a titania precursor titanium (IV) tetrabutoxide (TTBO) was dissolved in mixed acetonitrile / butanol. Then the aqueous gold nanorod dispersion was quickly injected into the TTBO solution under vigorous stirring. Immediately titania coating proceeds at the surface of gold nanorods, accompanied with color change due to an increase in the refractive index around nanorods. TEM and EDX confirmed a successful titania layer of ca. 3 nm thick on each gold nanorod[2].

Photocatalytic properties of titania-coated gold nanorods will also be presented at the conference site.

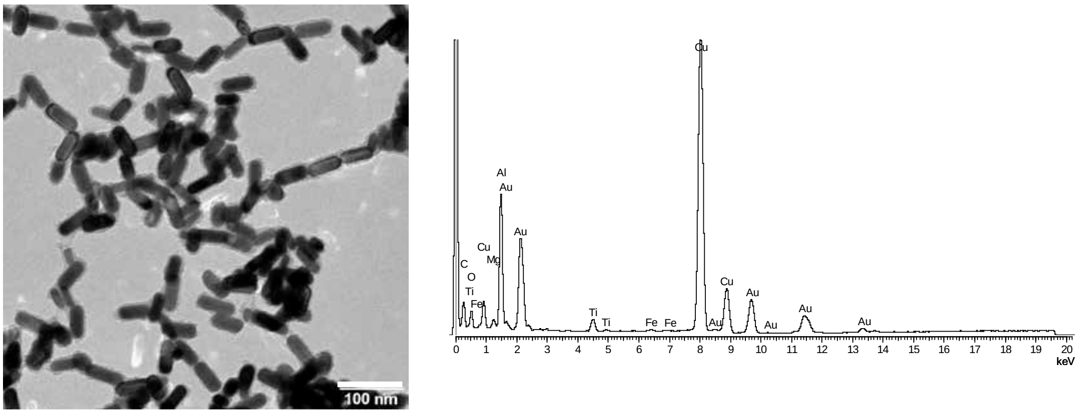

Fig. 1 **TEM image and EDX profile of titania-coated gold nanorods.**

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Kinetics of Fluorescent Latex Particle Deposition at PAH and PDADMAC Monolayers Determined by *in situ* Measurements

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A new flow cell was constructed for studying *in situ* kinetics of particle and macromolecule adsorption using fluorescence microscopy. Using the cell, calibration experiments were performed for fluorescent latex particles on mica coated by cationic polyelectrolytes: polyallylamine hydrochloride (PAH) and poly(diallyldimethylammonium chloride) (PDADMAC). Adsorption of PDADMAC on mica was determined for various ionic strengths and surface polyelectrolyte concentrations by the streaming potential method. The obtained results were quantitatively interpreted in terms of the 3D electrokinetic model. The bulk latex properties were determined by dynamic light scattering (DLS) and microelectrophoresis. The hydrodynamic diameter of particles varied in the range 528–574 nm, depending on ionic strength. The electrophoretic mobility measurements revealed that the zeta potential of particles was negative varying between -56 mV for $I = 10^{-4}$ M, and -42 mV for $I = 0.15$ M. The kinetics of latex particle deposition at mica coated by saturated polyelectrolyte layers was studied *in situ* as a function of ionic strength under diffusion-controlled conditions. The coverage was determined by direct enumeration of particles using the fluorescent microscopy and AFM technique. The experimental results were adequately interpreted in terms of numerical solutions of the mass transport equation with the blocking function derived from the random sequential adsorption (RSA) approach. Additionally, the dependence of integrated fluorescence intensity on particle coverage was determined, which enables a quasi-continuous measurements of particle deposition kinetics. It was concluded that the cell is versatile tool for determining mechanism of particle deposition at interfaces.

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Voltammetric Method for Determining Coverage of Densely Packed Spherical Particle Monolayer – Experimental View

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Deposition of microparticles at the solid/liquid interface leads to formation of a porous layer, which may have a noticeable effect on the ion transport from the bulk solution to the adsorption surface. Therefore, we can study adsorbed particle layers using the electrochemical method of cyclic voltammetry with a rotating disk electrode (RDE). The aim of this work was preparation and coverage determination of densely packed particle monolayers on a glassy carbon disk electrode (GC RDE). In our experiments we have used 3 µm monodisperse silica particles. We have carried out the particle deposition in a sedimentation cell to obtain monolayers at various coverage. Then, we have recorded cyclic voltammograms for various rotation frequencies to determine the limiting diffusion current at the RDE with each particle layer. We have conducted the electrochemical measurements at 298.15 K in the equimolar aqueous 1 mM $K_3[Fe(CN)_6]$ + $K_4[Fe(CN)_6]$ solution containing 1 M KCl as a base electrolyte. Finally, we have calculated each layer surface coverage from the measured values of the limiting diffusion current using equations derived in the limit of negligible convection. We have also compared the results with the electrode surface coverage determined by means of optical microscopy.

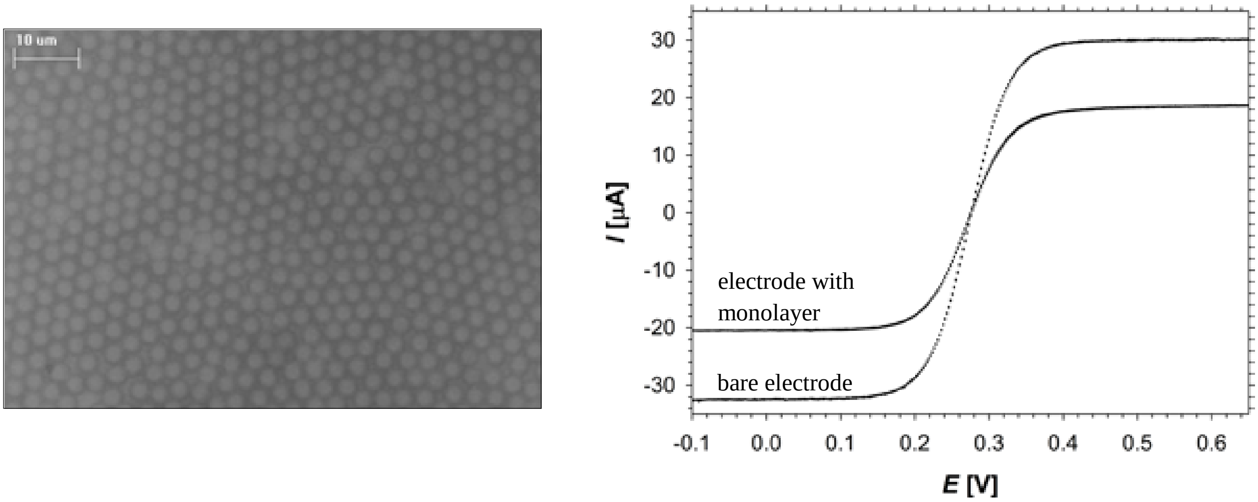

Fig. 1. Optical microscopy image and cyclic voltammogram of GC RDE with deposited particle layer at surface coverage $\theta = 0.813$.

We have found a good agreement between the monolayer parameters obtained by cyclic voltammetry and results from the optical microscopy in the range of surface coverage higher than 0.6, which confirms our underlying theoretical framework for densely packed monolayers. We have demonstrated that RDE cyclic voltammetry is a useful technique to determine the coverage of densely packed monolayers deposited on the electrode surface.

Acknowledgement:

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Effect of Particle Polydispersity on Limiting Diffusion Current

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Adsorption of large molecules at the solid/liquid interface leads to formation of a porous layer, which may have a visible effect on the ion transport from the bulk solution to the adsorption surface. Therefore, adsorbed particle layers can be studied using the electrochemical method of cyclic voltammetry with a rotating disk electrode (RDE). In our previous works we studied monodisperse colloidal particles [1, 2]. Particles in natural systems, however, such as colloids and bioparticles, are variable sized. So, the aim of this work is the preparation and electrochemical characterization of polydisperse particle monolayers on a glassy carbon disk electrode. In our experiments, we have used polydisperse glass beads in the micrometer size range. We have carried out the particle deposition in a sedimentation cell. Then, we have conducted cyclic voltammetry measurements of the limiting diffusion current at 298.15 K in the equimolar aqueous 1 mM potassium hexacyanoferrate(II) and (III) solution containing potassium chloride as a base electrolyte. For each layer we have recorded cyclic voltammograms at various rotation frequency. Next, we have determined the coverage of the electrode surface and the adsorbed particle size histogram using an optical microscope and scanning electron microscopy. Finally, we have calculated each layer surface coverage from the measured values of the limiting diffusion current using equations derived in the limit of negligible convection. We have also compared the results with the electrode surface coverage determined by means of microscopy. We have found a good agreement between the monolayer parameters obtained by cyclic voltammetry and results from the microscopy. Our research suggests that the effect of particle polydispersity on the limiting diffusion current is minor and can be neglected for the coefficient of variance less than 0.5. We have demonstrated that RDE cyclic voltammetry is a useful technique to determine the coverage of polydisperse particle monolayers deposited on the electrode surface.

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Acknowledgement:

The authors acknowledge the financial support of the EU Human Capital Operational Programme, Polish Project No. POKL.04.0101-00-434/08-00.

Effect of Nano-emulsions Composition on the Ursolic Acid Release

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Ursolic acid is a pentacyclic triterpene acid, present in many plants, including bearberry (Arctostaphylos uva ursi), sage (Salvia officinalis), rosemary (Rosmarinus officinalis) or apples. The most important properties of ursolic acid are: anti-inflammatory, anti-cancer effects, anti-atherosclerotic and anti-arrhythmic effects and anti-radical properties, regenerating, improving the appearance and elasticity of the skin [1]. Nanoemulsions are a new form of cosmetics products. They show some advantages comparing to classic emulsions: relatively easily penetrate into the skin, exhibit a high degree of hydration and soften the skin and have a very good user properties. They are one of the most promising formulations used to enhance percutaneous penetration of active substances as well as their bioavailability [2,3].

The aim of this work was to determine the release of ursolic acid depending on the applied formulations. The nano-emulsions based on caprylic/capric triglycerides, propylene glycol dicaprylate/dicaprate and oleic acid stabilized by Polisorbate 80 were compared. The nanoemulsions were prepared by stepwise addition of water to the mixture of polisorbate/oil/ursolic acid, at room temperature. The mean droplet size was determined by a dynamic light scattering measurment using Malvern Zetasizer Nano ZS. Drug release study of ursolic acid was carried out using the Spectra/Por Standard Regenerated Cellulose (RC) membrane, at the temperature $T=37^oC$. The concentration of ursolic acid in the receptor solution (i.e. Ethanol/PBS mixture) was analyzed by UV-Vis spectroscopy method. The results have shown that nanoemulsions can be used as carriers for controlled release of ursolic acid.

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2. The DSL analysis were carried by courtesy of Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, Cracow

The Influence of Active Substance Structure on their Release from Nano-emulsions

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The aim of this work was to determine the influence of active substance structure on their release from nano-emulsion system. Menthol (monoterepene), forskoline (diterpene) and ursolic acid (triterpene) were used as the actives. Terpenes are the largest group of natural compounds. Many of them showed biological activities against cancer, inflammation and infectious diseases [1], also they are known as active cosmetic ingredients. Nanoemulsions containing Caprylic/Capric Triglyceride as an oil phase, stabilized by Polisorbate 80, were used as the actives carriers. The oil used offers several functional benefits it is known as a non-greasy emollient and shows excellent penetration promoting.

The phase diagram of ternary system: Triglyceride/Polisorbate 80/water were determined to specify the area of occurrence of stable emulsion systems, with varying degrees of internal phase dispersion (microemulsions, nanoemulsion, liquid crystal systems), and to select the appropriate emulsions composition. The emulsions were prepared by phase inversion composition method, by stepwise water addition to the oil/surfactant mixture, at room temperature (25°C). The mean droplet size was determined by a dynamic light scattering measurment using Malvern 4700C Submicron Particle Analyzer**.** Stability studies were carried out using TurbiScan. Morfology of the liquid crystal was characterized by optical microscope. The release study of the active substances was carried out using the Spectra/Por Standard Regenerated Cellulose (RC) membrane**,** at the temperature T=37°C. The concentration of ursolic acid, forskoline and menthol in the receptor solution (i.e. Ethanol/PBS mixture) was analyzed by UV-VIS spectroscopy.

Kinetically stable emulsions with droplet sizes ranging around 116 nm were obtained. The results have shown that the structure of active substances has significant influence on the drug release form nano-emulsion system.

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Acknowledgements:

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Mechanism of Nanoparticle Deposition on Polystyrene Latex Particles Revealed by Electrokinetic, AFM and SEM Measurements

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Adsorption of positive amidine latex particles (average diameter 100 nm) on negative polystyrene latex particles (800 nm in diameter) was studied by SEM imaging, micro-electrophoretic and the concentration depletion methods involving AFM. The role of ionic strength varied between 10^{-4} to 10^{-2} M, NaCl was systematically evaluated. The number of deposited positive latex particles (surface coverage) was directly evaluated by a direct counting procedure exploiting the SEM images (see Fig. 1).

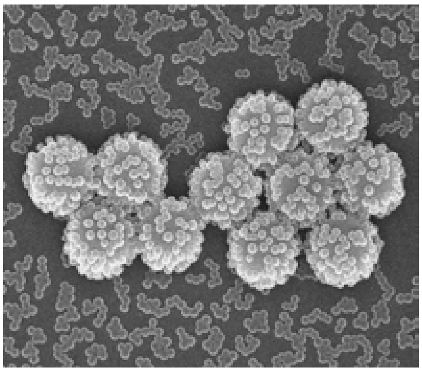

Fig. 1 SEM micrograph of negative polystyrene latex particles covered by positive amidine latex deposited on mica surface.

This allowed one to calibrate the results obtained by measuring the electrophoretic mobility of large latex particles covered by a controlled amount of the positive latex. These electrophoretic mobility vs. coverage dependencies obtained for higher ionic strength were quantitatively interpreted in terms of the 3D electrokinetic model previously used for planar interface. This allows one to precisely determine the coverage of nanoparticles on latex carriers as a function of ionic strength. For 10^{-2} M NaCl the maximum coverage was 0.52, close to the value pertinent to hard (non-interacting) particles. These results, which agreed with the SEM imaging and AFM determination of the residual latex concentration after deposition, were interpreted in terms of the random sequential adsorption (RSA) model. The increase in the maximum coverage with ionic strength was interpreted in terms of reduced electrostatic repulsion among positive latex particles. In this way the validity of the RSA approach for predicting maximum coverage of particles on curved surfaces was confirmed for the first time in the literature.

This finding has significance for basic science indicating that the results obtained for curved interfaces (polymeric carrier particles) by the micro-electrophoretic method can be exploited for interpreting deposition of nanoparticle and proteins on planar interfaces and vice versa.

A practical significance of the results stems from the possibility of developing a protocol of an accurate determination of nanoparticle and protein coverage on polymeric carrier particles based on the robust micro-electrophoretic measurements.

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Nacre-like Composite Materials Produced via Magnetically-controlled Sol-Gel Phase Separation

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Naturally occurring materials and structures have been always inspired scientists, who tried to either replicate or mimic them. Examples include gutta-percha, wood, opals, bones and nacre.

The latter has gained considerable interest in the last few years.Naturally occurring nacre is made of thin hexagonal platelets of aragonite, having a size of 10-20 ɱm and a thickness of 0.5 ɱm held together by a bio-polymer. This peculiar structure confers it excellent mechanical properties.

In this work we have prepared a new ceramic-polymer composite material inspired by the structure of nacre. This material is made from a monolithic skeleton of silica platelets (shown in the Figure) in a size range of 20-30 ɱm and a thickness of ~1ɱm reinforced by a polyetheramines based polymer. The silica platelets have been produced via a modification of the magnetically controlled phase separation in sol-gel process previously developed in our laboratories [1]. In this process polymer-magnetite nanoparticles produced via miniemulsion polymerization have been dispersed in an acidic solution where PEG and the silicon precursor TMOS have been previously dispersed. The obtained solution was then transferred to a mold and placed between the poles of an electromagnet. As shown in the literature, the application of a rotating magnetic field leads to the formation of two dimensional sheet-like structures. In our case we decided to rotate the sample inside a uniaxial magnetic field to mimic a rotating field. Once the monolith was formed it was functionalized with(3-aminopropyl)-triethoxysilane in order to promote the attachment of the polymer to the surface during the impregnation step.

The obtained structures have been analyzed with SEM microscopy and mechanical compression test before and after the polymer impregnation step. We have shown that the radial velocity plays an important role in the formation of the platelets structure and of the initial anisotropic mechanical properties of the materials. The impregnation step enhances these properties by making the material more stable.

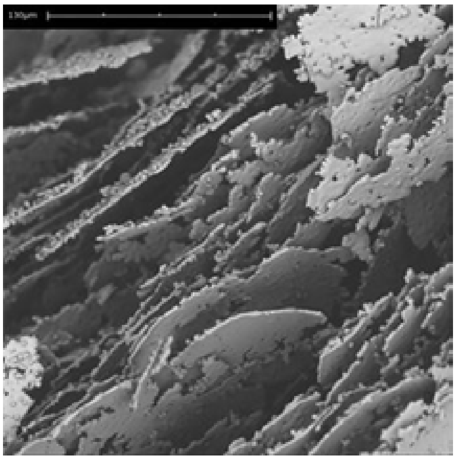

Fig. 1 SEM picture of a silica skeleton obtained in the presence of a rotating magnetic field

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Size Controlled Synthesis of Silver Nanoparticles based on Mechanistic Studies

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Metal nanoparticles have become a focus of extensive research based on their unique catalytic, optical and magnetic properties. These properties strongly depend on the particle size. Thus, size control provides one effective key to an accurate adjustment of colloidal properties. However, synthetic procedures for metal nanoparticles with precise size control are rare; especially for silver nanoparticles.[1] The common approach to size control is a simple trial and error testing of different reaction conditions. The particle growth mechanisms remain a black box.[2]

In this contribution we present a general approach to size control which is based on profound mechanistic knowledge. The approach comprises (i) the investigation of the principle growth mechanism including all relevant physicochemical processes, (ii) the investigation of parameter influences on the growth mechanism and (iii) the well-directed development of synthetic recipes. Small Angle X-Ray Scattering (SAXS) was shown to be a powerful tool to study nanoparticle growth processes.[3]

The presented approach is exemplified for a common silver nanoparticles synthesis: the wet-chemical reduction of silver perchlorate with an excess of sodium borohydride. Recently, we deduced a principle growth mechanism for this synthesis which comprises two separated steps of coalescence (illustrated in **Fig. 1**).[4] The second coalescent step is caused by the full consumption of residual BH_4^- which inhibits the formation of an oxidic layer. Surface oxidation after BH_4^- consumption decreases the colloidal stability and initiates particle growth until a stable size is reached. From the gained mechanistic knowledge a synthetic procedure could be deduced that enables the reproducible synthesis of silver nanoparticles in water in a range from 5 to 12 nm. To the best of our knowledge, this is the first time that silver nanoparticles which do not require additional stabilization agents can be produced with controllable size in this range.

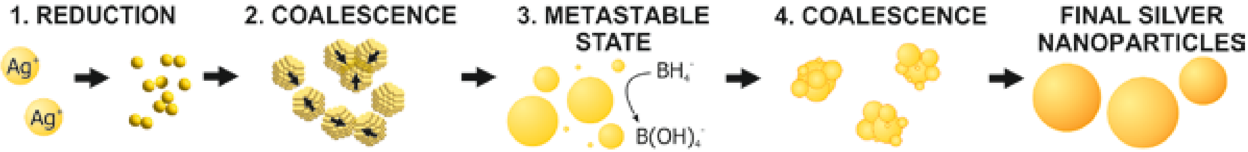

Fig. 1 Deduced growth mechanism for the wet-chemical reduction of $AgClO_4$ with $NaBH_4$

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Optical and Mechanical Properties of Hollow Silica Nanoparticles

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Hollow silica nanoparticles (HSNP) are simple building blocks for mesostructured materials with a wide range of interesting properties. HSNPs can be readily obtained by a sacrificial templating method using monodisperse polystyrene latex particles, which gives good control over the particle geometry, i.e. diameter and shell thickness. In this contribution we investigate the optical and mechanical properties of such well-defined HSNP particles and self-assembled arrays. Amorphous powders consisting of HSNPs with a shell thickness of only 15 nm exhibit an intriguing color effect, which depends on the particle diameter. This coloration is not caused by absorption or Bragg scattering, but is a direct observation of Mie resonances. Due to the ultralow refractive index ($n < 1.1$) in such disordered powders, multiple light scattering is largely suppressed and muted colors can be perceived by the naked eye (Fig. 1 left).[1]

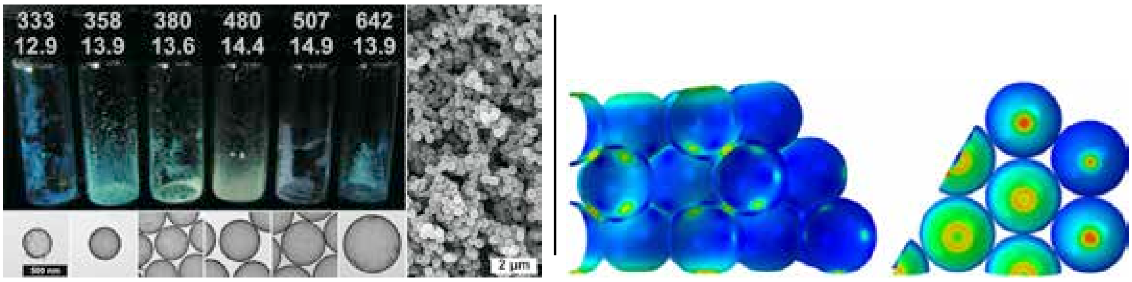

Fig. 1 Left panel: Direct observation of Mie resonances in disordered hollow sphere powders, depending on the particle size. Right panel: Stress contours of hexagonally ordered films of HSNPs upon compression with a spherical indentor.

HSNP particles can also be self-assembled into hexagonally ordered arrays. The deformation of such well-defined arrays upon mechanical compression has been investigated experimentally, theoretically and by modeling (Fig. 1 right). We find that under the premise of a constant film density (i.e. ratio of shell thickness to particle diameter is constant), smaller particles result in more stable films. Furthermore, the collective response of such films can be explained by the sequential contact and deformation of the spherical indentor with the constituting hollow spheres.[2,3]

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Bio-synthesis of Noble Metal Functionalized Nanoparticles Using Plant Extracts

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In recent years, noble metal nanoparticles have been the subject of extensive research due to their unique properties that are significantly different from those of bulk materials and find applications in the electronic, optical, chemical sector for catalysis, environmental protection, energy conversion, and drug delivery [1].

Metallic silver nanoparticles were synthesized using a rapid, single step, from aqueous silver nitrate through a simple and eco-friendly route using leaf broth of Arbutus Unedo, which acted as a reductant and stabilizer simultaneously. The aqueous silver ions when exposed to the leaf broth were reduced and stabilized over long periods of time resulting in the green synthesis of surface functionalized silver nanoparticles. The bio-reduced silver nanoparticles were characterized by UV-Vis spectroscopy and transmission electron microscopy (TEM). The results revealed the formation of single crystalline Ag nanoparticles with a narrow size distribution for each sample. The particles, although discrete, were predominately coated with the organic component forming small aggregates, which makes them stable over long time periods and highly appropriate for coatings or biomedical applications.

Transmission Electron Microscopy (TEM) experiments proved the formation of nanocrystalline silver particles, as shown in Fig. 1. The nanoparticles predominately adopt a spherical morphology. The obtained nanoparticles are quite uniform in size and up to 30 nm. In rare occasions, particles with higher sizes were also observed, but their population was rather low.

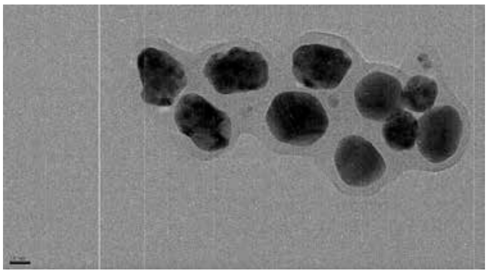

Fig. 1 Typical TEM image of Ag nanoparticles, synthesized by the proposed methodology

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Mesoporous Silica Nanocapsules and Loading of Dye Molecules into the Capsules

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Mesoporous silica hollow capsules (MSHC) are the candidates for drug carriers in drug delivery system. We had shown that a template-assisted synthesis provides the monodisperse MSHCs with excellent quality and the capsule diameter can be controlled from 450 to 80nm [1]. Although there are number of reports on the MSHCs, we could not find a direct evidence that the materials are loaded into the MSHCs expect the large capsules, which can be observed by the confocal laser scanning microscope [2]. One may doubt that the materials are not loaded inside, but they are merely adsorbed on the mesoporous shell. In the preset study, we propose a method to load dye molecules (alizarin) into our capsules, and the materials loaded inside the capsules are confirmed by the transmission electron microscope (TEM).

The MSHCs, whose average inner diameter was 48 nm and average diameter of the mesopores across the shell was 1.84 nm, were prepared [1]. The loading procedure is indicated in Fig. 1. The $\underline{x}$ mL of the resultant dispersion of the MSHC was dried and redispersed in the $\underline{y}$ mL acetone solution of alizarin (14 mM) by sonication for an hour. The acetone was then evaporated gradually under ambient conditions to precipitate alizarin inside the capsules, followed by a vacuum evaporation. After the evaporation, the capsules were redispersed in the saturated aqueous solution of alizarin (20 μM), followed by the filtration to separate the loaded capsules and the alizarin precipitates dispersed outside the capsules.

Fig. 2 clearly shows that the alizarin was precipitated inside the capsules. Although the hollow portion of the capsule was not filled with alizarin, the fraction of alizarin-loaded capsules reached almost 100%. To find the condition to achieve the 100% fraction, the ratio of y/x and the evaporation speed of acetone were varied, and it was found that the large amount of excess alizarin solution and the evaporation duration of three days are required. The release profiles of alizarin using the loaded MSHCs with different shell thickness will also be indicated.

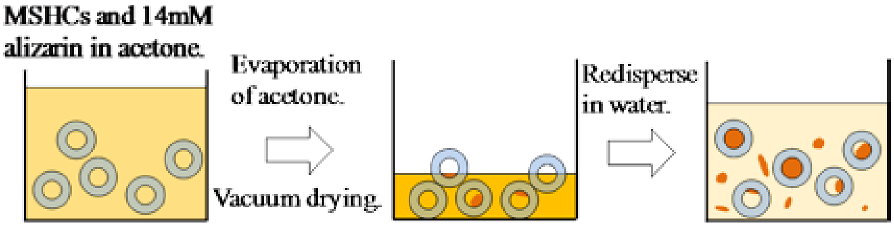

Fig. 1 Loading procedure of alizarin into MSHCs.

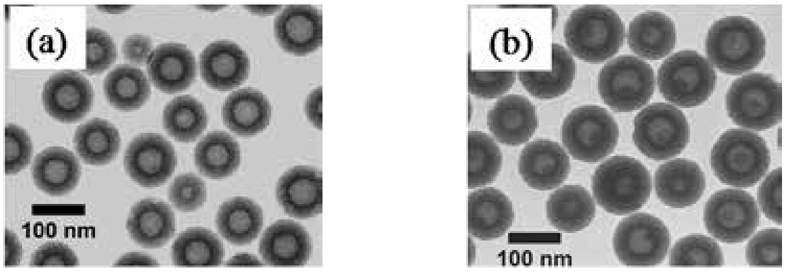

Fig. 2 TEM images of empty (a) and loaded (b) MSHCs.

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2. Y. Zhu, *Micro & Nano Letters* 6, 802-805 (2011).

Carbon Microspheres as Nanoparticle Scaffolds

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Susan J. Quinn[5] and David Hinds[5]

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Carbon materials and coatings are used for a vast range of applications in synergy with metal clusters or nanoparticles. Nanostructured carbon scaffolds such as foams, aerogels and mesoporous particles are particularly interesting as nanoparticle supports because the desirable chemical, thermal and electronic properties of carbon can be coupled to the high specific surface of these materials in order to deliver enhanced performance. Nanoparticle size, coverage and distribution at the carbon surface can play an important role in determining final properties and performance of the composite metal/carbon material, in particular for applications such as reactive adsorbents and heterogeneous catalysis. Therefore, there is great interest in developing new strategies for controlling nanoparticle growth at carbon nanostructured surfaces.

In this presentation we will discuss our results on the use of mesoporous carbon microspheres as supports for the growth of metal nanoparticles. We will discuss green approaches for the preparation of Pd/C and Ag/C composite particles. We have used a combination of microscopic, gravimetric and spectroscopic techniques for the characterization of these materials in order to understand what factors control size and distribution of metal nanoparticles and we will also present our preliminary work on their potential applications. Using surface catalysed processes, we have also developed methodologies for the synthesis of carbon supported Fe and Fe/FeOx particles. We will report on the structural characterization of these materials, in particular on the use of X-ray absorption techniques in order to determine their composition, and will discuss applications of these materials in environmental chemistry. Finally, we will also present results on the synthesis of Au/C composite materials with high specific area and with controlled loading and distribution for catalysis and biological applications.

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Transparent Silica Nano- and Microchannels with Circular Cross-Section

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Nano- and microchannels are widely used for defined and targeted material transport. Applications range from fluidic delivery systems to fluidic cell and particle separation, and drug delivery research. Cylindrical airtight channels are essential for fundamental studies of capillary filling, diffusion, or transport phenomena. Diverse techniques were used to prepare continuous tubular inorganic nano- and microchannels, such as coaxial electrospinning, template-assisted techniques or mechanical pulling. Although these techniques exist, it is still challenging to fabricate nanochannels with a defined, homogeneous diameter in an efficient and scalable process without compromising tightness.

In this work a simple template-assisted method to fabricate silica nanochannels is presented. The channels are tight, and possess a tunable, homogeneous diameter. To demonstrate the generic applicability of the method, we used artificial electrospun polymer and natural spider silk fibers as template and monitored the filling kinetics by laser scanning confocal microscopy.

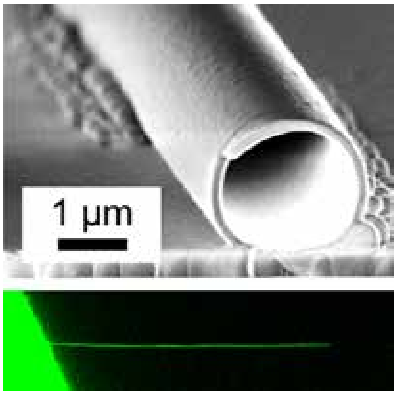

Fig. 1 Hollow silica microchannel. Spider silk was used as template, covered by silica using the Stöber method. After calcinations at 600 °C an air-tight hollow channel is created (top). Filling kinetics were studied by means of confocal microscopy (bottom) and described by the Lucas-Washburn equation.

Acknowledgements:

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Imaging NIR-Ellipsometry of Graphene

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Graphene is a two-dimensional crystalline solid consisting of only one atomic layer of hexagonally arranged carbon atoms with fascinating properties and a high potential for devices in various fields, for example flexible transparent electrodes for touch screens, solar cells, photo detectors, nano electronics and high frequency devices. Matković et al. (2012) used Spectroscopic imaging ellipsometry and Fano resonance modeling to characterize graphene. Albrektsen et al. (2012) characterized few-layer graphene by different imaging methods and showed clearly the capability of imaging ellipsometry to distinguish between single, double and few layer graphene. Wurstbauer et al. (2010) reported Imaging ellipsometry studies of graphene on SiO2/Si and crystalline GaAs. Variable angle spectroscopic ellipsometry is used to explore the dispersion of the optical constants of graphene in the visible range with high lateral resolution. Based on new developments, spectra with higher spectral resolution are available in the spectral range from 360 to 1700 nm.

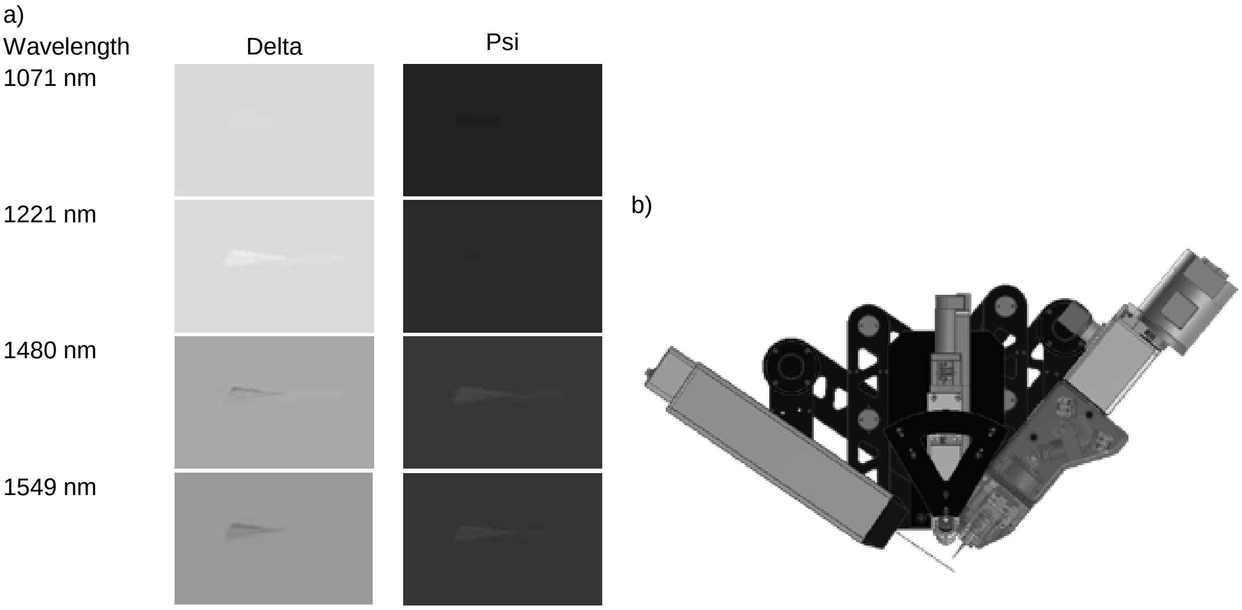

Fig. 1. Delta- and Psi-maps of graphene at different wavelength in the NIR (a) and technical drawing of a spectroscopic imaging ellipsometer equiped for the spectral range from 360 to 1700 nm (b).

In addition to an overview of information that can be obtained by imaging ellipsometry, new results like ellipsometric mapping in the NIR will be reported.

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Albrektsen et al. (2012) High resolution imaging of few-layer graphene. J. Appl. Phys. 111, 064305 ellipsometry:
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Preparation and Characterization of Halloysite/Polyhydroxyalkanoate Nanocomposites as Scaffolds for Bone Tissue Engineering

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Tissue engineering is a field that has recently gathered a lot of attention. An interdisciplinary approach, involving chemistry, physics, medicine and material science, is necessary to build up the knowledge required to produce biocompatible and active materials, able to replace the mechanical and biological functions of natural organs and to promote the reconstruction of damaged tissues.

In this contribution we present the design, preparation and characterization of a nanocomposite based on halloysite/polyhydroxybutirate-co-valerate (PHBHV) in view of its application as a scaffold for bone tissue engineering. Halloysite clay mineral is a natural aluminosilicate, consisting of cylindrical hollow tubules with nanometer cross sections having different chemical reactivity on inner and outer surfaces. Its choice as the inorganic filler in the nanocomposite was based on its biocompatibility, lightness, mechanical properties, and because of the nanotube structure, which could be exploited to deliver specific drugs. PHBHV, a polyhydroxyalkanoate entirely obtained by microbic fermentation, was chosen as the polymeric matrix as it is a biodegradable material, with natural origin, and its chemical and physical properties make it a suitable candidate as a resorbable material for biomedical applications.

The organic matrix of the nanocomposite is expected to spontaneously degrade over time, progressively exposing the halloysite nanotubes which should act as the substrate for the bone regeneration. This process is schematically shown in Figure 1.

Different methods for the preparation of the nanocomposite have been explored, trying to match the typical needing of biomedical devices. The degradation behavior and themorphological and structural properties of the nanocomposite were studied through a multi-technique approach, demonstrating that the prepared nanocomposite is a promising candidate for bone regeneration treatments.

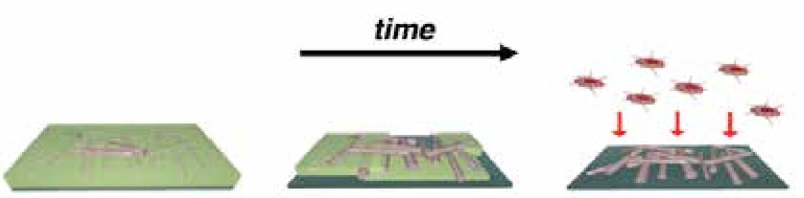

Figure 1. Sketch of the degradationprocess of the PHBHV matrix, taking to the exposition of halloysistesnanotubes.

Evolution of the Fractal Structure in Hydrating Cement Determined by Differential Scanning Calorimetry. Effect of Chemical Additives

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The assessment of the structural properties of solids plays a crucial role in solid state research, as the structure usually define different physical and chemical characteristics of the materials. Structurally disordered solids are complex systems, as they are not crystalline but at the same time not purely random. For this reason they cannot be investigated by means of the usual crystallographic methods nor by statistical calculations. One of the most diffuse and important disordered solid systems is cement. When hydrated, the initial heterogeneous mixture of calcium silicate and aluminate forms a rigid solid network with high mechanical resistance, mainly constituted by amorphous hydrated calcium silicate (briefly named C-S-H). This phase acts as "glue" between the grains (unreacted phases, inert fillers, crystalline hydrated products), and is the most relevant in affecting the mechanical properties of the final specimens. The most realistic picture of the C-S-H structure is provided by a fractal description. In particular, the precipitation of C-S-H is efficiently described by the *percolation theory* [1,2]. The methods of choice for the fractal nature of C-S-H are usually small angle scattering techniques because the length scale of the cement fractal microstructure (1-1000 nm) matches with the dimension of the probe (i.e. the inverse of the scattering vector) of a small angle scattering experiment. [3]

In this work we show for the first time that a very common and accessible technique like Differential Scanning Calorimetry can be used to extract most of the relevant information on cement structure and porosity. In particular, we show that low temperature calorimetric measurements performed in equilibrium conditions yield the fractal dimension of the pastes, with values in good accordance with small angle scattering measurements. We apply this method to monitor the development of C-S-H microstructure during the hydration of tricalcium silicate in presence of polycarboxylic esters (PCEs), estimating the *percolation threshold* of the porosity and the *fractal dimension*, directly related to the macroscopic characteristics of the material. Furthermore, through the analysis of the same DSC thermograms, we determine the volume of pores (capillary, large gel pores and small gel pores), monitoring it throughout the hydration. We deduce the influence of some of the commonly used additives on the structure and on the depercolation of the porosity. The development of methods that easily access the characteristics of cement microstructure during the hydration process is a task of primary importance, considering that several macroscopic properties of cement (degradation phenomena, elasticity, compressive strength, etc.) are influenced by the structure and the porosity of C-S-H. These results, apart the important information on the effect of additive on the curing process of cement pastes, show that the simple DSC analysis can provide a wealth of information on the fractal properties of this important material.

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Acknowledgements:

Authors thank CTG-Italcementi for providing the C_3S pure phase and for partial financial support and Dr. Stefan Becker and Dr. Joachim Pakusch (BASF AG, Ludwigshafen, Germany) for providing the PCE superplasticizers. Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, CSGI, is gratefully acknowledged for financial support.

Voltammetric Method for Determining Coverage of Densely Packed Spherical Particle Monolayer – Theoretical Study

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We have presented our research of the limiting diffusion current at a rotating disk electrode (RDE) covered with a dense layer of monodisperse spherical particles. We have derived simple equations for the diffusion permeability and limiting diffusion current at the RDE with a multilayer gel membrane, as well as gel membrane with variable diffusion and partition coefficients. Then, we have derived similar equations for a porous multilayer, as well as for a porous layer with variable tortuosity and porosity, under assumption of negligible convection in the layer. We have also demonstrated that the variation of limiting diffusion current with the porosity and tortuosity of porous layer can be characterized in terms of the equivalent thickness of stagnant solution layer, i.e., the average tortuosity / porosity ratio. Then we have found an approximate invertible relationship between the equivalent layer thickness and particle surface coverage, which is useful not only for predicting the diffusion current for a given coverage but also to determine the electrode surface coverage from the measurement of diffusion current. We have also demonstrated that the effect of dense particle layers adsorbed on the surface of RDE increases non-linearly with the surface coverage. Finally, we have tested our theoretical results experimentally by means of cyclic voltammetry measurements of limiting diffusion current at the RDE covered with a monolayer of monodisperse spherical particles. We have found good agreement in the range of particle surface coverage higher than 0.6.

Acknowledgements:

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Photocatalysis of Orange II by ZnO and TiO_2 powders and nanowire ZnO and ZnO/TiO_2 thin films

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The present study is focused on photocatalytic degradation of the organic azo-dye Orange II in water solutions using TiO_2 and ZnO powders or bare and TiO_2 doped nanowire ZnO thin films. Commercial anatase TiO_2 and ZnO are used for the photocatalytic experiments in slurry. The ZnO seeded substrates are prepared by repetition of four seed deposition cycles from zinc acetate solution using spin coating technique. The ZnO nanowire films are obtained via wet chemical method. The ZnO and ZnO/TiO_2 thin films are investigated by SEM and X-ray diffraction. The photocatalytic tests are performed in cylindrical glass reactors under UV or visible light irradiation. The pollutants concentrations are 20 ppm O II for slurry and 10 ppm for film photocatalysis. The photodegradation of Orange II dye is observed spectrophotometrically.

The observed higher rates of degradation with mixed TiO_2/ZnO than that with ZnO films fids explanation in: (i) higher contact area between the two semiconductor oxides; (ii) greater amount of effective illuminated photocatalyst surface and (iii) effective charge separation of the photogenerated charge carriers under light excitation.

Acknowledgements:

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Preparation and Optical Properties of Sol-Gel Microparticles Funtcionalized with Europium Complexes

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Sol-gel technology is a powerful method for preparation of doped oxide nanomaterials at room temperatures (below 150° C). By variation of synthesis conditions different kind of amorphous or nanocrystalline materials like hybrid composites, thin films,xerogels or aerogels can be obtained.Sol-gel chemistry also offers the amazing ability to tailor density, microstructure and shapes of samples prepared by control of the rate of hydrolysis and condensation reactions.Sol-gel derived inorganic network materials doped with rare earth ions display important optical properties such as luminescence, coloration and energy transfer[1,2].

A new method for functionalization of Eu^{3+} doped silica nanoparticles with 1,10-phenantroline is proposed in the framework of preparation of hybrid composites with quantum efficiency 20-40% [2]. In this way formation of optical centers, containing strongly emitting lanthanide takes place on the surface of the doped nanoparticles during adsorption of organic ligands.The optical properties of Eu^{3+} ions incorporated in silica are used to explore their site symmetry in the inorganic sol-gel network and hybrid composites. All the samples were characterized using UV / Vis spectroscopy, luminescence / excitation spectroscopy, X-ray diffraction, SEM / AFM microscopy, chemical analysis and quantum efficiency measurements. In the case of zirconia strong red emitting materials with quantum efficiency up to 48% or blue emitting samples are obtained depending on functionalization strategy.

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Fabrication and Optical Properties of Chitosan/Ag Nanoparticles Thin Film Composites

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Thin polymer coatings are widely used in optics and photonics due to relatively low costs and good processability of many polymers and the possibility to immobilize into polymeric matrix versatile optically active components, which change refractive index, light adsorption and reflection properties, and optical sensitivity of polymers to a wide range of analytes. Planar waveguide, which consists of dielectric film deposited on a dielectric substrate, is a basic element of integrated optics set-ups widely used for optical sensing. To assure light propagation in the waveguide, the refractive index of the polymer film must be higher than that of the substrate, whereas the film thickness must be comparable to the wavelength of the laser used in the optical scheme. Here we report on fabrication of optical waveguides using chitosan films with controlled thickness and show how refractive index of these films can be changed via doping with Ag nanoparticles.

To obtain chitosan films with the required thickness, polymer solutions were spin-coated on quartz supports (n=1.46). The correlation coefficients (k) for the dependence of resulting film thickness (h) on chitosan solution viscosity (η) and rotation speed (ω) - $h=k\eta\omega^{-0.5}$ - were found for several types of chitosan in acetic and citric acids. The refractive index of chitosan films was estimated as 1.53 using the dry state ellipsometry. Depending on the chitosan film thickness (in the range from 0.5 to 2.5 µm), single-mode and multi-mode optical waveguides were obtained. It was shown that changing the refraction index of the chitosan films is possible via doping polymer layers with Ag^+ ions followed by "in situ" reduction and formation of Ag nanoparticles with the size below 10 nm. Variation of contact time and concentration of Ag^+ ions in solution during the adsorption step allows precise control over the doping level, and, as a result, increase of the refractive index of the pre-formed chitosan coatings at the wavelength of HeNe laser (**Fig.**). Analysis of waveguiding properties of such composites revealed no scattering losses at Ag content up to 1 % (v/v). Due to increase of the refractive index chitosan/Ag, composite films can be used for waveguide fabrication using substrates, which are significantly cheaper than quartz, e.g. sodium silicate glass.

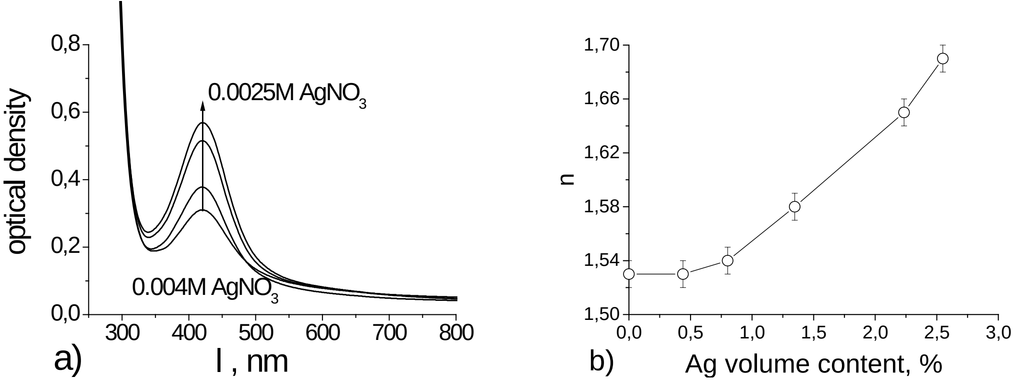

Fig. Absorption spectra of Chitosan/Ag composite films (a) and dependence of refractive index of the films on Ag volume content (b).

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Pentacyanoferrate(II) Complexes with N-Containing Derivatives of Chitosan and Polyallylamine: Synthesis and Cesium Uptake Properties

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Preparation and application of solid transition metals ferrocyanides for cesium removal have been extensively investigated over the last 50 years. Usually ferrocyanides are obtained as fine powders, which have superior sorption properties due to high surface area and fast kinetics, but are not suitable for the column application due to high flow resistance and low mechanical strength. These problems can be overcome by incorporation of ferrocyanides into the mechanically stable inorganic or organic polymeric matrix.

Here we report on synthesis of new organic-inorganic materials based on products of interaction between sodium aminoprusside and polymer ligands (chitosan (CS), N-2-(2-pyridyl)ethylchitosan (2-PC), N-2-(4-pyridyl)ethylchitosan (4-PC), N-(4-methyl-5-imidazolyl)methylchitosan (IC), N-(2-cyanoethyl)chitosan (CC), polyallylamine (PA), N-(2-pyridyl)methyl-polyallylamine (PMPA), N-2-(2-pyridyl)ethyl-polyallylamine (PEPA) and poly(2-vinylpyridine) (PVP)). The composition of the obtained materials was characterized using the element analysis and X-ray diffraction; the FT-IR spectroscopy and TGA data were used to propose the structure of the formed complexes. It was established that ion and ligand exchange were the main reactions at interaction of sodium aminoprusside with water-soluble polymer salts. Reactivity in complex formation reaction of unmodified polymers changes in a row: PA > CS > PVP. Modification of chitosan with 2-(4-pyridyl)ethyl and 2-cyanoethyl moieties enhance reactivity of chitosan to the level of PA, while introduction of 2-(2-pyridyl) and (4-methyl-5-imidazolyl)methyl moieties, on the contrary, decreases reactivity of chitosan to that of PVP. At the same time, functionalization of PA with 2-pyridylalkyl groups decreases its reactivity in reaction with aminoprusside ion. Thus, reactivity of all studied polymeric matrices changes in the row: PA ≈ 4-PC ≈ CC > CS > 2-PC ≈ IC > PMPA > PVP > PEPA.

The sorption capacity and distribution coefficients with respect to cesium ions have been determined for the synthesized complexes in cobalt(II) form. It has been shown that the complex of chitosan with pentacyanoferrate(II) has higher distribution coefficient with respect to Cs^+ ions, as compared to its N-derivatives and synthetic polymers. The maximum sorption capacity value for Cs^+ was found to be 0.3 mmol/g. Organic-inorganic materials obtained in the matrix of synthetic polymers have shown higher tendency to peptization and, therefore, lower sorption capacities and distribution coefficients. Functionalization of chitosan with N-containing moieties promotes the destruction of inner sphere of aminoprusside ion and results in formation of complexes with significantly lower cation exchange capacities compared to pentacyanoferrate(II) complex with unmodified chitosan.

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Adsorption of Gold nanoparticles into the Pores of Mesoporous Titania

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Background: Mesoporous Titania particles with crystalline framework and ordered pore arrangement can be obtained by mixing titanium oxosulfate and alkyltrimethylammonium bromide aqueous solutions.[1] On the other hand, many procedures have been proposed for synthesis of metal nanoparticles. But it is hard to obtain the monodispersed nanoparticles. So we attempted size separation of gold nanoparticles by mesopores.

Experimental: Mesoporous titania was prepared by mixing titanium oxosulfate and cetyltrimethylammonium bromide (CTAB) aqueous solutions at 40℃ for 1 day. Obtained white precipitation was filtered by membrane filter. The CTAB molecules in the pores were burnt out at 450℃. Gold particles with mean diameter of 1.5 and 4.2 nm were prepared according to the literature.[2,3] Then mesoporous titania powder was immersed into the gold nanoparticles dispersion. The size distribution and the amount of the gold particles left in the liquid phase was investigated.

Results and discussion: The color of the gold nanoparticles (1.5 nm) dispersion was weakened after immersion of mesoporous titania. On the other hand, the color of dispersion of gold nanoparticles (4.2 nm) was unchanged. Proportion of the number of small gold particles (1.5 nm) were decreased in the size distribution of the gold particles (mixture of 1.5 and 4.2 nm particles) after immersion of the mesoporous titania particles. Size separation of gold nanoparticles was successfully achieved with mesoporous powders. The pore volume of the mesoporous titania decreased after immersion in the gold particle dispersion. This shows that the particles were captured in the mesopores of titania particles and confirmed by TEM (Fig.1).

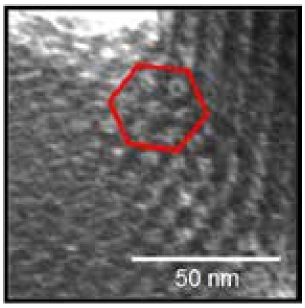

Fig. 1 Hexagonally packed structure of the mesoporous titania and adsorbed gold particles.

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Fabrication of Neuron-shaped Au Nanocrystals Using a Long-chain Amidoamine Derivative

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Controlling the morphology of metal nano-materials is essential to develop modern material chemistry because their physical and chemical properties can be easily and widely tuned by tailoring the size and shape. Among the unique shaped Au nanocrystals, one- and two-dimensional nanocrystals such as single crystal ultrathin Au nanowires (Au NWs) and highly branched dendritic Au nanowires (Au DNWs) have attracted considerable interest. In previous work [1-3], we has shown that an amphiphilic compound bearing two amidoamine groups (C18AA) acts as a low molecular weight organogelator and is a suitable phase transfer agent for Au NPs between organic solvent and water, because C18AA assembles as a lamellar structure in apolar solvents due to its hydrogen network structure and selectively adsorbs to specific Au surfaces of (100) and (110) facets. In this paper, we demonstrate that a single amphiphilic compound of C18AA enables the fabrication of water-dispersible ultrathin Au NWs by two steps [4-6]. The lamellar structure of C18AA can be used as a useful template for the formation of ultrathin Au NWs with diameters less than 2 nm and a few micrometers long, and moreover, the phase transfer ability of C18AA effectively forms water-dispersible Au NWs without a ligand exchange process. Further, we show the preparation of 2-dimensional dendritic Au NWs (2D Au DNWs) with diameters of 100-200 nm in an aqueous solution of C18AA, and they can be used as a seed to synthesize larger 2D Au DNWs with size 400-700 nm. We also present that seeded growth method can be applied to fabricate neuron-shaped Au NWs consisting of two DNWs dangling from the both ends of ultrathin Au NWs (Fig.1). C18AA is very useful for the preferential growth of Au from the (111) crystal facet. Since the both ends of ultrathin Au NWs prepared in the toluene gel of C18AA have (111) crystal facet, thus, we applied the seeded growth method to ultrathin Au NWs to obtain a hybrid nanostructure of straight NWs. In order to apply the seeded growth method to ultrathin Au NWs, 2wt% C18AA-water and HAuCl4 were added to the resulting aqueous dispersion of the ultrathin Au NWs and the mixed solution was left at room temperature for 3 day. We then successfully obtained novel neuron-shaped Au nanocrystal (Fig.1).

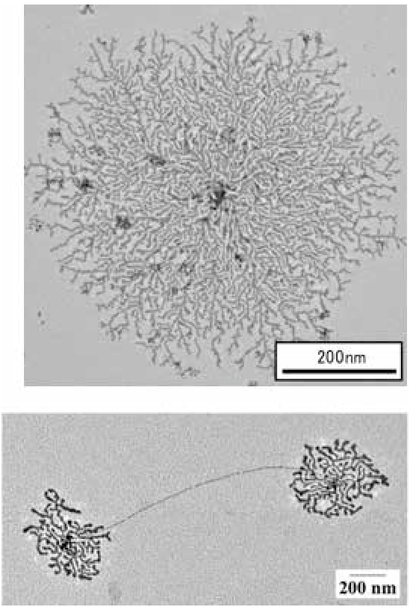

Figure 1. TEM images of 2D dendric Au NWs and neuron-shaped Au nanocrystal.

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The Modification of Polyelectrolyte Coatings for Biomedical Applications

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Bioseparation systems, diagnostic devices, drug delivery systems, a variety of biomedical implants are used in direct contact with biological fluids. There are a number of problems associated with such use of materials. One of the most significant is associated with the fact that on the surfaces exposed to solutions containing biological material the process of biofouling occurs. Biofouling is a common term used to describe the unwanted, non-specific adsorption of proteins on artificial surfaces, which significantly decreases the performance of modern biomaterials. Therefore, the development of the “antifouling” coatings protecting against non-specific protein adsorption is an important area of research within a broader field of biointerface science. A variety of approaches has been developed for modification of surfaces in order to eliminate or reduce protein adsorption. Immobilization of neutral hydrophilic polymers at a surfaces is one of the accepted methods to reduce non-specific adsorption of proteins, and one of the promising components that are suitable for surface modification aimed at preventing non-specific protein adsorption is poly(ethylene glycol) (PEG). On the other hand, the sequential adsorption of charged nano-objects e.g. polyelectrolytes or nanoparticles, method called layer-by-layer, is considered as one of the most promising techniques of surface modification and formation of highly tailored functional thin films for the wide range of applications, including nanomedicine. Multilayers thin films for such a purpose should be non-toxic and show minimal interaction with immune system, i.e. by the minimal non-specific adsorption of proteins. Therefore the goal of this work was to explore the method direct immobilization of PEG layer to reduce/eliminate non-specific adsorption of proteins at surface of polyelectrolyte multilayer thin films. Synthesized copolymers of poly(glutamic acid) or poly(L-lysine) with grafted PEG chains with various grafting ratio and various chain lengths, were used for that modification by formation of the external layer of films. The biofouling process was investigated by studying the adsorption of different proteins e.g. HSA, fibrinogen as well as proteins from Human serum, using QCM (Quartz Crystal Microbalance). The influence of the pegylated external layer on the permeability of polyelectrolyte multilayer film was determined by the electrochemical techniques (e.g. cyclic voltamperometry)

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Study of Interface and Stress Evolution in Cu/Au Bilayers Using Molecular Dynamics Simulation

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Multilayer thin film material systems play a prominent role in numerous applications in microelectronics, optoelectronics and magnetic recording. Irrespective of the deposition technique applied stresses are commonly generated during the process of deposition of thin films. One of the parameters influencing the stress in thin film systems is a mismatch of the lattice constants between the substrate and films. It is obvious that the stress evolution of thin films at early stage growth is open to discussion. The aim of this work is to investigate an interface effect on stress evolution in bilayers systems (flat and with strips/grains) using different kind of interactions. We used model with the Lennard-Jones potential and model based on embedding atom method [1].

Molecular dynamic simulations are used to study of interface and the evolution of stress during the deposition of Cu atoms on the (100) plane of Au. The Au substrate consists of an unmoved layer and a regular strips as a grains. We considered two cases of the substrate: substrate with different lateral correlations, and substrate with different size of grains. The simulation is carried out for three-dimensional systems with x-y periodic boundary conditions. The simulations were performed at different temperatures. During simulation the films grow according the Volmer-Weber mode with grains of nanometer size.

From the results of this study the following conclusion can be drawn [2]:

- For larger distances between strips/grains larger compressive stress is generated in systems.
- The grain size effect plays an important role in stress generation. With an increase in the grain size, the value of compressive stress decreases.
- The appearance of tensile stresses during the deposition of layers is associated with the coalescence of copper grains with gold grains during the layer growth.

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Enhanced Signaling in Thermoresponsive Microgels: New Opportunities in Electrogenerated Chemiluminescence

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Stimuli-responsive hydrogels, and especially bioresponsive ones, have already demonstrated their interest in biosensing applications using various transduction methods, including luminescence as an easy readout. These highly swollen networks undergo volume phase transition upon stimulus application, which modifies many of their physical properties. Among them, various hydrogels or microgels have been designed to perform a change in fluorescence upon network expansion or contraction.

Another way to generate luminescence is electrogenerated chemiluminescence (ECL). ECL is the process of light emission by the excited state of a luminophore that results from an initial electrochemical reaction at the electrode surface. It is a remarkably versatile and ultrasensitive method that has emerged in various research fields[1] and it has already proved its performances in immunoassays and multiplexed arrays[2].

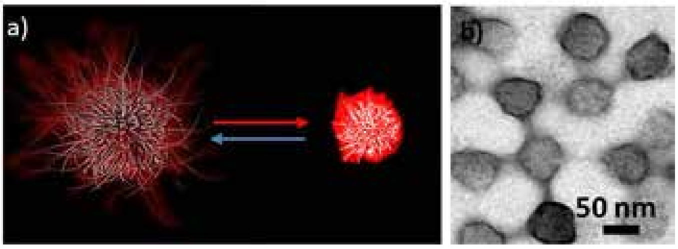

Fig. 1 a) Concept of luminescence enhancement upon microgel collapse at the swell-collapse transition; b) Image of Transmission electron microscopy of microgels.

In the present work, we synthesized microgels based on poly(N-isopropylacrylamide) (pNIPAM) copolymerized with a Ruthenium ($Ru(bpy)_3^{2+}$ monomer) complex. The electrochemistry, photoluminescence and electrogenerated chemiluminescence (ECL) of these thermoresponsive redox microgels were investigated. For the first time, reversible ECL enhancement is demonstrated in stimuli-responsive 100-nm microgel particles[3]. Such an unexpected amplification reaches 2 orders of magnitude and it is intrinsically correlated with the collapse of the microgel particles. The swell-collapse transition decreases the average distance between adjacent redox sites and favors the electron-transfer processes in the microgels resulting in the enhanced ECL emission. This study opens new perspectives towards applications in ultrasensitive bioassays.

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Growth and Dissolution of Equally-Sized Insulin Crystals

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A protocol for growing sets of nearly uniform size crystals was devised and tested experimentally [1]. The method was centered on insulin because of its medical significance however it is applicable to other crystalline drugs as well. An analytical model is developed now to describe quantitatively both growth and dissolution (in pure solvent) of equally-sized crystals; in the latter case it is based on Noyes-Whitney equation. The emphasis is put on the case when crystals number and/or size are sufficiently large to secure reaching solubility, while some non-dissolved crystalline substance is still remaining. Quantitative results were obtained for the relations between dimensionless values of crystal size, solution concentration and time elapsed, the assumption simplifying the calculations being that the crystals retain their shape during the entire dissolution process. Insulin binding to its receptors was taken into account as a next step in model elaboration. Under the assumption of insulin consumption in human body being a first order chemical reaction, stationary concentration level was established, which should settle due to the opposing action of crystal dissolution and consumption. It turns out that equilibration between them should establish upon achieving half the value of drug solubility, or closely to it. A conclusion was made that insulin crystals can dissolve sufficiently slowly to provide a long-term therapeutic effect.

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Acknowledgements:

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Synthesis and Surface Modification of Rod-Like and Spherical Silica Particles

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Micro-/nanoparticles with shape anisotropy have received considerable attention as compared with their spherical counterparts owing to their fascinating optical, electronic, and magnetic properties in materials sciences.[1] In particular, silica materials have several important properties that make them unique for many applications such as energy storage, chemical and biological sensing, food processing, drug delivery, and catalysis.[2]

We present in this poster the synthesis of rod-like and spherical shaped silica particles using sol-gel method. We performed a systematic study to modify the surfaces of these silica particles with functional groups to achieve minimal nanoparticle aggregation.

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Electro-Optic Properties of Liquid Crystal Devices Doped with Cucurbituril-protected Zirconia Nanowires

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Much attention has been paid to nanoscience and nanotechnology leading to nanodevices, because their developments are requested for the information technology revolution. Nanomaterials protected by organic molecules are now creating a novel architecture of materials different from either conventional bulk materials or atoms.1) Cucurbiturils, a series of cyclic oligomers of glycoluril doubly bridged by methylene linkers, have a pumpkin-like shape with all the ureido oxygen atoms being situated on both portals. The cavity is hydrophobic while the portals are hydrophilic. This study aims to synthesize cucurbituril-protected nanowires having high solubility into liquid-crystal matrices and to develop novel liquid crystal devices (LCD).

Zirconia protected by cucurbituril (CB-ZrO_2) nanowires were prepared by using a microwave reactor equipped with ultrasonic nozzle mixing at 240 ºC for 30 min in a tetraethylene glycol solution of zirconium (IV) ethoxide in the presence of CB. Transmission electron microscopy (TEM) images were observed with a JEOL TEM 1230 at accelerated voltage of 80 kV. The average width and length of CB-ZrO_2 nanowires are 240 nm and 13.7 mm, respectively (Fig.1). CB-ZrO_2 nanowires were mixed with 4'-pentylbiphenyl-4-carbonitrile at room temperature resulting in a liquid crystal sol of 4'-pentylbiphenyl-4-carbonitrile containing 0.075 wt% of total metal. The sols were injected into an empty cell for a TN mode with a cell gap of 5μm. A twisted nematic liquid-crystal device was fabricated by doping LC host matrices with CB-ZrO_2 nanowires. CB-ZrO_2 nanowires have high solubility into the liquid-crystal medium. The response time of this LCD in the presence of CB-ZrO_2 nanowires is faster than that in the absence. This result suggests that the presence of CB-ZrO_2 nanowires in liquid crystal makes it easy for liquid crystal molecules to change the viscosity probably due to the inclusion effect of CB upon intermolecular interactions among liquid crystal molecules.

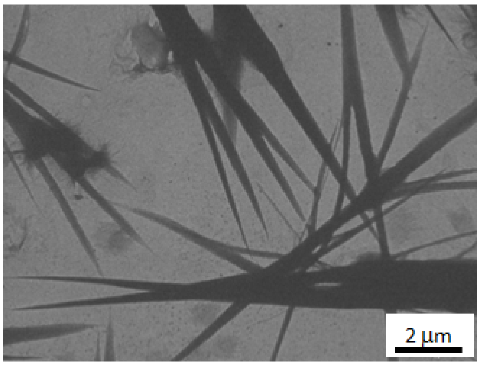

Fig.1 Transmission electron micrograph of cucurbituril-protected ZrO_2 nanowires

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Gold-Lustrous Organic Crystals Formed from Azobenzene Derivatives

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There is little research on low-molecular-weight organic compounds with golden luster. In this study, gold-colored crystals were prepared from low-molecular-weight compounds with an azobenzene group, i.e. bis[4-(3-methyl-butoxy)phenyl]diazene (**DC-azo, Figure 1a**). It was postulated that it would be essential for the plate-like single crystals to have smooth surfaces, and that these crystals must stack in order to obtain gold-lustrous crystals (**Figure 2a**). Recently, gold-colored organic crystals with luster were successfully prepared and formed from another azobenzene derivative (**bCOOEt-azo, Figure 1b**). In this study, the structure of gold-colored crystals formed from **bCOOEt-azo** was analyzed using spectroscopy and the method of synthetic organic chemistry. The influence of the thickness of layered crystals on gold luster expression was also investigated.

Azobenzene derivatives were synthesized, and the color and luster of the crystals were investigated by UV-vis measurements. The molecular arrangement in the crystal was estimated by X-ray diffraction (XRD) measurements.

Derivative **bCOOEt-azo** was recrystallized from a mixture of acetone and water. The precipitated **bCOOEt-azo** was yellow-colored, clear, and contained film-like crystals. The crystals were collected on filter paper and the thin film formed showed a gold-luster (**Figure 2b**). However, gold-colored crystals were not obtained from other azobenzene derivatives, which were synthesized with different molecular lengths and substituents. Total reflectance measurements in the visible light range indicated that the color of the **bCOOEt-azo** crystals was similar to that of metallic Au. In addition, the maximum specular reflectances of the gold-colored crystals were ca. 18% over the visible light range. XRD measurement revealed that the long-range *d*-spacing in the gold-colored **bCOOEt-azo** crystals was 1.41 nm. Considering the molecular length of **bCOOEt-azo**, the result indicates that the azobenzene moieties are oriented diagonally with reference to the crystal surfaces.

Next, the influence of the thickness of the **DC-azo** crystals on gold luster was investigated. The thickness of the **DC-azo** crystals was independent of the specular reflectance. However, the spectral shapes of the total reflectance in UV-vis measurements changed with the thickness of the **DC-azo** crystals. This indicates that the color of the **DC-azo** crystals varied from yellow to red through gold.

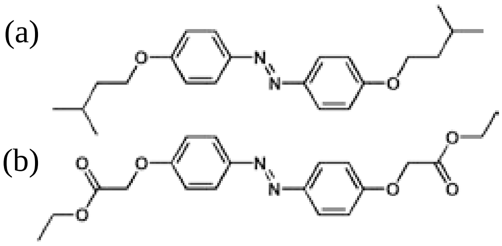

Figure 1: Chemical structure of (a) **DC-azo** and (b) **bCOOEt-azo**.

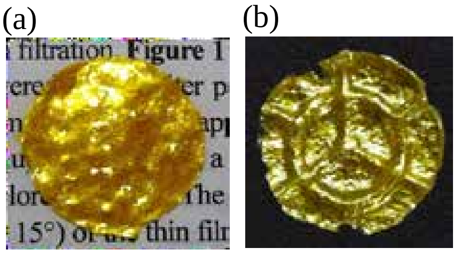

Figure 2: Gold-colored crystals formed from (a) **DC-azo** and (b) **bCOOEt-azo**.

Thin Film Formation of Colloidal Organic Semiconductor Materials Using Electrospray Deposition Method

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Organic semiconductor materials (OSMs) are materials of great interest for the development of new electronics, such as field effect transistors (FETs), light-emitting diodes (LEDs), and photovoltaics (PVs). Polymer semiconductor thin films are currently formed by spin-coating or ink-jet printing of a solution of polymer semiconductor dissolved in an organic solvent**.** Small molecules are mostly deposited by high-vacuum sublimation process. Photoelectric properties of OSM thin film are correlated to the nanoscale morphology in the inside of films. Controlling the molecular order in whole area of film is very difficult for any established thin film formation process. The use of colloidal OSMs proposes an attractive methodology for the production of organic electronics because they offer an opportunity to segregate the morphology control of organic molecules from the film formation process. In this manner, the electronic and structural properties of the OSMs could be optimized in the dispersions before the device is fabricated.

This study focuses in the formation and electronic property of colloidal organic photoconducting materials dispersed in water. In our experiment, colloids of OSM are generated from different types of OSMs, *i.e.* poly(3-hexylthiophene) (P3HT) and phenyl C61-butyric acid methyl ester (PCBM), by reprecipitation method, in which THF solution of the OSM is injected into vigorously stirred hot-water. The precipitate was filtered off and both THF and excess water were removed under vacuum. The resulting aqueous dispersions were coated on indium tin oxide (ITO) coated glass substrates by using electrospray deposition (ESD) method under a room temperature and atmospheric pressure. ESD method can be used to produce nanometer-scale thin films by electric repulsion of fine droplets.[1] The image of atomic force microscopy and scanning electron microscopy showed that electrospray-deposited films were composed of many nanoparticles arranged closely and disorderly (Fig 1). The time-photocurrent characteristics of Schottky cell (ITO/P3HT/Al) fabricated by ESD method was comparable to that of the cell fabricated using typical spin-coating method (Fig. 2). These results imply that the aqueous colloidal processing is a promising candidate for the manufacturing technique of organic electronics.

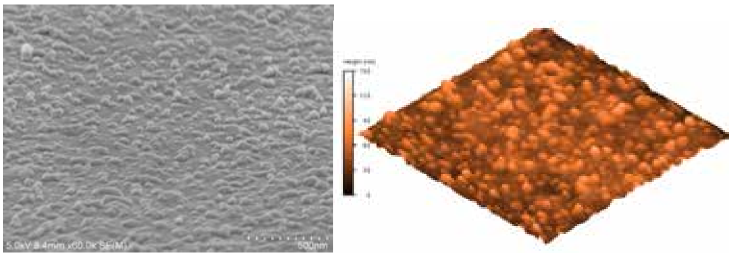

Fig.1 SEM (left) and AFM (right) images of colloidal P3HT film formed by ESD method.

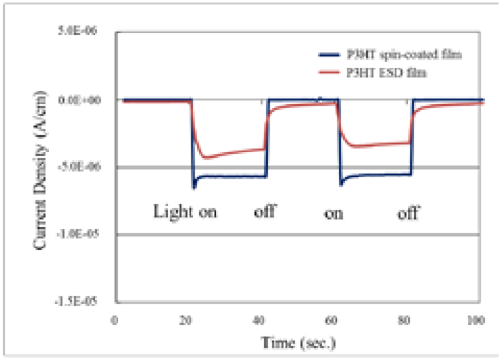

Fig. 2 Photocurrent response of Schottky cells composed of P3HT film formed by spin-coating or ESD method.

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Liquid Phase Synthesis of Highly Crystalline Transparent Conductive Oxide Nanoparticles

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Tin-doped indium oxide (ITO), an n-type transparent conducting oxide (TCO), have been extensively investigated due to many ITO applications as typified by a flat panel display technology and electrical paper, which utilize the unique properties of the high optical transparency of ITO in the visible region and its controllable low resistivity. In general, ITO electrode is industrially prepared by sputtering or laser deposition method followed by chemical etching process. On the other hand, in tandem with the penetration of a flat panel display, the world-wide demand for indium as a TCO has been remarkably increased so that the saving and utilization of indium becomes task of pressing urgency. In this regard, TCO nanoink, obtained by extremely stable disperse of ITO nanoparticles (NPs) into medium, has been paid attention as an alternative to the conventional processes, and the preparation of ITO NPs with high crystallinity and well-defined particle morphology is of particular technological interest to improve the resistivity of the ITO electrodes.[1,2] In the present study, we have investigated the solvothermal synthesis of ITO NPs with use of quaternary ammonium hydroxides.[3] As a result, monodispersed highly-crystalline ITO NPs with a cubic shape were prepared through a one step process from ethylene glycol solution mixture of indium and tin salts (**Fig. 1**). Their blue-coloured compacts exhibited low resistivity as a TCO. The formation of a gel intermediate, obtained by mixing with the indium/tin salts and quaternary ammonium hydroxides in the ethylene glycol solution, have been identified as a decisive factor for the precise control in size and shape of the resulting ITO NPs. Further, as indium-free TCOs, we have also investigated liquid phase synthesis of highly crystalline antimony-doped tin oxide (ATO), aluminium-doped zinc oxide (AZO), and gallium-doped zinc oxide (GZO) NPs. In particular, as shown in **Fig. 2**, cubic-shaped single-crystalline ATO nanoparticles were successively obtained in the presence of amine derivatives. Resistivity as well as ink property of TCO NPs thus obtained has been also investigated for the development of TCO nanoinks with low sintering property.

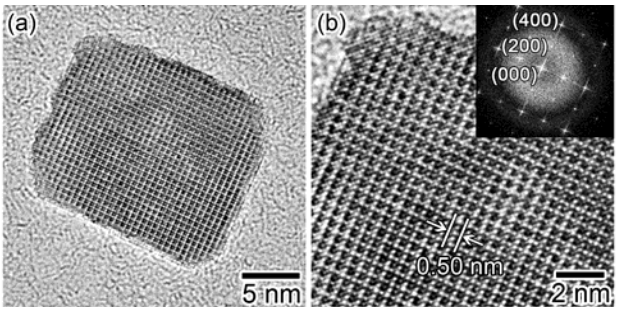

Fig. 1. (a) A HRTEM image of an ITO NP with a cubic shape; (b) A magnified and a FT images (inset) of the ITO NP exhibited in **Fig. 1a**.

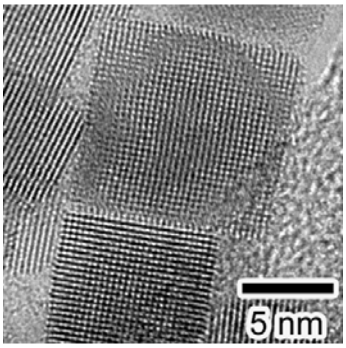

Fig. 2. A HRTEM image of an ATO NP with a cubic shape.

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Microgels in Membrane Technology: Thermoresponsive Membranes

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Microgels[1] represent hydrated polymer networks, whose binding capacity for water depends on their degree of crosslinking and upon solution pH and ionic strength. They are highly porous, mostly spherical particles with average diameter that can range from nano- to micrometer size and which form stable dispersions in aqueous phase. Recently aqueous colloidal microgels became a very important class of polymeric particles and found useful applications in different areas such as coatings, agriculture and medicine. Their potential for membrane applications lies in their modifiable and adaptive properties.

We recently surface-engineered flat sheet membranes via the layer-by-layer (LbL) assembly[2] of polyelectrolyte multilayers to enhance the performance of membranes.[3,4] In the present work, we investigate the potential of microgels in membrane technology, especially for filtration applications. The poly(vinylcaprolactam)-based microgels[5] exhibit thermoresponsive behaviour and were employed to modify ultrafiltration hollow fibre membranes by dead-end infiltration (inside-out as well as outside-in filtration). We will discuss experimental results such as real time transmembrane pressure (TMP) evolution during microgel filtration, clean water permeability tests, and the stability of such microgel-membranes not only as a function of time, but also of temperature. Indeed, we show that the thermoresponsive microgels retain their reversible sensitivity to temperature even when they are confined within the pores of the membrane. In addition we investigated the stability of the microgel coating under varying hydrodynamic conditions such as crossflow and backwashing. The permselectivity of the thermoresponsive membrane with regards to rejection of humic acid will be discussed as a function of temperature.

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