

# Synthesis of environment friendly biosurfactants based on vegetable oils and characterization of interfacial properties for cosmetic and household products formulations

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Recently, interest in biosurfactants has been steadily increasing due to their diversity, environment friendly nature such as nontoxicity and excellent biodegradability, possibility of large-scale production, selectivity, performance under extreme conditions, and potential applications in environmental protection [1]. Due to their unique functional properties, biosurfactants have been used in various industries including agriculture, fertilizers, petroleum, petrochemicals, cosmetics, pharmaceuticals, personal care products, food processing, beverages, textile manufacturing, metal treatment and processing, pulp and paper processing, paint industries and many others [2,3]. In this study, amino acid based biosurfactants were synthesized from renewable vegetable oils. The structure of the resulting products was elucidated by FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopies and environmental compatibility such as biodegradability and acute oral toxicity was evaluated. The interfacial properties of synthesized surfactants have been also examined such as critical micelle concentration (CMC), static and dynamic surface tensions, interfacial tension, wetting property, emulsion stability, viscosity, and foam property. The results indicated that synthesized surfactants have excellent interfacial properties.

Detergency test has been performed with newly synthesized surfactants by using an agitation/mixing type detergency tester at 25°C. The results suggested that the newly synthesized surfactants show moderately good detergency. Acute oral toxicity (LD<sub>50</sub>) measurement showed that newly synthesized surfactants are very mild compared with conventional nonionic and anionic surfactants used in detergent and cosmetic formulations such as polyoxyethylene (9) lauryl ether (PLA) and dodecylbenzene sulfonic acid (LAS). The primary biodegradability of newly synthesized surfactants has been found to be greater than 95%, suggesting that newly synthesized surfactants are acceptable for cosmetic and detergent applications. Both acute dermal irritation and acute eye irritation tests revealed that surfactants are mild. In particular, the prescription test in shampoo formulation prepared with synthesized biosurfactants indicated better sensory feeling and excellent foaming ability compared with conventional surfactants used such as silicon. The patch test also indicated no irritation during 48 hours, indicating potential applicability in cosmetic and household products.

**Acknowledgements** This work was supported by "the Technology Innovation Program 10050496", funded by the Ministry of Trade, Industry & Energy, Korea.

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# Clear solutions of Rebaudioside A and Sodium Oleate at neutral pH

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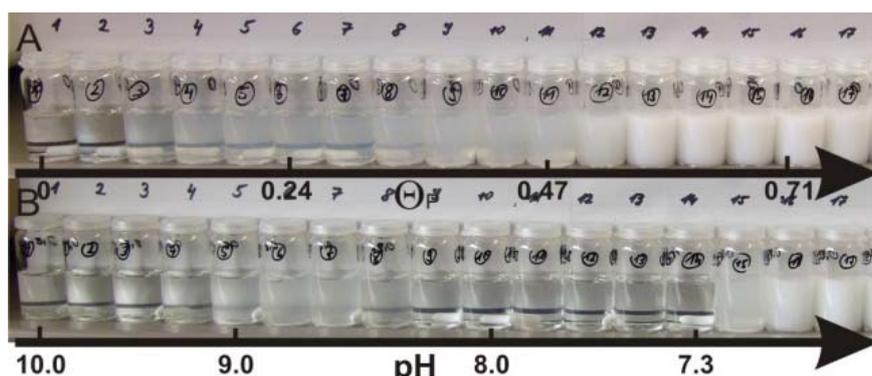
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Herein, we present a novel method for the preparation of highly translucent and macroscopically stable aqueous long chain soap solutions at neutral pH values[1]. This is for the first time that a long-chain soap could be really solubilised in water at neutral pH. The consequences for manifold now possible applications is evident, e.g. in food and cosmetics, whenever neutral pH values are mandatory.

Using the (food) emulsifier sodium oleate (NaOl), clear and stable aqueous solutions can only be obtained at pH values higher than 10. A decrease in the pH value leads to turbid and unstable solutions [2, 3]. This effect is not compatible with the formulation of stable aqueous formulations with a pH value lower than 8.5. In this work, we report on the effect of the (edible) bio-surfactant and high efficiency sweetener Rebaudioside A ("Stevia"), on the macroscopic and microscopic phase behavior of simple aqueous sodium oleate solutions at varying pH values. The macroscopic phase behavior was investigated by visual observation and turbidity measurements. The microscopic phase behavior was analyzed by acid-base titration curves, phase-contrast and electron microscopy.

We observed very interesting changes in microscopic and macroscopic phase behavior of the mixed NaOl/RebA/water systems compared to the pure aqueous NaOl system. In particular, it turned out that even at neutral pH, such systems are completely clear and stable for more than 50 days at room temperature. Figure 1 shows the difference in the macroscopic appearance of aqueous 1 wt % NaOl solutions at different neutralization states  $\Theta_p$  of NaOl without RebA (A) and with additional 0.8 wt% RebA (B). With soaps having a chain-melting temperature above room temperature, such as sodium dodecanoate and tetradecanoate, the effect of RebA was not observed due to the formation of crystals. At last, these findings were applied to prepare stable, highly translucent and drinkable aqueous solutions of omega-3-fatty acids at a pH value of 7.5.



**Figure 1:** The macroscopic appearance of aqueous 1 wt % NaOl solutions at different neutralization states  $\Theta_p$  of the soap without RebA (photo A) and with additional 0.8 wt% RebA (photo B) after 21 days of aging. The pH scale is only valid for the lower picture, since the addition of RebA reduces the pH value of aqueous NaOl solutions at a given neutralization state  $\Theta_p$ .

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# Polyelectrolyte induced swelling of an amphiphilic lamellar phase

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Oppositely charged polyelectrolytes and surfactants can associate to form a complex, with simultaneous release of counterions [1]. We have studied complexation of the cationic surfactant, didodecyldimethylammonium chloride (DDAC) and the anionic polyelectrolyte, sodium polyacrylate (PAANA) in water. Small angle x-ray scattering (SAXS) and polarizing optical microscopy (POM) studies reveal a unexpected transition between collapsed and swollen lamellar phases with decreasing water content. This transition can also be driven by the addition of NaCl at high water content. The swelling behaviour is observed only for low molecular weights of PAANA. On replacing DDAC by didodecyldimethylammonium bromide (DDAB), the system showed a transition from a collapsed lamellar phase to a swollen sponge phase [2]. These results indicate the influence of the adsorbed polyelectrolyte on the elastic moduli of the amphiphile bilayer.

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# Incomplete capsid formation: coarse-grained and elastic modeling

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We study the formation of stable incomplete capsids self-assembled from capsomers in solution by means of coarse-grained simulations and an elastic model. We show that during self-assembly, the favorable capsomer-capsomer binding energy competes with the unfavorable stresses generated by the rim of the caps and the elastic stretching due to the spontaneous curvature of the capsid. As a result of that competition, ribbon-shaped and incomplete capsids may emerge as stable structures on very specific conditions. We analyze the conditions required for this process to occur and the influence of the presence of an adsorbing surface in in vitro self-assembly.

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# Small-angle X-ray scattering studies on the structure of disc-shaped DPPC/Triton X-100 bicelles

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Disc-shaped bicelles can be formed spontaneously by mixing long-chain lipids with short-chain lipids at suitable ratios. The long-chain lipids form the bilayer core of the bicelle while the short-chain lipids form the rim of the bicelle. The typical mixed lipid bicelles have a relatively uniform diameter around 20 nm [1]. Bicelles can be doped with charged lipids to vary their surface charge density for encapsulating DNA for biomedical applications [2-4]. Other than using short-chain lipids, it is also possible to use bile salts to mix with the long-chain lipids to form bicelles, such as using the bile salt analogue CHAPSO. CHAPSO/lipid bicelles have a better structural stability than the mixed lipid bicelles. Recently, it was shown that adding Triton X-100 to lipid membrane could form well-aligned and stable bilayers that could improve the resolution of the solid-state NMR spectra of proteins. Although the non-ionic detergent Triton X-100 has been widely used in solubilising the lipid membranes, it is not clear whether it is possible to form bicelles with the Triton X-100 or not. In this study, we employed the small-angle X-ray scattering to investigate the structure of the mixed DPPC/Triton X-100 self-assembled aggregates at different mixing ratios. It was found that disc-shaped bicelles can be formed at a Triton X-100 to DPPC molar ratio around 1 to 2. As compared with the diC7PC/DPPC bicelle, which can be formed for a diC7PC to DPPC molar ratio around 0.2 to 1, it seems that it takes more Triton X-100 than the short-chain lipid to form bicelles for a fixed amount of DPPC. The diameter of the Triton X-100/DPPC bicelle is found to be significantly smaller than the diC7PC/DPPC bicelle and the thickness of the bicelle is also slightly smaller. Since the Triton X-100 has a high partition coefficient in lipid bilayer, part of the added Triton-X100 molecules are incorporated in the bilayer core region and it causes the average bilayer core thickness to become smaller. Since the Triton X-100 is a single chain detergent, it seems that Triton X-100 prefers to form the rim with a higher curvature (smaller bicelle).

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# Photomodulation of bacterial growth and biofilm formation using carbohydrate-based surfactants

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Naturally occurring and synthetic carbohydrate amphiphiles have emerged as promising class of antimicrobial and antiadhesive agents. Recently, light triggered antibacterial compounds have been used as an alternative to traditional antibiotics for controlling bacterial infections. In particular, the *trans-cis* photo-isomerization of azobenzene chromophore is a unique and powerful strategy for triggering changes in the molecular geometry and self-assembly of surfactant monomers. Herein, we incorporate variable carbohydrate head groups with hydrophobic *n*-butylazobenzene tail group to make an array of photoswitchable surfactants. The applicability of the azobenzene *trans-cis* photo-isomerization in these carbohydrate-based surfactants for effecting spatial and temporal control over bacterial activity was evaluated.

Through the reversible azobenzene *trans-cis* photo-isomerization, we achieved structural and stereo-chemical modification of the carbohydrate head group and revealed dramatic differences in the self-assembly and interfacial activity. By the aid of light illumination, these surfactants were assessed as modulators of bacterial growth and biofilm formation against multi-drug resistant (MDR) *Pseudomonas aeruginosa*, methicillin-resistant *Staphylococcus aureus* (MRSA) and Gram-negative *Escherichia coli*. These photoswitchable carbohydrate-based surfactants displayed dose-dependent, as well as bacteria- and photo-isomer specific biological activity, which suggests that these amphiphiles possess a selective mode of action. To further probe the mechanism of bioactivity, we evaluated the impact of *trans-cis* photo-isomerization in these surfactants on bacterial motility and revealed photo-modulated enhancement in swarming motility in *Pseudomonas aeruginosa*.

Such light-responsive amphiphiles will attract significant interest as a new class of antibacterial agents and as investigational tools for probing the complex mechanisms underpinning bacterial adhesion and biofilm formation.

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## Syntheses and Surface-Active Properties of New Amphoteric Photosensitive Surfactants Containing Azobenzene Moiety

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### ABSTRACT

New amphoteric photosensitive surfactants containing azobenzene moiety, which are surface-active and photosensitive, have been easily synthesized from alkyraniline by incorporating the glycidyl ether with an epoxy group into photochromic materials such as azobenzene compounds. The photoisomerization of the synthesized alkylazobenzene-4'-(oxy-2-hydroxypropyl)-N-methylaminoethyl sulfonate surfactant have been easily monitored by <sup>1</sup>H-NMR and UV/vis spectrophotometry. Methylazobenzene-4'-(oxy-2-hydroxypropyl)-N-methylaminoethyl sulfonate solution as well as azobenzene-4'-(oxy-2-hydroxypropyl)-N-methylaminoethyl sulfonate solution is isomerized to about 93 % *cis* form generated by 30 seconds of UV irradiation at 350 nm. The spectrum of the solution was regenerated by irradiation of the *cis* solution in the visible region ( $\lambda > 445$  nm). The *trans* form surfactant was regenerated and the total *trans* content was about 74 %. The critical micelle concentration (cmc) of the *trans* form of methylazobenzene-4'-(oxy-2-hydroxypropyl)-N-methylaminoethyl sulfonate surfactant is about  $1.50 \times 10^{-4}$  mol/L. Especially, the ratio of cmc *cis* to cmc *trans* of the synthesized derivatives is about 2.81 and 4.41 which is proportionally increased with the chain length of alkyl group. The minimum average area per molecule ( $A_{\min}^{a/w}$ ) for the *trans* and *cis* isomers of the surfactant is 0.75 and 0.83 nm<sup>2</sup>, respectively. The difference in the  $A_{\min}^{a/w}$  for the *cis* and the *trans* forms may be attributed to the effect of structure between planar *trans* azobenzene and bent *cis* azobenzene. Also, various physical properties such as critical micelle concentration (cmc), emulsion stability and foaming test of the synthesized surfactants have been carried out with respect to changes before and after the UV/vis light irradiation.

**Key words :** azobenzene, surfactant, surface-activity, photo-responsive, sulphonate

# New micelles of ionic carbosilane dendrons

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A novel family of amphiphilic ionic carbosilane dendrons containing fatty acids at the focal point have been designed, synthesized and characterized. A representative structure of an anionic dendron with palmitic acid at the focal point of the third generation can be seen in Fig. 1. Cationic dendrons with hexanoic acid at the focal point and homologous anionic dendrons have been also obtained. These dendrons spontaneously self-assemble in aqueous solution into micelles in presence of salt, as confirmed by surface tension, conductivity, and DLS measurements. CMC values ranges from 2 to 25  $\mu\text{M}$ . The results show that not only the length of the aliphatic chain but also the carbosilane scaffold play important roles in the self-assembly process. In such way, it is not necessary to include large hydrophobic tails in the carbosilane dendritic structure to observe an ordered aggregation behavior. It is enough with small lipophilic fragments and the use of high dendritic generations. Therefore, an optimal balance between hydrophobicity and hydrophilicity is required. So that, the amphiphilic dendrons built up from micelles with diameters of c.a. 4-6 nm.

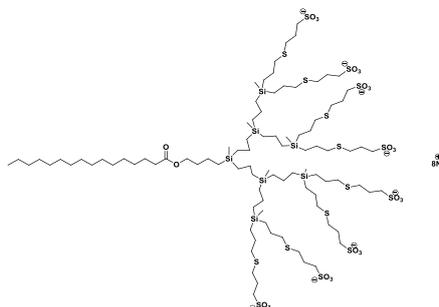


Fig. 1. Representative structure of an anionic dendron with palmitic at the focal point

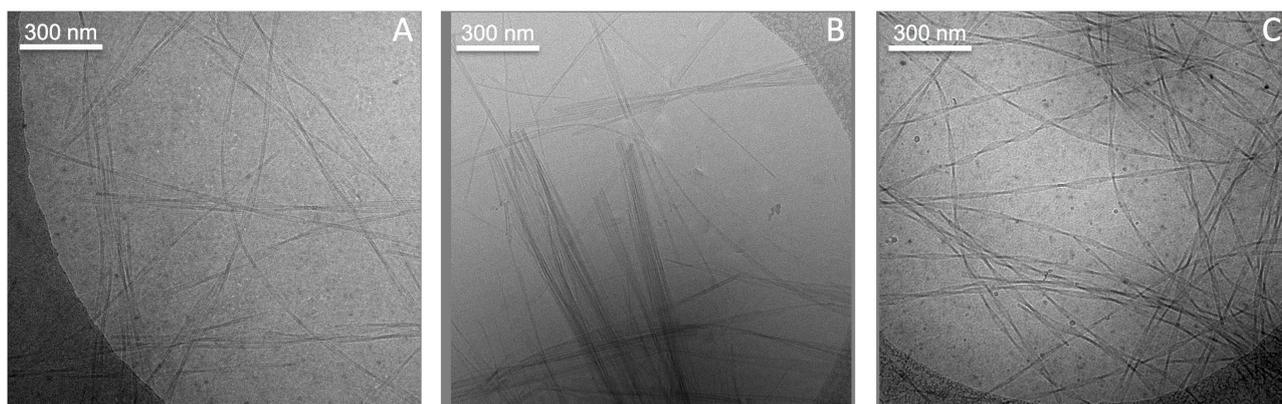
# Self-assembling properties in aqueous solution of the lipopeptide lauryl-Gly-Gly-D-Ser-D-Asp-NH<sub>2</sub>

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Lipopeptides are a remarkable class of amphiphilic biomolecules obtained by conjugating lipid chains to hydrophilic peptide sequences that are able to self-assemble into well-ordered nanostructures useful for biomedical applications. Lipopeptide self-assembly depends on the hydrophile/lipophile balance of the molecules and on the peptide portion that are able to adopt predesigned secondary structure and respond to external stimuli such as pH, temperature, and ionic strength [1,2]. Herein, the self-assembling properties of the lipopeptide lauryl-Gly-Gly-D-Ser-D-Asp-NH<sub>2</sub>, where the peptide moiety is designed to assume  $\beta$  sheet conformation, are investigated. The amphiphilic conjugate was synthesized by solid-phase synthesis and its self-aggregate features were investigated by NMR, circular dichroism (CD) and fluorescence spectroscopies, rheology, TEM and Cryo-TEM microscopies at various temperatures and pH and in the presence of divalent magnesium and copper ions. Cryo-TEM images showed that at room temperature in buffer solution, at pH=7.4, the lipopeptide is organized in twisted ribbons (Figure 1A); this result is supported by a very high molar ellipticity measured by CD spectroscopy. Heating the sample above 40 °C leads to a strong decrease in ellipticity, and upon re-cooling a sol-gel transition took place as clearly indicated by rheological measurements. Moreover, the effects of magnesium and copper ions added after the lipopeptide had already assembled in buffer were investigated. Cryo-TEM images showed that in the presence of Mg<sup>2+</sup> ions the lipopeptide self-assembled in well ordered flat ribbons where the supercoiled structures almost completely disappeared (Figure 1B). The molar ellipticity decreased accordingly. Instead, Cu<sup>2+</sup> addition to self-organized lipopeptide provided supercoiled ribbons with a highly regular pitch as shown by cryo-TEM images (Figure 1C). All these features along with the biocompatibility make this lipopeptide a promising candidate for biomedical applications.



**Figure 1** Cryo-TEM micrographs of lauryl-Gly-Gly-D-Ser-D-Asp-NH<sub>2</sub>: in buffer solution at pH 7.4 (A); in the presence of Mg<sup>2+</sup> (B) and Cu<sup>2+</sup> (C) ions.

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# INFLUENCE OF SURFACTANT STRUCTURE ON HIGHLY CONCENTRATED EMULSIONS STABILITY AND DRUG RELEASE

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Highly concentrated emulsions constitute an interesting class of emulsions because of the large internal volume fraction of the dispersed phase which is higher than 0.74, value corresponding to critical volume fraction of closely packed monodisperse spheres [1-2]. Due to their high internal phase ratio, the droplets are polydisperse and could show deformed polyhedral foam-like microscopic appearance. They are also called high-internal-phase ratio emulsions (HIPREs), or gel-emulsions since they present high viscosity and viscoelastic behavior.

The present work describes the influence of two different non-ionic surfactants, Cremophor RH40 and Tween 20, on stability of HIPREs and drug release. Formation of highly concentrated emulsions had been studied in water/non-ionic surfactant/Miglyol 812 systems by SAXS and optical microscopy. Liquid crystalline structures formed were characterized. Diclofenac sodium (DS) was incorporated in selected HIPREs and visual appearance, droplet size, morphology, rheological behaviour (viscosity,  $G'$  in the linear viscoelastic (LVE) region,  $G'$  in the critical deformation and  $G'$  as a function of frequency). DS in vitro release experiments were performed by Franz diffusion cells at 32°C using cellulose acetate membranes [3]. HIPREs stability was assessed by optical microscopy and rheology as a function of time. The results obtained showed a higher stability for HIPREs prepared with Cremophor RH40. Conversely, HIPREs prepared with Tween 20 showed changes in the microstructure and  $G'$  values were highly reduced. Stability differences could be related to the formation of liquid crystal structures in the water/Cremophor RH40/Miglyol 812 system. DS was released from HIPREs and slight differences observed could be attributed to emulsion structure.

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# Perfume solubilization effect on rheological properties of wormlike micellar gel in bio-based isosorbide surfactants systems

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We already reported the viscosity behavior of wormlike micellar system with hydrophilic anionic surfactant, sodium dodecyl sulfate (SDS) and hydrophobic POE-type nonionic surfactant, C<sub>12</sub>EO<sub>3</sub> by added perfume molecular structure [1]. In this work we chose a bio-based wormlike micellar system with hydrophilic anionic surfactant, sodium 5-*O*-dodecyl isosorbide sulfate (SDSS) and hydrophobic nonionic surfactant, 5-*O*-dodecyl isosorbide (5-DS). 9-Decen-1-ol and *p*-Cymene were added to the above wormlike micellar system as perfume compounds. Fig.1 shows viscosity behavior of the 3wt%NaClaq./SDSS/5-DS system with or without perfumes at constant surfactant concentration (5wt%). The perfume-free system gives the highest viscosity when the weight fraction of 5-DS in total surfactant ( $X$ ) was 0.18. On the other hand, perfume added systems, the maximum  $\eta_0$  shifts to lower  $X$  in following order 9-Decen-1-ol < (9-Decen-1-ol + *p*-Cymene) < *p*-Cymene. The relaxation time ( $\tau_R$ ) can be obtained by fitting the data from oscillatory-shear measurements to the Maxwell equations. The maximum  $\tau_R$  shifts to lower  $X$  in the same order as the maximum  $\eta_0$ .

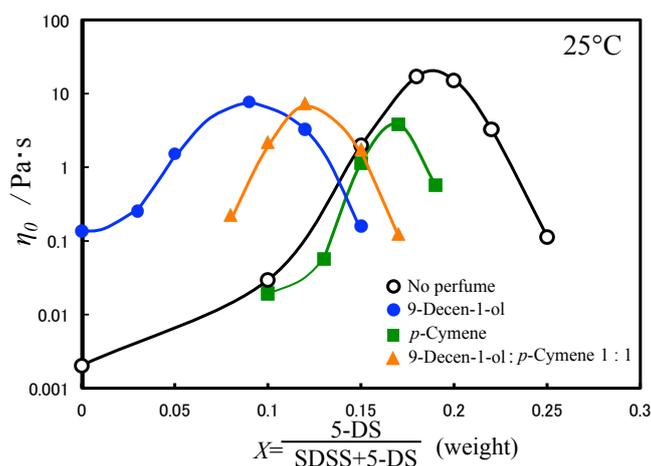


Figure 1 Zero-shear viscosity  $\eta_0$  plot against surfactant mixing fraction with or without perfume addition (0.25wt%).

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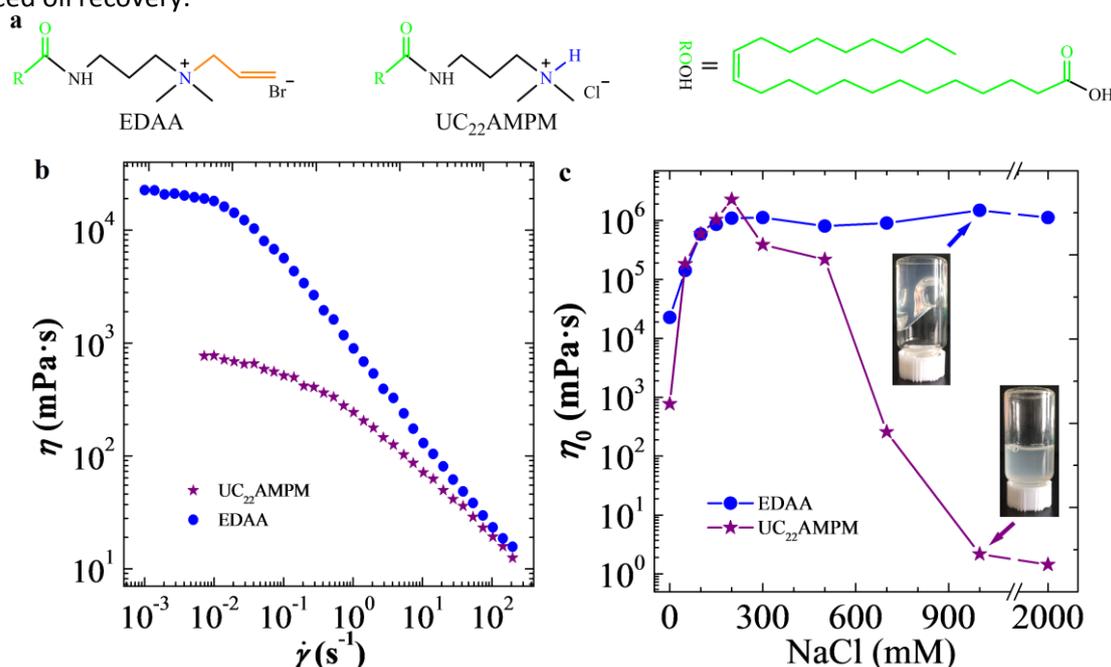
# The N-allyl substituted effect on wormlike micelles and salt tolerance of an cationic surfactant with C<sub>22</sub> unsaturated tail

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Wormlike micelles (WLMs) have been observed in a wide variety of cationic surfactants, but the research on the effect of substituent on the performance of cationic surfactants is relatively few [1-3]. Here we developed an N-allyl substituted cationic surfactant with an unsaturated C<sub>22</sub>-tail, N-Erucamidopropyl-N,N-dimethyl-N-allyl-ammonium bromide (EDAA), and compared with UC<sub>22</sub>AMPM. The surface activity, viscoelasticity and aggregate microstructure of solutions were investigated by surface tension, rheology and Cryo-TEM measurements. It was found that N-allyl substituent enabled EDAA to exhibit a lower critical micelle concentration and a higher viscosity without any hydrotropes. Upon increasing the concentration of NaCl, the viscosity of wormlike micelles in the solutions continuously increased and reached  $\sim 1.10 \times 10^6$  mPa·s at 200 mM. Further increasing the concentration of NaCl to 2000 mM, the viscosity remained at  $\sim 1.00 \times 10^6$  mPa·s without any reduction. The rheological experiments also indicated that the rheological behavior of EDAA solutions could be controlled by concentration and temperature. Cryo-TEM revealed the presence of giant WLMs in EDAA samples at room temperature. Besides, the EDAA worms also show some advantages such as low overlapping concentration ( $\sim 2.2$  mM) and stable over the whole pH range. EDAA has self-assembled into long flexible WLMs on its own and avoid the “chromatographic fractionation” occurs in multicomponent displacing fluids which shows more appealing potential for applications in enhanced oil recovery.



**Figure 1** (a) The chemical structure; (b) steady rheological curves; (c) effect of NaCl concentration on the zero-shear viscosity  $\eta_0$  for 30 mM EDAA and UC<sub>22</sub>AMPM solutions at pH 6.17 and 25 °C.

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# Thermodynamic study for micellization of imidazolium based surface active ionic liquids in water: Effect of alkyl chain length on N3 position

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The great potential of surface active ionic liquids (SAILs) for investigation of thermodynamics of micellization process in solutions due to possible variations in the structure of chain length and counter-ions has been demonstrated recently [1]. In many ways, their behaviour was found identical to those observed by “usual” surfactants: the critical micelle concentration is decreasing with the length of hydrophobic chain and expresses a minimum in the temperature dependence. The micellization process is endothermic at low temperatures and exothermic at high temperatures, but the extremely important role of counter-ions was observed. It was confirmed that the hydrophobicity of counter-ions evidently contribute to the heat capacity change and the water accessible surface area removal upon burial of non-polar group from the contact with water at micellization process. Even more, it can be assumed that all hydrophobic anions are partially incorporated in the micelles.

Whereas in recent work the influence of length of alkyl chain length and counter ion on the micellization properties of the 1-alkyl-3-methyl imidazolium SAILs in water was studied, in this contribution the investigation will be extended to a systematic study of influence of the alkyl chain length on the N3 position. The thermodynamic study of the micellization process of newly synthesized 1-dodecyl-3-ethyl- and 1-dodecyl-3-butylimidazolium bromide in water will be carried out by isothermal titration calorimetry in a broad temperature range. Experimental data will be analysed by help of corresponding model [1, 2, 3] and the obtained results will be compared to the values reported for 1-dodecyl-3-methylimidazolium bromide in water [1].

**Acknowledgements:** This work was financially supported by the Slovenian Research Agency through grant No. P1-0201 and Ministry of Education, Science and Technological Development of Serbia under project contract ON172012.

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# Synergistic micellar growth in mixed surfactant solutions: Rheology and cryo-TEM imaging

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L. Abezgauz<sup>2</sup>, I. Lieberwirth<sup>3</sup>, K. Koynov<sup>3</sup>, P.A. Kralchevsky<sup>1</sup>

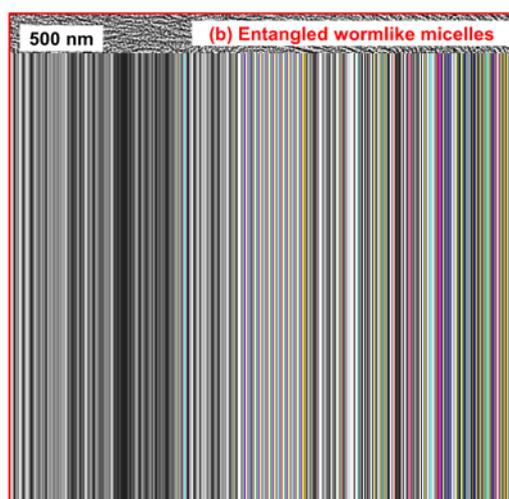
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We studied the synergistic growth of giant wormlike micelles in ternary solutions, which contain a zwitterionic surfactant (CAPB, cocamidopropyl betaine), an anionic surfactant (SLES, sodium lauryl-ethersulfate) and a fatty acid. For a given fatty acid concentration, the viscosity  $\eta_0$  exhibits a sharp and high peak (Fig. 1), which in the case of octanoic acid (HC8) reaches 41 000 times the viscosity of water [1]. The peak height decreases as a function of the fatty acid chainlength until it completely disappears for hexadecanoic acid. Experiments with polarized-light microscopy and NMR showed that all examined solutions are isotropic, rather than liquid-crystalline. The cryo-TEM imaging revealed complex phase behaviour: (i) growing rod-like micelles to the left of the peak; (ii) entangled wormlike micelles at the peak (Fig. 1); and (iii) multi-connected structures for octanoic acid versus shape transition into disc-like micelles for dodecanoic acid after the peak [1,2]. The two scenarios in (iii) explain the viscosity reduction by making a direct correlation between rheology and microstructure.



**Figure 1:** Viscosity peak and microstructure in the presence of octanoic acid (HC8).

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# Preparation of sugar based vesicles by injection method: role of the solvent chain length

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Within the different ways of preparing vesicles, the ethanol injection method is one of the key methods. It consists of the vesicle formation by the mixture of two phases, one of which containing the surfactant dissolved in ethanol. [1]

Sorbitan esters (Span) are nonionic surfactants with low HLB values, thus compatible with lipophilic materials. Niosomes are nonionic vesicles that have been attracting various studies to their incorporation in pharmaceutical products. [2]

The Span used in this work are Span 20, 40, 60, 65, 80 and 85, all of them were solubilized in methanol, ethanol and propanol, and the solutions were then injected in water, at 70 °C, 80 °C and 100 °C, respectively, and 1000 rpm, to form non-ionic sugar vesicles. The influence of the solvent chain length on the vesicular size and emulsification index was investigated. The obtained results indicate that the chain length of the alcohol - where the surfactants are solubilized - has a crucial role in vesicular size and emulsification ability of non-ionic vesicles.

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# Gemini-bolaform hybrid-type lipids as efficient nanocarriers in gene therapy

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Genetic disorders involve a high percentage of total number of diseases, so a suitable and economic treatment is essential to eradicate them [1]. In the last decades, researches are focused on solving these diseases through the substitution or silencing of the damaged gen. However, due to the DNA negative charge, the interaction with the cell membrane is strongly hampered. In order to overcome this barrier, a wide variety of cationic vectors has been designed and developed. In particular, gemini cationic lipids (GCLs) have been extensively used due their low toxicity, easy of manufacturing and high versatility for biological applications [2]. On the other hand, bola-amphiphile lipids (BA) are other type of cationic vectors, normally used on pharmaceuticals research [3]. In this work, we have evaluated the performance as a gene vector of a mixed system consisting of the commonly used DOPE, as adjuvant and fusogenic lipid, and a gemini-bolaamphiphilic lipid (GBA), with a hybrid structure between that of a gemini lipid (GCL) (as it contains two secondary amine-type cationic heads attached to two short hydrophobic chains of 6 C atoms), and that of a bolaamphiphile (BA) (in the sense that these cationic heads are connected by a long spacer of 22 C). The disproportion in the length of the hydrophobic chains (6C) with respect to that of the spacer (22C) causes the latter to potentially play a leading role in the self-aggregation process on which the posterior formation of the lipoplex is based when the DNA is present. This lipid-type nanocarrier (designated as C<sub>6</sub>C<sub>22</sub>C<sub>6</sub>) has been used in this work to compact and transfect two DNA plasmids to COS-7 cells *in vitro*: one encoding GFP (pEGFP-C3) and another encoding Luciferase (pCMV- Luc). The study has been carried out using several biophysical experimental methods, such as electrophoretic mobility/zeta potential, gel electrophoresis, small angle X-ray scattering (SAXS) and cryogenic electronic transmission microscopy (cryo-TEM) to determine the charge, size, structure and compaction capability of the vector, together with several biochemical experiments, such as FACS, cell viability/cytotoxicity, and protection against DNases assays to evaluate its potential as an efficient and safe gene nanocarrier. The whole ensemble of biophysical and biochemical outcomes of C<sub>6</sub>C<sub>22</sub>C<sub>6</sub>/DOPE-pDNA lipoplex indicates that this system may open a novel and promising via in the gene therapy field using gemini bolaamphiphilic vectors.

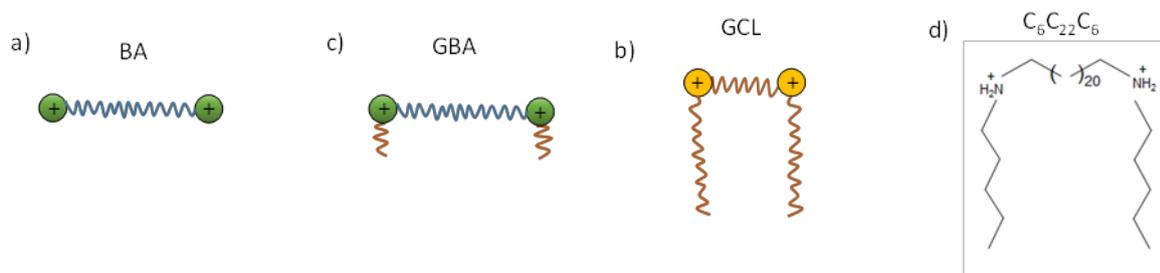


Figure 1. Schematic draw of: a) Bolaform lipid (BA); b) Gemini lipid (GCL); c) Gemini bolaform lipid (GBA) and (d) structure of C<sub>6</sub>C<sub>22</sub>C<sub>6</sub>.

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# Natural aging of LbL films containing associative polymers or their complexes with surfactants

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# SYNTHESIS OF KERATIN FOAMER AND THE INFLUENCE OF SURFACTANT ON ITS FOAMING ABILITY

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According to statistics, every year more than 40 thousand tons of wools, hooves and horns are got rid of as waste from slaughterhouse in Republic of Kazakhstan. The thrown away wastes from slaughterhouse such as wool, horn, hoofs cause the environmental pollution and it might be harmful to human's health. Proteins from the different classes of wool keratins possess characteristics that give them unique advantages in specific applications. Wool and hair are examples of hard  $\alpha$ -keratin. All keratins are characterized by a high level of the sulphur-containing diamino-acid cystine, which acts as a cross-linking point between protein chains. This feature of a high-level of interchain crosslinking through cystine gives the keratins, especially the hard keratins, their characteristics of toughness, durability, resistance to degradation, and desirable mechanical properties. Cystine contents vary widely in the keratins, which is reflected in their variation in mechanical properties [1-4].

The samples of technical foamers based on keratin materials were obtained by method of alkaline hydrolysis. The optimum temperature of reaction is 403K. Conducted by IR spectroscopic studies of the hydrolysis reaction products were shown the identify of the samples of keratinic foaming agents, obtaining at 403K and at 433K. Proposed structure of the samples has  $\alpha$ -helical configuration of laying chain and samples of amin acids with peptide bonds.

As it is known the efficiency of foaming and foam-stabilizing action increase for compositions of surfactant with water soluble polymers [5,6]. The effect of surfactant - cetyltrimethylammonium bromide (CTAB) on the foaming and foam-stabilizing ability of keratin foamer was studied. In mixtures with increasing concentration of CTAB before CMC ( $10^{-3}$  mol / l) lifetime foam rises to 30-40 minutes and reaches 600 ml due to the formation of mixed adsorption layer at the water-air interface, wherein the low molecular surfactant (CTAB) reduces the surface tension and keratinous foaming increases the viscosity of inter layer liquid.

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# Soft nanostructures based on antennary peptide amphiphiles

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Antennary peptide amphiphiles are synthetic products, produced recently as a result of preliminary molecular design [1]. They are biocompatible and nontoxic to life organisms thus having high potential for e.g. bioanalytic and biomedical applications, design of electronic and smart materials, water-purity-control applications and etc. [2-4]. These molecules constructed as two or three oligoglycine chains of equal length (Gly<sub>n</sub>, n=1-9) attached to a branching core (either  $\alpha,\omega$ -diaminoalkane, NH(CH<sub>2</sub>)<sub>2-10</sub>NH, or triaminomethyl carbinol, [NHCH<sub>2</sub>]<sub>3</sub>CCH<sub>3</sub>, units). The peptide chains that are usually terminated with amine group, comprise hydrophilic portion of the molecules, whereas the core is their hydrophobic part. The described peptide amphiphiles are capable of spontaneous assembly in solution forming extended flaky nanoaggregates (tectomers) or at interfaces generating ultra-smooth layers or coatings. The key phenomenon driving the formation of these nanoscale structures is the onset of specifically ordered inter- and intramolecular systems of H-bonding on very high cooperativity level (the so-called Polyglycine II type of structure). Noteworthy, length of the peptide chains and nature of the core unit are expected to modulate supra-molecular properties of the peptide amphiphiles.

A combined procedure is developed, including the registration of inception and stability of the bulk aggregates of various sizes and charges, examination of the properties of the interfacial layers at the solution/air boundary and the drainage characteristics of microscopic foam films, as well as and solution/solid plate and wetting films. The experimental methodology includes the application of various research techniques: Profile Analysis Tensiometry, microscopic thin foam and wetting films, Contact Angle measurements, Scanning Electron Microscopy, Dynamic Light Scattering. Due to the specific structure and properties of the obtained nanostructures, these complex fluid systems are prone to smart regulation by mild changes of pH, the wetting properties of the solid surfaces and/or the addition of charged additives (low-molecular-mass electrolytes or high-molecular-mass substances).

The obtained results add new knowledge to structure-properties relationships of the investigated aqueous formulations and give important hints related to the effect of specific composition of the systems and the approach to fine-tuning of their performance. The experimental observations are related to possible applications in medicine, pharmaceutical industry, environment protection development, etc.

## Acknowledgements

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# Annealing in polyelectrolyte multilayers: influence of entanglements

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Polyelectrolyte multilayer films were assembled by the layer-by-layer (LbL) technique using poly(styrene sulfonate) PSS as polyanion and poly (diallyldimethylammonium) (PDADMA) as polycation. The first compartment of the film is built with protonated PSS, the second compartment with deuterated PSSd. To understand the microscopic dynamics of entangled synthetic polyelectrolytes in a dense liquid of diffusing, interpenetrating random walks, the films were annealed in 1 M NaCl and the time dependent intermixing was recorded with neutron reflectivity. Thus, the diffusion coefficient of PSS was determined. The molecular weight of PDADMA and the salt concentration of the deposition solution were varied. If the deposition solution contained 0.1 M NaCl, the diffusion constant was largest when PSS and PDADMA had the same degree of polymerization. The diffusion constant dropped by two orders of magnitude, if  $M_w(\text{PDADMA})$  was decreased. The slowed down center of mass movement of long PSS chains is attributed to entanglement with different PDADMA molecules. The diffusion constant increased by more than one order of magnitude, if the polyelectrolyte multilayer was built from a deposition solution with 0.005 M NaCl. With these preparation conditions, PSS is adsorbed flatly with little entanglements. To summarize, the diffusion constant could be varied by four orders of magnitude. The results highlight the influence of entanglements on the diffusion of polyanions within polyelectrolyte multilayers and indicate ways to tune the diffusion constant.

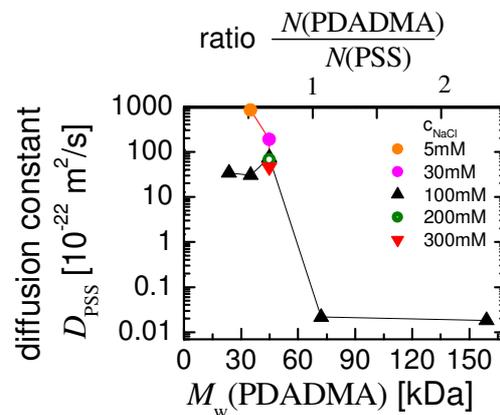


Fig. 1. The diffusion coefficient of PSS in a polyelectrolyte multilayer immersed in 1 M NaCl solution. Shown is the dependence on the molecular weight of PDADMA ( $M_w(\text{PSS}) = 76$  kDa). Varied is the salt concentration in the deposition solution as indicated.

# Study of Structure of Mixed Reversed Micelles on the Basis of Polyoxyethylene (4) Lauryl Ether and Sodium Cholate

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Reversed micelles are successfully used as microreactors for enzymatic catalysis, as well as for mimicking biological membranes. The additives of biological surfactants bile salts are of special interest because of wide spectrum of their application, e.g. they are used in micellar and biopartitioning liquid chromatography, also in micellar capillary electrokinetic electrophoresis [1]. Micelles of bile salts solubilize cholesterol, fat-soluble vitamins and bilirubin in the intestine [2]. Bile acids influence drug absorption and transmembrane transport and they are called as absorption enhancers [3,4]. It is found that bile salts effect percolation and size of reverse micelles [5]. Bile salts can act as an organogelator in the process of self-aggregative organic gel formation [6].

The purpose of the presented work was study of influence of structure of the water droplets of mixed micelles based on polyoxyethylene (4) lauryl ether (Brij-30) and sodium cholate.

The microstructure of Brij-30 reverse micelles at different concentrations of sodium cholate was investigated with an infrared spectroscopy method. Deconvolution of the O-H stretching vibrational absorption spectra in the region of 3000-3800  $\text{cm}^{-1}$  into three subpeaks (free, bound and trapped water fractions) with a Gauss fitting program and Monte Carlo method was accomplished. Results show, that suppression of free water fraction takes place in the water pockets of the reverse micelles with increasing of concentration of sodium salt of cholic acid.

The microenvironment of mixed reverse microemulsions (Brij-30+sodium cholate) was investigated with an ultraviolet-visible spectroscopy by using of ortho-nitroaniline and methyl orange as molecular probes. The values of binding constants and association degrees of ortho-nitroaniline and methyl orange with Brij-30 reverse micelles at different concentrations of sodium cholate were determined.

Different parameters viz. volume fraction of the water droplets, their relative density, the concentration of micelles, aggregation number, etc. were calculated on the basis of viscosity measurements. Viscosity was measured with an Ostwald viscometer. The viscosity of microemulsions was related to the volume fraction of water droplets by the equation given in literature [7]. The abovementioned parameters were calculated by the methodology described in the same work. In addition, density changes of water droplets of the reverse microemulsions under the influence of additives of sodium cholate were estimated.

Results may be useful in the investigations of water structure, when it is confined to nanometer-scale cavities.

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# Aggregation of colloidal spheres mediated by Janus dimers

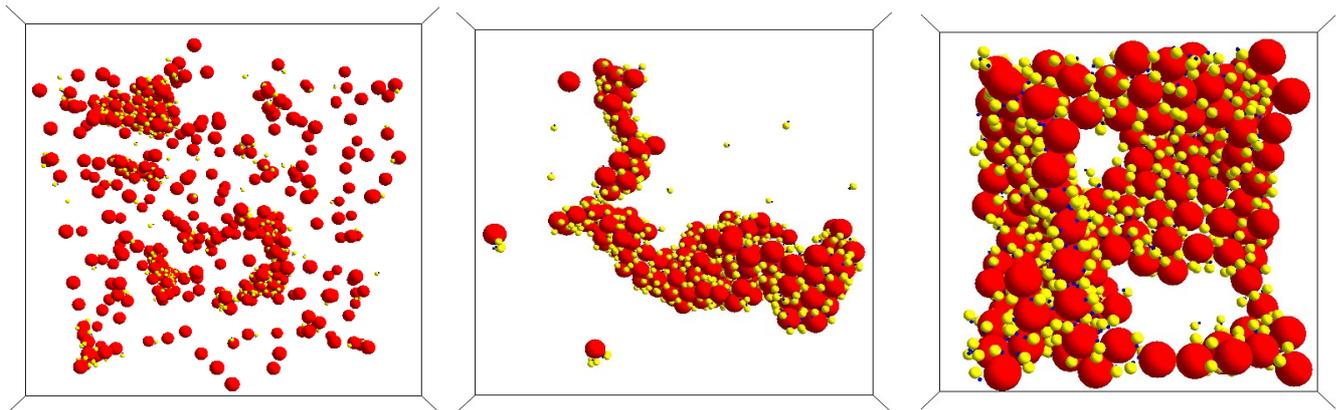
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The phase behavior of colloidal mixtures is currently one of the most investigated topics in soft matter. This is especially due to the large variety of superstructures that can be found in such mixtures under proper conditions: it has been observed experimentally that when cooled to a sufficient degree, colloidal mixtures may phase separate/demix [1] or form aggregates (micelles, clusters, lamellae, etc.) [2], as a result of the attractive forces between the particles. From a theoretical point of view, colloidal solutions can be modeled as systems of macroparticles with effective interactions implicitly accounting also for the solvent.

Here we investigate by Monte Carlo simulation the structure and self-assembly of a mixture formed by asymmetric dimers and larger spherical particles. In our model, dimers and spheres interact through a monomer-specific short-range attraction, in addition to hard-core repulsion. The interaction properties are chosen so as to mimic features of real colloidal mixtures. Within our choice of interactions, the dimer behaves as made of a solvophobic particle, namely the small monomer, and an inert large monomer, whence the designation of Janus (i.e. amphiphilic) dimers [3]. We find that the dilute mixture is characterized by the onset of low-temperature aggregates: when the sphere concentration is sufficiently high, such aggregates are in the form of clusters of spheres glued together with dimers; for lower concentrations, a liquid-vapor phase separation takes place. Upon increasing the density, a sponge-like structure eventually emerges for intermediate concentrations. If the attraction between dimers and spheres is switched off, leaving only depletion forces to act, neither phase separation nor demixing are found.



**Figure:** Low-temperature phase behavior of the mixture: cluster structures (left), gas-liquid phase separation (centre) and sponge-like structures (right).

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# Alkylglycoside surfactants with oligomeric head-group: investigation of self-assembly and its implications for future applications

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The increased effort to preserve the environment has driven extensive research toward the identification of surfactants that are nontoxic, biodegradable, and synthesized from sustainable resources[1]. Alkylglycosides, which have a head-group consisting of one or several sugar moieties, promise to meet these demands. Alkylglycoside surfactants with functionalised oligomeric head group (>3 sugars) have recently proved possible to synthesize by enzymatic means[2,3]. This novel class of surfactants has been specifically designed to ensure biocompatibility and controlled biodegradability, and hence lend themselves to applications within the life sciences.

Our study focused on a surfactant comprising a long alkyl chain, 16 carbons, and a long glucose chain, 8 glucose units, which is referred to as C<sub>16</sub>G<sub>8</sub>. Since the functionalities and possible applications of C<sub>16</sub>G<sub>8</sub> can compete with the widely used Polysorbate 80, we investigated thoroughly the self-aggregation mechanism. We characterised the system with several techniques, such as light scattering, both static (SLS) and dynamic (DLS), NMR, SAXS and SANS. Light scattering showed the presence of large aggregates ( $R_H \sim 60$  nm), whereas data from NMR diffusometry are compatible with aggregates that are ten times smaller. SANS was crucial to collect information on the structure of both aggregate types at the same time, and to quantify their relative presence. The larger aggregates have a disc-like shape, most probably a portion of bilayer lamella, while the small aggregates have an elongated shape. Consequently, C<sub>16</sub>G<sub>8</sub> is a surfactant in which two different modes of self-aggregation operate side by side.

We will discuss the effect of temperature and concentration on the size and shape of the aggregates and, furthermore, the effect of different anomeric configurations. The combination of these techniques allowed us to reveal the features of this novel sugar surfactant and build a fundamental knowledge required for identification and development of applications.

## Acknowledgements

This work has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 606713. The SANS study was allowed by allocations of beam time at the ILL (Grenoble, France).

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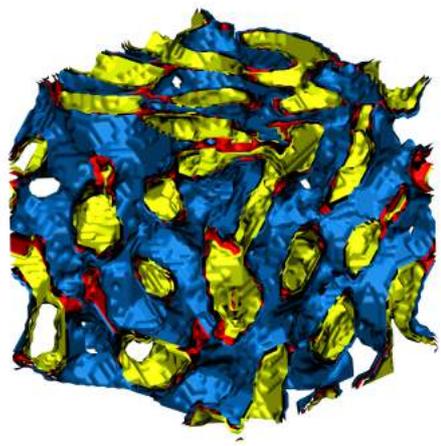
# Modelisation of microemulsion for liquid-liquid extraction.

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Random wave models of microemulsions with high spontaneous curvature and weak aggregation (high CMC or CAC) have been recently shown to capture the features of scattering measured and going from Ornstein-Zernike to a Porod limit [1]. Moreover, domains of local stability in a triangle can be found, using a rough approximation of the bending energy [2]. Last but not least, the previously unexplained “jump” between frustrated and unfrustrated local microstructures has been explained [3]. However, all these results were obtained using two level cuts with a zero order approximation of the entropy, valid only around 50% of polar phase. The vast majority of microemulsions used in Winsor II regime have typically 10-20% of polar domain and a spontaneous curvature of the order of the chain length. The bending energy is harmonic in packing parameter and the free energy of transfer between pseudo-phase cannot be neglected near the Lifshitz line. We present in this work the results obtained combining film entropy, and frustration combined with the transfer of extractant from the bulk to the interface as well as complexation or electrostatic interaction.



**Figure 1** Example of microemulsion generated with our code (only interfaces are shown, water in blue, oil in yellow)

**Acknowledgements** The financial support of the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement n. [320915] "REE-CYCLE": Rare Earth Element reCYCling with Low harmful Emissions.

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# Droplet Drying Kinetics: Inter-particle Interaction

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The evaporation of a droplet of colloidal suspension has attracted considerable research attention because of its inherent complexity as well as its important industrial applications such as coating, printing and layering processes [1,2]. In particular, there has been great interest in controlling the well-known 'coffee-ring' effect, in which the contact line of a drying drop is pinned on the substrate so that dispersed particles are deposited onto the triple point contact line [1]. Our aim is to explore the role of inter-particle forces on this evaporation-induced particle deposition by studying the drying of highly charged non-polar suspensions.

The surfactant, dioctyl sodium sulfosuccinate (AOT), was used to produce controllable long-range electrostatic interactions in a suspension of monodisperse, fluorescent poly(methyl methacrylate) (PMMA) in a series of alkanes. Confocal Light Scanning Microscopy (CLSM) was used to characterise the deposition of the particles onto hydrophobically-modified glass. The existence and extent of a coffee-ring deposit was studied over a wide range of AOT concentrations.

For higher volatility solvents, hexane in this case, the PMMA deposition is always influenced by the fluid flow at all AOT concentrations. With increasing AOT concentration, particle deposition becomes more uniform over the droplet radius. Meanwhile in dodecane, the addition of AOT in the system contributed to a number of effects namely, electrostatics and particle-substrate interactions and also contact line mobilization. These affects differently to the drying droplet patterns. The particle charging effect on the 'coffee-ring' suppression is also clearly seen in the hexane system, using the highly-charged poly(ionic liquid) PMMA particles.

The drying patterns are largely influenced by the evaporation rate of the solvent (drying kinetics) and concentration of AOT added (particles-substrate and particle-particle interactions), which contribute to the electrostatic charging of the system (electrokinetics).

We would like to thank the Ministry of Higher Education Malaysia and University of Science Malaysia for research funding.

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# Viscosity increase and control of N,N-dialkylamide extractants in presence of uranyl

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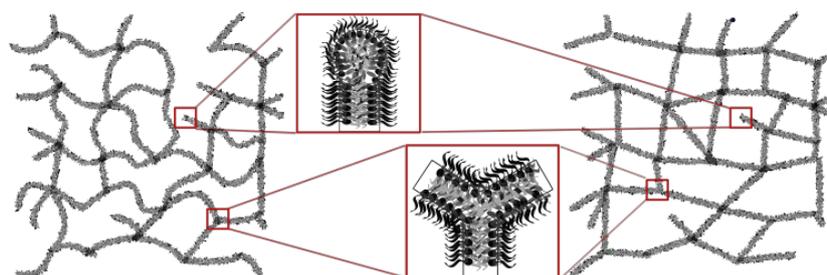
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Liquid-liquid extraction is the central technology in metal recycling. An important application is the recovery of major actinides – Uranium and Plutonium – in the framework of the required closing of the nuclear fuel cycle by using fast neutrons in the future. Emulsification and demulsification in extraction devices are only efficient when the difference in viscosity between organic and aqueous phase is small. Even if the processes using Tributyl phosphate (TBP) as selective extractant are known since world-war II, economic and technical reasons motivate the research for alternative extractants. One promising approach is the use of N,N-dialkylamides which also have a high affinity towards Uranium and Plutonium and significant advantages over TBP. The main disadvantage of N,N-dialkylamides is the viscosity of the organic phase which increases exponentially when processes are intensified by increasing uranyl and extractant concentration.

By combining scattering and phase analysis, we show that the viscosity increase with uranyl concentration can be rationalized by the formation of a three-dimensional living network of a 1D ionic liquid made by alternate cation-nitrate chains embodied in a bottle-brush structure. The main component is a cylinder in equilibrium with some end-caps of strong curvature and junction units with high Gaussian curvature. The number distribution of each unit is given by the chemical potential associated with the defects as gliding junction points and end-caps. The skeleton made of the alternating ions are enclosed in this structure at a well-defined distance. The effective viscosity is related to the mean distance ratio between end-caps and junctions. If this ratio is small, end-caps are close and shearing of the network is facilitated. If the ratio is high, junctions are close and inhibit shear flow. This work finally shows how models developed twenty-five years ago for giant micelles in water by Candau<sup>[1]</sup>, Cates<sup>[2]</sup> and Safran<sup>[3]</sup> can be extended to connected water tubes in solvents.



**Figure 1** Schematic drawing of the structure at the origin of the viscosity increase of the organic phase observed upon loading with actinides or lanthanides. Left: flexible and Right: stiff cylinder units between junction points.

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# Structure of block copolymer frozen micelle in gold solution

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<sup>4</sup> Laboratoire de Sciences et Ingénierie de la Matière Molle Physico-Chimie,

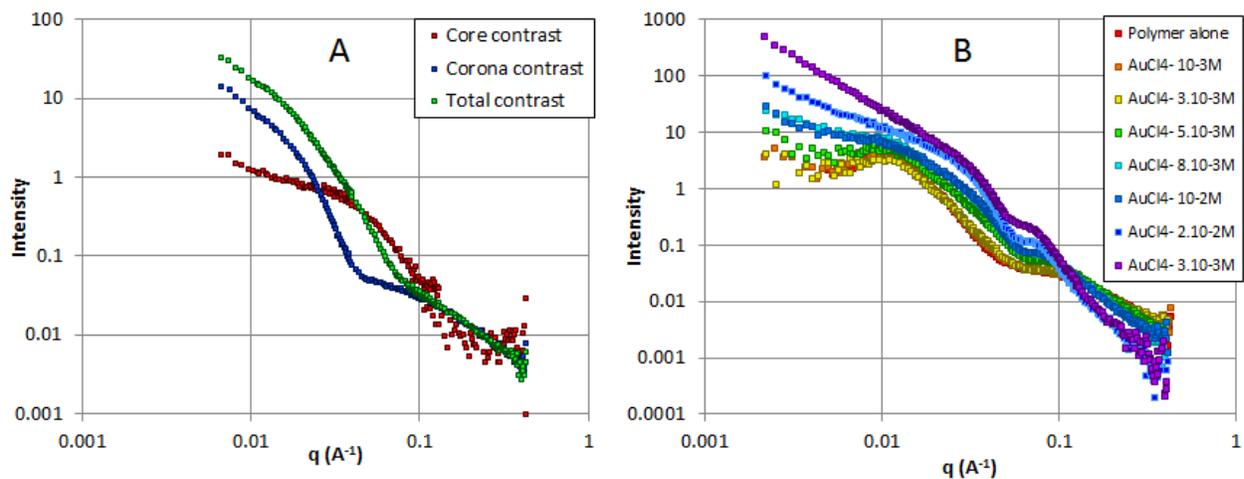
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The reduction of gold ions trapped into constraining media, such as block copolymer micelles, allows the formation of a variety of nanoparticles and inorganic/organic hybrid structures. We studied a system composed of block copolymer frozen micelles and  $\text{AuCl}_4^-$  ions in acidic water. The copolymer used is a polystyrene-*b*-poly(2-dimethylaminoethyl methacrylate), PS-*b*-PDMAEMA. The PS part is insoluble in water under 95°C while the PDMAEMA is a hydrophilic block, positively charged at acidic pH. A rapid cooling of the copolymer from 95°C to ambient temperature induces a condensation of the PS block to form a dense core surrounded by charged, extended chains of PDMAEMA. Those chains are expected to interact with the negatively charged gold ions.

We performed SANS measurements on the PAXY spectrometer at LLB to probe the micelle structure evolution as the gold ions concentration raises. Neutron spectrometry allows the selective probing of the micelle core or corona providing one copolymer block is deuterated. The corresponding SANS spectra are shown on FigA. As the gold ions concentration rises, the extended chains of charged polyelectrolyte collapse leading to the formation of a core-shell structure of the micelle. The corresponding SANS spectra are shown on FigB. Moreover we observed on this figure a transition from repulsive micelle at low gold ions concentration to aggregated sphere at high concentration.

These systems will then be used to synthesize gold nanoparticles around the micelle.



**Figure: (A)** SANS spectra of the block micelles depending on the contrast **(B)** SANS spectra of the block micelles in corona contrast depending on gold concentration

# A shear-induced network of aligned wormlike micelles in a sugar-based molecular gel

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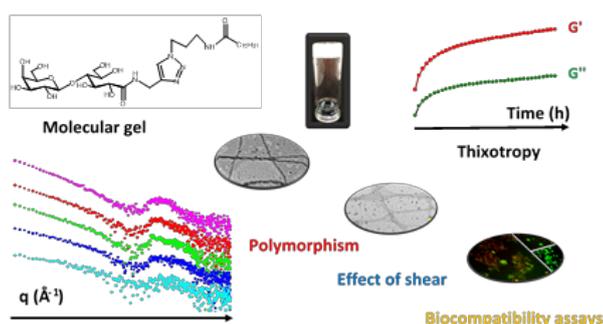
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A new low molecular weight hydrogelator with a lactobionic polar head linked by azide-alkyne click chemistry [1,2] was prepared in three steps. Its gelation behaviour in water was at first a bit puzzling. It was not obtained reproducibly by conventional heating-cooling cycles and instead was obtained by shearing the aqueous solutions, from 2wt% to 0.25 wt%. This method of preparation favored the formation of a quite unusual network of interconnected thin 2D-sheets (7 nm-thick) formed by the association side-by-side of long and aligned 7 nm diameter wormlike micelles. It was responsible for the reproducible gelation at the macroscopic scale. A second network made of helical fibres with a 10-13 nm diameter, more or less intertwined was also formed but was scarcely able to sustain a macroscopic gel on its own. The gels were analysed by TEM, cryo-TEM, DSC, SAXS and rheology. Molecular modelling was also used to highlight the possible conformations the hydrogelator can take. The gels displayed a weak and reversible transition near 20°C, close to room temperature, ascribed to the wormlike micelles 2D-sheets network. A second transition near 50°C, was ascribed to the network of helical fibers. The gels were thixotrope, but slowly: they recovered their initial elastic modulus few hours after injection through a needle. Stable gels were tested as scaffold for neural cell line culture, showing a reduced biocompatibility.



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# Studying the interaction of hydrophobically modified ethoxylated urethane (HEUR) polymers with sodium dodecyl sulphate (SDS) in aqueous solution

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Hydrophobically modified (ethoxylated-urethane) polymers (HEURs) are widely used to control the rheological profile of formulated particulate dispersions. However, HEURs, interact with other components in the formulation, in particular surfactants, leading to substantial perturbations in behaviour. Surface tension, rheology, fluoresce, electron paramagnetic resonance, small-angle neutron scattering, and pulsed-gradient spin-echo nuclear magnetic resonance have been employed to quantify how molecular-level interactions between the polymer, and surfactant define the macroscopic behaviour of the polymer/surfactant mixture. Acrysol RM2020E, HEUR C6-(EO100-I) 9-C6, has been studied with SDS at  $C_{\text{polymer}} < C^*$  (critical overlap concentration) and  $C_{\text{polymer}} > C^*$ . Below the HEUR  $C^*$  monomeric anti-cooperative and micellar cooperative binding of SDS has been detected. Evidence of polymer conformational changes has been observed as a function of [SDS]. Above  $C^*$  the two SDS binding mechanisms, as well as the polymer conformational changes, have been observed with shifting to higher SDS concentration. The insights gained in this work attempts to define macroscopic and nanoscale structure-property relationship of HEUR/SDS interaction.

**KEYWORDS:** Hydrophobically modified polymer, sodium dodecyl sulphate, rheology, pulsed gradient spin echo nuclear magnetic resonance, surface tension, fluorescence and small-angle neutron scattering.

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**Figure 1** Figure legend.

**Acknowledgements** The financial support of the University of Greenwich, and Akzonobel Company

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# Supramolecular amphiphilic systems based on calix[4]arenes

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The nanosized particles based on macrocyclic amphiphiles have been widely applied in biomedical applications such as drug delivery and release [1]. Their main advantages are nanoscale dimensions, low aggregation threshold, easy preparation and ability to encapsulate a water-insoluble drug, the controlled and efficient release of which is an essential technique developed in order to increase the effectiveness and decrease the side effects in long-term administration of therapeutic agents [2]. Our studies represent that calix[4]resorcinol-based amphiphiles have been applied to the delivery systems.

To generate resorcin[4]arene-based nanocontainers for hydrophobic compounds, we chose water-soluble resorcin[4]arene cavitands consisting of four viologen units on the upper rim of resorcin[4]arene platform and different tail lengths (methyl, n-pentyl, n-decyl) on the lower rim. Among three structurally similar cavitands with a different number of methylene groups at the lower rim, different self-assembly behavior was observed. The influence of nature of the counterion on their self-assembly properties was also shown. The replacement of the chloride counterions by iodide ones promoted cavitand self-assembly. However, interactions of cavitands with benzoate resulted in a more marked increase in the assembly due to additional stabilization of the supramolecular structure. The solubilization data for amphiphilic cavitands make them an ideal choice for use as nanocontainers.

The recognition abilities of calix[4]resorcinols enable them to be applied in the design of amphiphiles constructed from non-covalent bonds (supramolecular amphiphiles) [3]. We studied how calix[4]resorcinols can promote the self-assembly of the single-chain surfactants by regulating the degree of order in the assemblies. Supramolecular surfactants were able to self-assemble at concentrations much lower than that corresponding to pure surfactant. When calix[4]resorcinol is added to the surfactant micellar solution, it is observed the formation of vesicles. Thereby, the structure of supramolecular species is determined by relative fractions of components and, hence, could be selectively controlled. The found properties can be used for the design of nanocontainers with the controlled cavity size.

**Acknowledgements** This work is supported by Russian Scientific Foundation, grant no. 17-73-20253.

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# Aggregation states of glycoconjugated dyes in water

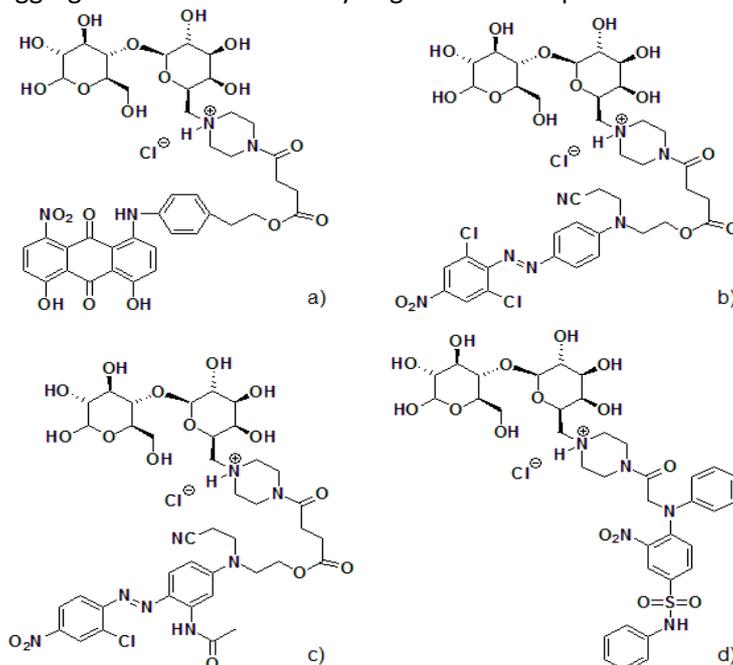
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The dyes object of the present study a class of compounds obtained through glycoconjugation of several specifically modified chromophores with a lactose unit.[1], [2] The lactose is obtained by crystallization from dairy farm whey, while the several starting chromophores are isolated from commercial formulations of disperse dyes. As such, disperse dyes are insoluble in water, but the introduction of a sugar moiety imparts them an amphiphilic character and enhance their water solubility. This is particularly important in view of their end use in leather and textile dyeing, resulting in a dramatic decrease of the environmental impact of the dyeing step. In fact, aqueous solubility avoids the addition of large amounts of inorganic salts and surfactants, necessary to stabilize disperse dyes in water. Glycoconjugated dyes form self-assembled structures in solution, mainly through stacking interactions between the conjugated hydrophobic cores. However, despite the presence of these aggregates, their dyeing efficiency, tested on leather, polyester, hair and polyurethane, was very good, as well as their light fastness. Aim of this study was to understand the influence of such self-assembled structures on the dyeing process. The assemblies were characterized using UV-visible spectrophotometry, light and X-rays scattering and circular dichroism. The effects of solvents and additives on aggregate formation and on the interaction with several substrates were also addressed. The formation of J and H aggregates was confirmed. However, the self-assembly took place only in water and the dimensions of the aggregates varied with the dyeing mixture composition.



**Fig. 1:** Chemical structures of the four glycoconjugated dyes object of this study: NB27 (a), NO30 (b), NR202 (c) and NY42 (d).

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# Spectroscopic study of aqueous solutions of nonionic surfactants, derivatives of D-sorbitol

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Fluorescence spectroscopy (also known as spectrofluorometry) is a type of electromagnetic spectroscopy which analyses sample fluorescence. It involves using a beam of light, usually ultraviolet that excites electrons in the molecules of certain compounds and causes them to emit light; typically, but not necessarily, visible light. A complementary technique is absorption spectroscopy. In the special case of single molecule fluorescence spectroscopy, intensity fluctuations from the emitted light are measured from either single fluorophores, or pairs of fluorophores [1].

Surface active agents are often studied by spectrofluorimetry, a technique based on the measurement of the intensity of fluorescence radiation emitted after appropriate excitation of the fluorescence probe. It is possible to determine, for example, the critical concentration of surfactant micellization (CMC) [2], the micropolarity of the system with the increase of surfactant concentration and the temperature or the apparent dielectric constant [3]. As the literature presents the contradictory data concerning the values for the nonionic Tween surfactants, the aim of the presented study was to determine them over a wide range of temperatures (293-318K) by obtaining and analysing the emission spectra of pyrene, ANS (8-anilino-1-naphthalenesulfonic acid ammonium salt) and pyronin Y in surfactant solutions of this type (Tween 20, 60 and 80) at different concentrations. The variation of these parameters with the concentration and temperature was also discussed in terms of intramolecular interactions in the solution of the surfactants under examination.

**Acknowledgements** This work was supported by the National Science Centre, Poland, Project no. 2014/15/B/ST4/05086.

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# Interaction of the saponin aescin with cholesterol in DMPC vesicles.

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Phospholipids are the main component of biological membranes. The interaction of drugs, membrane bound proteins, and receptors are of major interest in industrial and pharmaceutical research. The function of membrane bound proteins depends on the structural properties such as the bilayer thickness ( $d_z$ ) of the membrane. Here, we study the bilayer properties of small unilamellar vesicles (ULVs) consisting of the phospholipid 1,2-dimyristoyl-*sn*-glycero-phosphocholine (DMPC). DMPC molecules undergo a phase transition at  $T_m=23.6$  °C from a rigid gel to a 2D flexible fluid structure so that both phases are experimentally accessible. The properties of a biological membrane can be affected by the type of inserted molecule into the membrane, for example leading to an increase of  $d_z$  or stiffening [1] upon cholesterol insertion. Saponins are a divers class of plant-derived surfactants with a peculiar molecular structure made of a hydrophobic backbone similar to that of cholesterol and a hydrophilic oligosaccharide chain. They are widely used in the food and pharmaceutical industry and are naturally available in natural foods such as nuts and chick peas. Together with a phospholipid and cholesterol immune stimulating complex matrices (ISCOMS) are formed being carrier cages for e.g. vaccines. Here, we study the effect of mixtures of the saponin aescin and cholesterol on phospholipid membranes by scattering methods such as small-angle X-ray and neutron scattering. We demonstrate the concentration dependent structure formation of non-equilibrium and equilibrium structures upon incorporation of larger amounts of aescin and complexation in the presence of cholesterol.

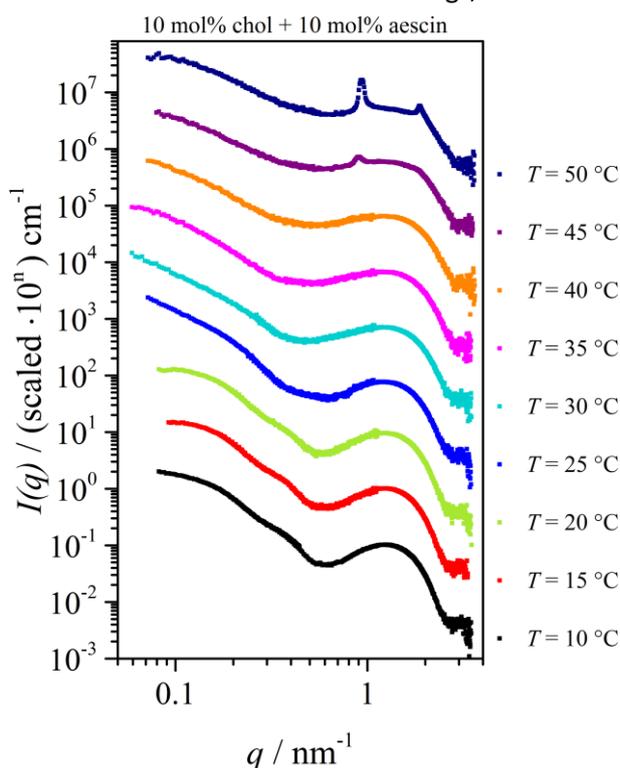


Fig. 1: Form factors of DMPC vesicles incorporating aescin and cholesterol measured by small-angle X-ray scattering.

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# Adsorption Layer and Bulk Properties of Two-antennary oligoglycine C8-T2: pH dependency

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The molecule of two-antennary oligoglycine C<sub>8</sub>H<sub>16</sub>(-CH<sub>2</sub>-NH-Gly<sub>5</sub>)<sub>2</sub>\*HCl consists of two oligoglycine units (T2) linked to a hydrocarbon chain (C8). This structure implies amphiphilic properties: onset of bulk and interfacial self-assemblies. The interfacial properties of aqueous solutions of C8-T2 have been investigated after two, twenty four and forty eight hours after preparation of the solutions. Dynamic, equilibrium and rheological properties of adsorption layers are studied by Profile Analysis Tensiometer. The investigated concentration interval is 1x10<sup>-5</sup>M to 1x10<sup>-3</sup>M for aqueous solutions. For investigating of the pH dependency buffer solutions are used. pH of the solutions is changed in the interval from 3 to 11. During investigation it has been found the maximum pH of the solutions is pH=8.7. Film drainage and stability of foam films from aqueous and buffer solutions of C8-T2 are studied by the microinterferometric method of Scheludko and Exerowa. The onset of bulk assemblies is largely dependent on the charge of the amino groups, located at the ends of the oligoglycine tails, thus the presence of electrolyte and the pH dependency are crucial for understanding of the properties of the system. Investigation on the bulk nanostructures (tectomers) is conducted via DLS, as well.

The initial results add important new knowledge about the nature of these new substances and outline its specific characteristics in view of possible applications in complex fluid preparations, including drug delivery and/or extraction of various impurities from water media.

**Acknowledgements** The financial support of BG05M2OP001-2.009-0023 is gracefully acknowledged.

# LIPID BASED LIQUID CRYSTALLINE NANOPARTICLES AS POTENT THERAPEUTIC MODULES FOR ANTI LEPROSY DRUGS

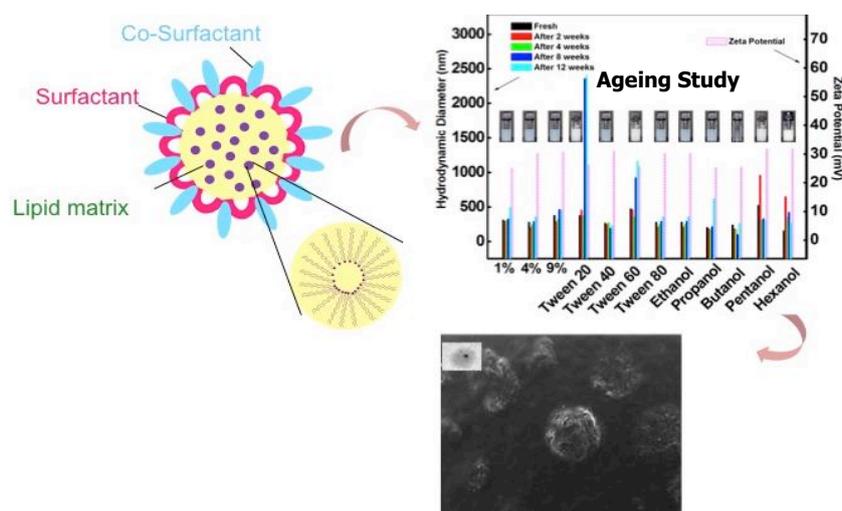
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This report aims at unveiling the potential of nanostructured lipid-based liquid crystalline systems for improving the therapeutic efficiency of anti-leprotic drugs i.e. Rifampicin and Dapsone. Lipid based liquid crystalline nanoparticles (LCNP) have been fabricated by employing the hot micro-emulsification methodology in which the hot microemulsion becomes rapidly diluted by water [1]. Dialkyldimethylammonium bromide ( $D_x$ DAB) surfactants (where,  $x=12,14,16,18$ ) as the liquid crystalline solid lipid part and oleic acid as the liquid core, are employed owing to their contribution towards the enhancement of encapsulation and release property of hydrophobic drugs. The effect of  $D_x$ DAB as a function of the chain length of the double alkyl chain on the characteristics of LCNP was investigated to completely understand its physicochemical aspects in association with its *in-vitro* release performance. In depth characterization of the LCNP placebo has been done by using various techniques such as DLS, SLS, ZP, TEM, SEM, AFM and SANS etc [2]. *In-vitro* cytotoxicity evaluation put forth that toxicity is totally concentration dependent phenomena and LCNP with less than 50  $\mu\text{g}/\text{mL}$  is preferred for better *in-vivo* tolerance. High encapsulation efficiency and *in-vitro* release has been achieved by employing these LCNP nano vehicles for drug delivery. Therefore, this class of  $D_x$ DAB based LCNP has become a potent candidate for anti leprosy medicaments as carriers, targeting for pharmaceutical and medicinal purposes. In summary, these LCNPs are an interesting way of colloid formulation for delivering a large variety of different active agents.



**Figure 1.** Schematic representation of optimized lipid based liquid crystalline nanoparticles (LCNPs) formulation verified by TEM and SEM analysis.

**Acknowledgements** The financial support of DST PURSE II Grant, CSIR and DAAD.

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# Biomolecules in Deep Eutectic Solvents

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The investigation of the behavior of biomolecules in the absence of water has experienced a recent upsurge, with special emphasis on deep eutectic solvents (DES).[1] These solvents are generally formed from a eutectic mixture of organic compounds, where the melting point of the resulting mixture is considerably lower than those of the individual precursors. DES have been recently postulated as matrix where biomolecules may remain active, even in extreme conditions (e.g. cryogenic temperatures or total absence of water). Following on our previous work in surfactant self-assembly,[2,3] we have started a systematic study on phospholipid and protein behavior in pure and hydrated DES. Here we report the behavior of phospholipid monolayers at the air-liquid interface, and the conformation of proteins in DES.

We have employed Neutron and X-Ray reflectometry to study the behavior of DPPC, DMPC and DMPG has been investigated at the air-liquid interface on a choline chloride:glycerol subphase. Circular dichroism and small-angle neutron scattering were used to examine the structure and conformation of bovine serum albumin and hen egg-white lysozyme in choline chloride-based DES.

Our investigations have shown the formation of stable, well-defined phospholipid monolayers of variable thickness and solvation depending on the surface coverage. The conformation of the proteins has been studied for pure and hydrated solvents. Our results have shown that proteins remain partially folded in pure DES, whereas in the presence of hydrated DES the protein effectively folds as in buffer, even at high DES concentrations.[4]

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# Selective Protein Adsorption on Stimuli-Responsive Polymer Brushes Studied by ToF-SIMS and Gel Electrophoresis

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Protein adsorption on solid surfaces provides either beneficial or adverse outcomes depending on the application. Therefore, the desire to predict, control, and manipulate protein adsorption on different surfaces has been the main driving force in this area.

In this work, the adsorption of human serum albumin (HSA - 66 kDa, iep at pH 4.7), human fibrinogen (Fb – 340 kDa, iep at pH 5.8), and Lysozyme (Lys – 14 kDa, iep at pH 10) was investigated on stimuli-responsive brushes composed of poly(ethylene oxide) (PEO), poly(acrylic acid) (PAA), and/or poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) formed on a gold substrate. Polymer brushes were characterized by X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM), and water contact angle measurements. PEO inhibits protein adsorption. PAA and PDMAEMA are weak anionic and cationic polyelectrolytes, respectively, featuring a variable density of negative or positive charges depending on pH .

Polymer brush formation and protein adsorption/desorption were further studied by Quartz Crystal Microbalance (QCM). Protein adsorption was performed at pH 7.4-9.0 and ionic strength of  $10^{-3}$ - $10^{-2}$ M, while desorption was carried out by rinsing with a sodium chloride solution at pH 9.0 and ionic strength of 0.15 M. Firstly, protein adsorption was measured from single protein solutions. It was observed that at pH 9.0 and in the ionic strength range  $10^{-3}$ - $10^{-2}$ M, Fb and Lys adsorb on mixed PEO/PAA brushes, while the adsorption of HSA was not observed. Significant adsorption of HSA and Fb was observed on the mixed PEO/PDMAEMA brushes while the adsorption of lysozyme (Lys) was not observed.

Next, adsorption was performed from mixtures of two or three proteins. Time-of-flight ion mass spectrometry (ToF-SIMS) and gel electrophoresis coupled with silver staining were used to identify the adsorbed proteins. Principal Component Analysis (PCA) was used to obtain a more detailed interpretation of the ToF-SIMS spectra. It was proved that selective adsorption of Lys from the mixture of Lys/HSA/Fb on the PEO/PAA polymer brushes is possible at pH 9.0 and ionic strength  $10^{-3}$ M, while Lys and HSA, but not Fb, were adsorbed at ionic strength  $10^{-2}$ M and pH 9.0. Further work is now focused on the performances of PEO/PDMAEMA brushes.

This study shows that by controlling both pH and ionic strength, it is possible to tune protein adsorption/desorption on stimuli-responsive polymer brushes, and that selective adsorption can be achieved from protein mixtures.

## Acknowledgements:

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 659391.

# Ultrasonic studies of aqueous solutions of nonionic surfactants at different temperatures

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One of the most important properties of surfactants is their ability to form aggregates in solutions above the critical micelle concentration (CMC). Micelles, which are formed from surfactants, are thermodynamically stable aggregates. Their shape, size and charge (for the ionic ones) can be modulated by other components and/or by varying the surfactant concentrations, pressures, temperatures and so on. Temperature has a very significant effect on the supramolecular arrangements of the surfactants in their aqueous solutions [1,2]. The nonionic surfactant - Tween 80 is a clear and odourless liquid at room temperature. It is derived from polyethoxylated sorbitan and oleic acid. Tween 80 is used in foods and cosmetic as well as pharmaceutical industry [3,4]. The presented studies include the measurements of speed of sound, density and refractive index of aqueous solutions of Tween 80 and Triton X-114 over the entire range of concentrations at 293,298,303,313 and 318K under the atmospheric pressure. Steady state fluorescence measurements have been also made using pyrene as a probe.

**Acknowledgements** This work was supported by the National Science Centre, Poland, Project No. 2014/15/B/ST4/05086.

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# Physical characterization of bilayer lipid membranes doped with cholesterol

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One of the primary roles of cholesterol in the biological cell is to modulate the physical, in particular optical, properties of the bilayer phospholipid membrane. Furthermore, the effect of cholesterol on lipid bilayers is strongly dependent on the concentration, and as a result it can easily adapt to changes of the cell's temperature. Incorporation of cholesterol in membranes induces diverse changes in the bilayer properties, including alteration of the bilayer thickness and changes in lipid order. Taking in consideration these physical and structural characteristics of the doped with cholesterol lipid membranes, as well as their underlined optical birefringence, we apply the typical structural methods for studying these complex biological systems. We have performed a number of studies, involving Fourier transform infrared (FT-IR) and polarization micro-Raman spectroscopies, as well differential scanning calorimetry (DSC), aiming to discover the specific physical characteristics of the doped with cholesterol lipid membrane. The analysis of the far FT-IR spectra (below  $100\text{ cm}^{-1}$ ) indicated that hydrogen bonds exist between the hydroxyl group of cholesterol and the phosphate head group of phospholipid. Besides the trivial H-O hydrogen bond, we were able to detect the complex hydrogen bonds involving C and N elements in the complex bilayer membrane. The evaluation of the standard physical parameters, like enthalpy, energy, entropy and strength of the hydrogen bonds (responsible for the bilayer structure and function modification) gives us possibility to apply molecular dynamic simulation for assignment of the new physical and structural characteristics of the complex lipid membrane.

**Acknowledgements** The authors acknowledge support from the Ministry of Education and Research, Bulgaria (National Science Fund, Grant DN 08-02/2016).

# Determination of Nanostructures of Block Copolymer Self-Assemblies via Simultaneous Use of Small Angle X-ray and Neutron Scattering Measurements

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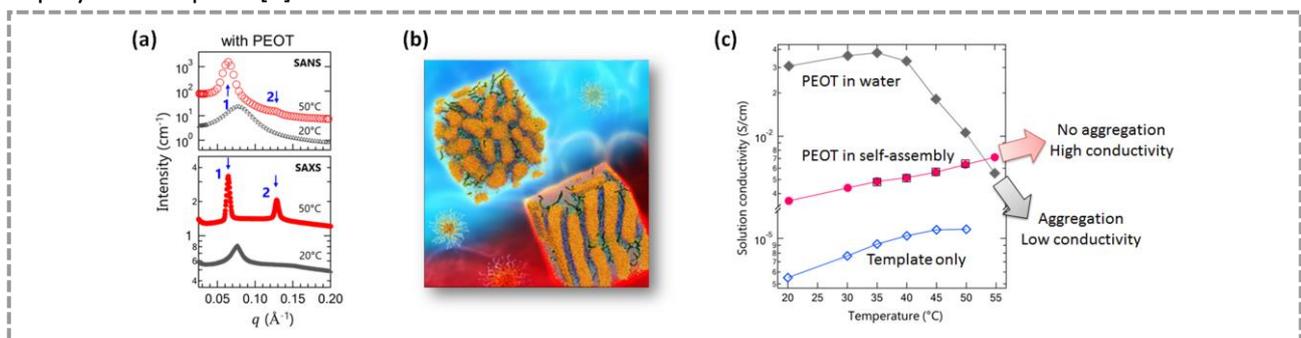
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Various nanostructure and nanoscale building blocks are being fabricated using soft-materials targeting unique physical, chemical, and mechanical properties by controlling orientations, densities, or locations of constituting molecules via self-assembly [1]. Small angle neutron scattering (SANS) combined with a unique leverage on the scattering contrast by isotope replacement can provide structural information on the self-assembled ordered systems that is much more than just periodic length scales. Here, we show examples of structural analysis using contrast-varied small angle scattering methods on a few selected block copolymer self-assemblies. The scattering contrast can be varied either by using deuterated materials or by combining x-ray and neutron measurements. For examples, lamellar structure of aqueous solution of block copolymers is generally considered to have alternating stacks of hydrophobic and hydrophilic layers. By changing the scattering contrast of the solvent, we reveal that there are sub-domain level structures that can fully explain the measured scattering profiles [2]. When isotope replacement is not an ideal choice, the scattering contrasts can also be made by combining the neutron and x-ray scattering measurements. Using this approach, self-assembled structures with conjugate polymers and block copolymers are identified, providing better understanding on how the thermos-reversible conductivity is influence by the distribution of conjugated polymers and the structure of the block copolymer template [3].



**Figure 1** (a) Scattering intensities from SANS and SAXS show different profiles for identical structures at 20 °C and 50 °C, respectively. (b) Self-assembled structures from scattering analysis agree with molecular dynamics simulations. (c) Self-assembling with block copolymer leads to better conduction behaviour at high temperature.

**Acknowledgements** This material is based upon work supported by the U.S. Department of Energy, Office of Basic Energy Sciences under contract number DE-AC05-00OR22725. This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

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# The properties of water-alcohol solutions of quercetin and rutin

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Flavonoids are hydroxylated phenolic substances and are known to be synthesized by plants. The chemical nature of flavonoids depends on their structural class, degree of hydroxylation, other substitutions and conjugations, and degree of polymerization. Recent interest in these substances has been increasing because of their potential health benefits [1]. Flavonoids are widely distributed in plants, performing many functions. Flavonoids are the most important plant pigments, they are also engaged in UV filtration, symbiotic nitrogen fixation and floral pigmentation in high plants [2].

Quercetin and rutin are two of the best known flavonoids. The in-vivo and in-vitro studies have shown that rutin and quercetin exhibit anti-inflammatory, anti-diabetic, anti-bacterial, anti-mutagenic and antioxidant properties [3]. However, the solubility of quercetin and rutin as well as of many other flavonoids in aqueous solutions is low eg 0.17-7.7  $\mu\text{g} / \text{ml}$  for quercetin [4]. Hence, much attention is paid to the increasing of solubility and transport mechanism of these compounds. It is worth emphasizing that the isolation process of biologically active compounds from raw materials (fruit and vegetables), including quercetin and/or rutin, is based on extraction performed under different conditions and with the addition of various solvents, mainly alcohol. These alcohols, depending on their concentration, can act as co-surfactants or co-solvents [6,7]. As so far quercetin-alcohol and rutin-alcohol interactions have been neglected in the literature, the purpose of the presented study was to investigate the properties of quercetin ( $C_{qe}=4 \times 10^{-5} \text{M}$ ) and rutin ( $C_{ru}=4 \times 10^{-5} \text{M}$ ) solutions with methanol (MeOH), ethanol (EtOH) and propanol (PrOH) ( $C_{alcohol}=0-80\%$ ) at 293, 303 and 313 K based on the registered absorption and emission spectra.

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# Meniscus Depth in Capillaries under the Influence of Gravity

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One of the important elements in surface science is the equilibrium shape of fluid menisci. In the presence of gravity or other external fields, a meniscus does not have a spherical shape and by integrating the Young–Laplace equation numerically the shape of the meniscus can be found. Typically, the apex of the interface is chosen as an initial point for the integration. However, this choice is not adequate to find the meniscus shape in capillaries with large Bond numbers which have the central part of the interface flattened. Here we considered a point on the three-phase contact line as the initial point for the integration and evaluate the curvature at the three-phase contact line ( $R_{mo}$ ) with two novel approaches: a large capillary size method and a free energy calculation method.

We provide some important information about  $R_{mo}$  and this information is the pre-requirement to solve the Young–Laplace equation. It was found that  $R_{mo}$  is the highest acceptable curvature that satisfies the equilibrium condition since it has the smallest free energy. In addition, the deviation of curvature at the three-phase contact line from that of a spherical shape is examined and it was found that the highest deviation from spherical, which is about 0.83, happens at a Bond number of approximately 13. The capillary meniscus depth is found for two systems of liquid–vapour and liquid–liquid menisci for various values of capillary radius and contact angle which is providing insights into the dependence of meniscus depths on the various variables.

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# Conformational behavior of graft copolymers in selective solvents and their sorption on lyophobic surface

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Conformational behavior of graft copolymers and their sorption at surfaces interacting selectively with the backbone is a result of a number of synergic and antagonistic effects. The conformations are affected not only by the interactions of grafts and backbone with the solvent, but also by interactions of the copolymer with the surface. We performed an extensive series of coarse-grained computer simulations. We used dissipative particle dynamics (DPD) and studied copolymers differing in grafting density and in the lengths of grafts and varied solvent quality for the backbone. The attractive interaction of the surface with the backbone and repulsive interaction with grafts were kept constant in all simulations.

Results of systematic simulations allowed us to construct phase diagrams which show regions (combinations of solvent selectivity and the lengths of grafts) where the copolymers are strongly or weakly adsorbed, or fully dissolved in bulk solvent. The description of the behavior is supplemented by conformations typical for individual regions. The complexity of the behavior is mainly due to the competition of following factors: (i) Poor quality of the solvent for the backbone lowers the overall copolymer solubility and promotes the adsorption, (ii) but it simultaneously causes the contraction of the backbone and lowers the probability of backbone-surface contacts. During the lecture, the behavior will be discussed in detail and important conclusions concerning the experimental chromatography of copolymers and other separation techniques will be also presented.

New pieces of information provided by simulations are not only interesting from the theoretical point of view, but they facilitate the prediction and tuning the adhesion in technological applications of graft copolymers. Last, but not least, they help to interpret results of modern chromatographic methods used for the characterization of copolymers which combine the separation mechanisms of size-exclusion chromatography with different variants of interaction chromatography.

**Acknowledgements.** The authors acknowledge the support by the Grant Agency of the Czech Republic (Grant No. 17-04258J).

# Hydrophobicity of acetylcholine and related ions examined using ion transfer voltammetry at a polarized ionic liquid membrane

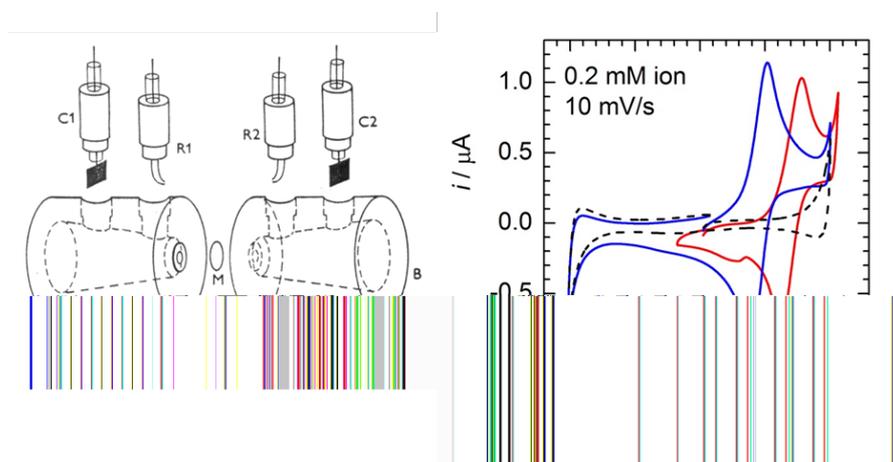
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Ion transfer voltammetry at a polarized ionic liquid membrane can be used to evaluate the standard Gibbs energy of ion transfer from water to an ionic liquid (IL),  $\Delta_{\text{w}}^{\text{L}}G_{\text{i}}^0$  [1]. This quantity exhibits a correlation with the standard Gibbs energy of ion transfer from water to an organic solvent (o),  $\Delta_{\text{w}}^{\text{o}}G_{\text{i}}^0$  [2]. They both can be considered as a measure of the ion hydrophobicity, which is one of the factors playing a role in the physiological activity of the ion. The aim of this work was to compare on this basis the hydrophobicity of acetylcholine ( $\text{ACH}^+$ , neurotransmitter), choline ( $\text{CH}^+$ , precursor for  $\text{ACH}^+$ ), muscarine ( $\text{MUS}^+$ , agonist of the muscarinic  $\text{ACH}^+$  receptors), atropine ( $\text{AT}^+$ , antagonist of the muscarinic  $\text{ACH}^+$  receptors), and  $(\text{CH}_3)_4\text{N}^+$  ( $\text{TMA}^+$ , a model tetraalkylammonium ion). Cyclic voltammetric measurements were carried out using a 4-electrode cell shown in Fig. 1 (left) with the IL membrane (M) composed of highly hydrophobic tridodecylmethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (TDMATFPB), see ref. 3 for methodology.

Fig. 1 (right) shows cyclic voltammograms of the reference tetraethylammonium ion ( $\text{TEA}^+$ ,  $\Delta_{\text{w}}^{\text{L}}G_{\text{i}}^0 = -3.3$  kJ/mol) and  $\text{MUS}^+$ . Analysis of the voltammetric data provided the values of  $\Delta_{\text{w}}^{\text{L}}G_{\text{i}}^0$  (in kJ/mol in parentheses) following the order  $\text{TMA}^+(14.6) < \text{ACH}^+(16.2) \sim \text{AT}^+(16.4) < \text{MUS}^+(20.3) < \text{CH}^+(24.1)$  indicating only minor differences in hydrophobicity of  $\text{ACH}^+$  and related ions.



**Figure 1** (Left) Scheme of the 4-electrode cell with two reference (R1,R2) and two counter (C1,C2) electrodes for the voltammetric measurements at the TDMATFPB membrane (M), thickness 112  $\mu\text{m}$ . (Right) Cyclic voltammograms of 0.2 mM  $\text{TEA}^+$  (blue), 0.2 mM  $\text{MUS}^+$  (red), and the background electrolytes (black).

**Acknowledgements** The financial support of the Czech Science Foundation (project number 15-03139S) is acknowledged.

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# Spontaneous adsorption of microgels at model liquid interfaces and link with Pickering emulsion stabilized thereof

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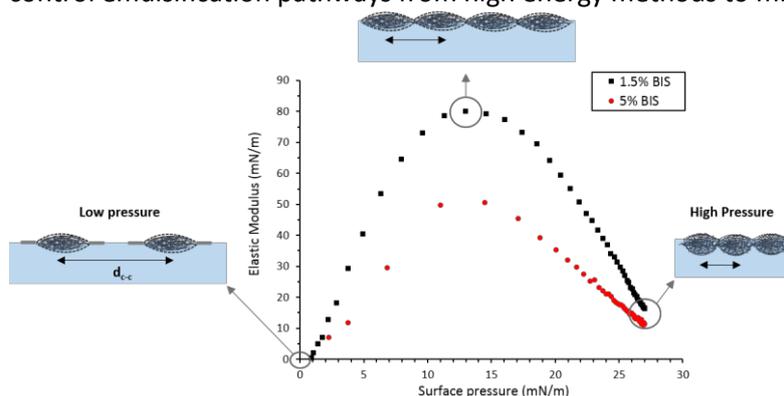
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Microgels are soft and deformable colloidal particles which can be swollen by a solvent and adsorb at liquid interfaces. The well-known poly(N-isopropylacrylamide) (pNIPAM) microgels are thermo-sensitive and exhibit a volume contraction when the temperature is raised above the volume phase transition temperature (VPTT). These particles have shown high potential as Pickering emulsions stabilizers: emulsions could be stable at temperatures below the VPTT and be destabilized on-demand above it [1]. In order to improve understanding of the emulsion stabilization mechanism, the role of microgels adsorption at model liquid interfaces has been studied [2, 3].

In the present work, we study the spontaneous adsorption of charged and uncharged microgels with different cross-linking densities, at liquid interfaces (air-water and oil-water) and in various aqueous conditions (pH, electrolyte concentrations). We also discuss interfacial properties such as surface tension, pressure and elasticity of more or less rigid, charged and neutral pNIPAM microgels. To investigate their interfacial adsorption, we measure the dynamic interfacial tension using the pendant-drop technique. We show that the bulk microgels concentration has an influence on the spontaneous adsorption of charged pNIPAM microgels, modifying both the kinetics of adsorption and the value of the spontaneous interfacial tension at equilibrium (long times). Moreover, for different cross-linking densities microgels, we attempt to correlate the surface elasticity with the microgel morphology at the interface by dilatational visco-elasticity measurements using the oscillatory drop method. We show that the maximal dilatational interfacial elastic modulus increases as the cross-linking density decreases.

Microgels deformation and adsorption at the liquid interface have consequences on emulsion macroscopic properties. Spontaneous adsorption of our systems can be compared with constrained interfaces [3] to imitate the microgels conformation in emulsions or foam films in which microgels are locked into various conformations. Taking into account the kinetics of adsorption at the interface and processing conditions, we could control emulsification pathways from high energy methods to microfluidics.



**Figure 1:** Elastic modulus as a function of surface pressure for microgels at 1.5% (black square) and 5% of cross-linker (red circle) and scheme of their profile view in different conformations at different surface pressures.

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# Monolayers of PBA Homopolymers and PEG-PBA Diblock Copolymers at the Air/Water Interface: Isothermal Compression and Structure Formation during Collapse

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Poly (butyl acrylate), PBA, readily spread at the air/water interface and its properties are already well studied.<sup>[1]</sup> It forms stable films that become elastic at high surface pressures (20–30 mN/m).<sup>[2]</sup> For intermediate pressures, their thickness is found to be of the order of 1–2 nm. We prepare Langmuir monolayers of PBA and the diblock copolymer poly (ethylene glycol)-poly (butyl acrylate), PEG-PBA, with different molecular weights ranging from 5–30 kg/mol. In this series the PEG block acts as a small hydrophilic anchor and its size is constant for all diblock copolymers ( $M_N = 0.3$  kg/mol). We perform in-situ Brewster-Angle-Microscopy (BAM) and in-situ X-Ray reflectometry (XRR) to get a thorough understanding of the film structure, as-well as Langmuir-Blodgett measurements to understand the compression behaviour of the film.

In the semi-dilute regime each polymer exists as an isolated collapsed disk and a single monolayer structure can be identified for both, homo polymers and diblock copolymers, by XRR and BAM as expected from an acrylate polymer.<sup>[1]</sup> Upon compression those disks frequently collide, leading to an increasing surface pressure that can be described with the well-known scaling behaviour stated by de Gennes in 2D.<sup>[3]</sup> We find that the PEG block in the diblock copolymers can tune the air/water interface from a poor solvent to good solvent conditions. In the concentrated regime, a phase transition from a 2D continuous water-free monolayer to a more complex structure occurs. Increasing surface pressure to the concentrated regime, we observe a phase transition on a macroscopic length scale. BAM images show bulk-like polymer in flattened globular structures at the interface and their size varies between several  $\mu\text{m}$  and 100  $\mu\text{m}$ . Complementarily, we observe a periodic inter-particle distance of a few  $\mu\text{m}$  within the surface by off-specular XRR. Furthermore, hysteresis cycles show that one part of the phase transition for homopolymers and diblock copolymers is a reversible deformation while a second part is irreversible. To conclude, the collapse is accompanied by the appearance of flattened globular structures over a wide range of length scales and the fractional removal of polymer from the film.

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# Evaluating the influence of surface topography on bacterial adhesion using spatially organized microtopographic surface patterns

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The influence of surface topography on bacterial adhesion has been investigated using a range of spatially organized microtopographic surface patterns fabricated on polydimethylsiloxane (PDMS) and three unrelated bacterial strains suspended in phosphate buffer solution. The results presented indicate that bacterial cells actively choose their position to settle, differentiating upper and lower areas in all the surface patterns evaluated. Such selective adhesion depends on the cells' size and shape relative to the dimensions of the surface topographical features. Moreover, it was found that all the topographies investigated provoke a significant reduction in bacterial adhesion (30–45%) relative to the smooth control samples. This remarkable finding constitutes a general phenomenon, occurring in both Gram-positive and Gram-negative cells with spherical or rod shape, dictated by only surface topography. Interestingly, preliminary experiments performed with one of the strains investigated suspended in nutritionally rich media further revealed that fully active bacterial cells choose their position to settle based on a basic principle: cell-surface contact points maximization. Accordingly, cells were found, for example, to display a marked preference for the square corners and convex walls of recessed surface features rather than the flat or concave walls of equal protruding features. In terms of reduction values, higher reduction values were found in rich media (~ 85%) than in phosphate buffer solution. Therefore, the results presented in this study collectively demonstrate that bacterial cells actively respond to spatially organized microtopographic surface patterns, which might represent a new and promising approach to controlling/inhibiting bacterial adhesion and biofilm formation.

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# Interactions between parabens and membrane lipids in monolayers at the air/aqueous solution interface

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Parabens (PBs) constitute a family of p-hydroxybenzoic acid esters which are widely applied as preservatives in processed food and beverages, personal care products and pharmaceuticals [1]. PBs possess well documented, broad antimicrobial activity, which together with low costs of their synthesis, chemical stability and no perceptible odor and taste, makes them good additives in commercial products [2]. Unfortunately, at present it is becoming clear that they exert series of adverse effects when introduced to the living organisms [3]. The side effects of PBs were investigated in cell culture studies, which demonstrated that PBs are able to increase breast cancer development [4]. PBs modify the integrity of cellular membranes leading to their disruption and induce potassium release from the cell [5]. Nevertheless, the exact mechanism of PBs activity is still not clear. In our studies on lipid • PB interactions we applied the Langmuir monolayer technique together with Brewster angle microscopy and Grazing incidence X-ray diffraction. We showed that PBs interact with monolayers formed by the membrane phospholipids.

We found that the magnitude of interactions depends on the esters chemical structure, on the class of membrane lipid and on the concentration of PB solution. The largest influence of PBs was found for monolayers being in the low degree of condensation, whereas in the case of LC state, the effect was weaker and observed only for periodically ordered domains. The strongest modification of the monolayer characteristics was found for BuPB. Because of the largest hydrophobic fragment BuPB is able to disrupt monolayer organization leading to its collapse at relatively low surface pressure.

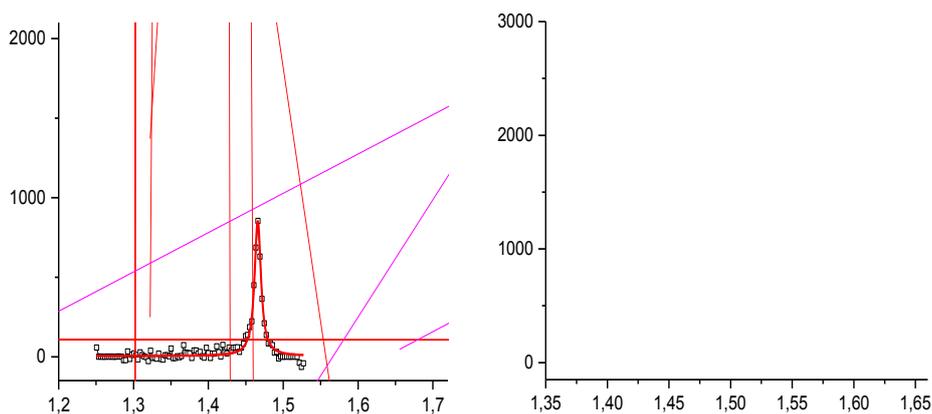


Figure 1. Diffraction signals (Bragg peaks) registered for DPPC (a) and SOPE (b) monolayers spread on pure water surface ..... well as .....

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# Natural molecules to protect membranes against dehydration: Osmolytes and dehydrin proteins

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Nature has many mechanisms to protect living organisms from dehydration. One common mechanism used by many living organisms is the accumulation of small polar solutes with low vapor pressure that stabilize the cell membranes in cases of osmotic stress.<sup>1</sup> These molecules are known as osmolytes. Among other mechanisms, plants also synthesize dehydrin proteins, which are found in vegetative tissues, and that are believed to protect membranes from conditions like desiccation or cold stress.<sup>2</sup> However, little is known about the molecular mechanism of neither osmolytes nor dehydrin proteins on the membrane, which in turn may affect membrane function.

Scattering experiments were used to study the effect that the dehydrin protein Lti30 has on the swelling limit of a charged lipid lamellar phase at high water contents. Proton transfer solid-state NMR was also performed for selected samples. The second set of experiment focuses on how two osmolytes, urea and TMAO, influence dehydration-induced phase transitions. Scattering experiments were performed in a lipid system that exhibit a  $L_{\sigma}H_{II}$  phase transition upon dehydration.

Our results show that Lti30 interacts with the lipid membranes preventing them from swelling at high water contents. In the case of dehydration conditions, Lti30 does not have any effect on the phase transition of the lipids but it increases the swelling of the phases. Urea stabilizes the fluid lipid bilayers at low water activities, where otherwise a phase transition to a solid state would occur. Moreover, the swelling of the fluid lipid bilayers increases significantly in the presence of urea. Adding TMAO to the lipid model system stabilizes the reverse structures by shifting the phase transition to higher water contents.

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# Surface Properties of Triblock Semifluorinated n-Alkanes

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Symmetrical triblock semifluorinated *n*-alkanes of the general formula:  $F(CF_2)_m(CH_2)_n(CF_2)_mF$ , (in short  $F_mH_nF_m$ ), where  $m=4, 6, 8, 10, 12$  and  $n=6$  have been synthesized and investigated at the air/water and air/solid interface. The studied molecules have been subjected to Langmuir monolayer characterization including surface pressure and electric surface potential measurements under a variety of experimental conditions such as spreading volume, subphase temperature and compression speed. The textures of insoluble films obtained on water surface were visualized by Brewster angle microscope (BAM). Our results show that molecules with longer perfluoroalkyl chains ( $m=10$  and  $12$ ) are capable of monomolecular monolayer formation at the air/water interface. Meanwhile the molecules with shorter perfluorinated moieties ( $m=4, 6$  and  $8$ ) do form stable surface domains with shape characteristic to every homologue. These domains are also stable and reproducible on mica surface after transfer on solid support by Langmuir-Blodgett technique as proven atomic force microscopy (AFM).

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# Manipulation of Structural Forces via Temperature

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Structural forces arise when liquids or dispersions are confined between two smooth surfaces. In-between this surfaces, molecules and dispersed particles can form specific structuring, usually layers parallel to the surface. During approach, these layers will be ruptured resulting in an alternating attraction and repulsion. Therefore, the interactions between the surfaces cannot be described by the well-known DLVO theory only. An additional force has to be taken into account. Due to the origin of this interaction, it is often called structural force. This can be experimentally observed with dispersions containing polyelectrolytes [1], micelles [2] or nanoparticles [3]. Israelachvili *et al.* have been the first to detect those forces by confining long chained alkanes between surfaces of negatively charged mica in the surface-force apparatus. [4]

Control over structural forces can be a powerful tool to change the behavior at the interface. This opens many possible applications, including a better control over emulsion stability, an improvement in solubility of otherwise low soluble substances and even a tailored affinity of particles towards each other.

Here we present, that the use of temperature sensitive polymer-particles in aqueous solution introduces control over structural forces utilizing their volume phase transition at a specific temperature. Upon heating, the reduction of size and increase of surface potential results in a better ordering of gel-particles at the silica-water interface. Using Colloidal Probe atomic force microscopy (CP-AFM) reveals, that at room temperature, no structural forces are observable whereas at 60 °C a pronounced oscillating force profile is detected. The reversibility of this effect is shown by multiple heating-cooling-cycles.

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# Influence of the hydrodynamic conditions, surfactant type and surfactant concentration on solution foaminess

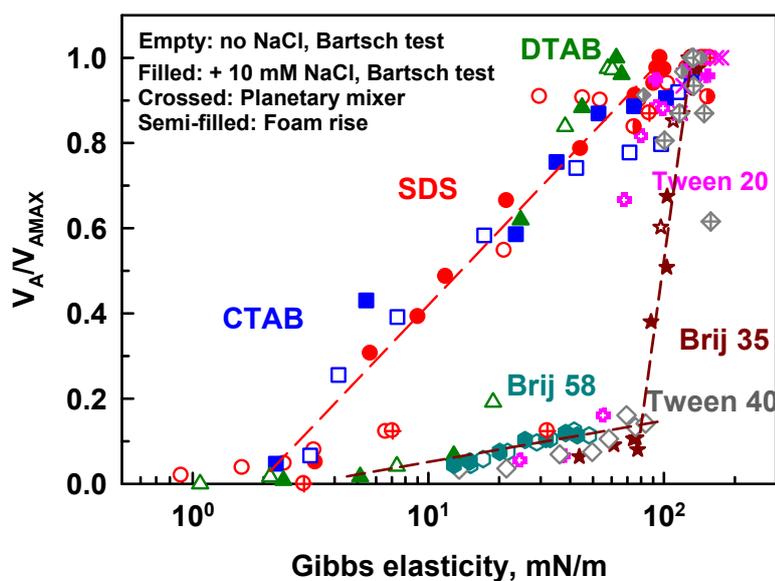
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Surfactants are essential ingredients in many personal and household care products, and in various technological applications. Major aim of the current study is to clarify the role of the hydrodynamic conditions, surfactant type and surfactant concentration on the foamability of solutions. Experiments were performed at low and high surfactant concentrations, below and above the critical micelle concentration, using one anionic and two nonionic surfactants which differ in their hydrophilic head-groups and in the length of their hydrophobic tails. We applied three experimental methods for foam generation which differ significantly in their hydrodynamic conditions – automatic Bartsch test, foam rise method, and a planetary mixer. To explain the obtained results, the surface properties of the studied solutions were characterized in terms of their equilibrium and dynamic surface tensions, and surface dilatational modulus.

The foamability of the solutions of ionic surfactants is higher in the Bartsch test, whereas the nonionic surfactants are much more efficient when the foam is formed in a planetary mixer. These trends are explained by the very different characteristic times of the foaming process in these two foaming methods. In the Bartsch test the surfactant adsorption is in the millisecond range, whereas the properties of the (almost) equilibrium adsorption layers are important for the foaming in the planetary mixer. All experimental data obtained with different surfactant solutions from different foaming methods fall around two universal curves (one for ionic and another one for nonionic surfactants) when the foam volume is presented as a function of the Gibbs elasticity of the dynamic adsorption layers, formed on the bubble surface in the respective foaming method.



**Figure 1.** Correlation between the dimensionless foam volume and the Gibbs elasticity of the dynamic adsorption layers. Foams produced in Bartsch test: empty symbols: no electrolyte, filled symbols: 10 mM NaCl; Planetary mixer (crossed symbols) and foam rise method (semi-filled symbols).

# Boundary lubricants prepared from mixtures of saturated and unsaturated phosphatidylcholine lipids: Lubrication and self-healing

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A series of phosphatidylcholine lipids (PCs) has been proven to be good boundary lubricants due to the hydration lubrication mechanism.[1][2] Both saturated and unsaturated PCs in human synovial fluid (SF) are considered as major contributors to joint lubrication;[3] however, the underlying synergistic effect is not clear. In this work, two main components of PCs in SF,[4] DPPC (C16:0-C16:0) and POPC (C16:0-C18:1), were selected to study how saturated and unsaturated PCs mixtures behave as boundary lubricants. AFM imaging shows that small unilamellar vesicles (SUVs) prepared from DPPC-POPC mixtures (8-2, 5-5, 2-8, molar ratios) form continuous bilayers on a mica surface. Normal and shear forces between two mica surfaces bearing DPPC-POPC SUVs were measured by a surface force balance (SFB). Relatively low friction and reproducible approaches after “rigid-coupling” were observed for the studied mixtures.

**Acknowledgements** We thank the Koshland Foundation and McDonald-Leapman Grant for their support to this work.

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# Triesters of phosphatidylcholine as a potential antibacterial drug - the impact of EPOPC on model bacterial membranes

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Antibiotics are often used in inappropriate manner or administered in unsuitable cases. As a result, many bacteria exhibit multi-drug resistance. For this reason, new drugs of antibacterial properties, are sought. In this context the interest of cationic lipoids is increased due to amphiphilic structure and positive charge of these compounds, which can change the properties of bacterial membranes and demonstrate antibacterial activity. The triesters of phosphatidylcholine are the new class of cationic lipoids that similarly to natural phosphocholines, show low cytotoxicity to human cells. [1-3] Despite the lack of systematic investigations on antibacterial properties of these compounds, it is believed that, by analogy to other cationic amphiphiles, they also exhibit this kind of activity.

The purpose of our studies was to verify the effect of the one of phosphatidylcholine triester derivatives on model bacterial membranes. The research included the analysis of the influence of 1-palmitoyl-2-oleoyl-sn-glycero-3-ethylphosphocholine (EPOPC) on monolayers and bilayers consisting of lipids naturally occurring in bacterial membranes, mixed in proportions reflecting the lipid composition of biomembranes.

The obtained results showed that the incorporation of EPOPC molecules into model bacterial membranes leads to significant increase of their fluidity as well as to decrease of the ordering of the phospholipid *acyl* chains. Moreover, the presence of EPOPC in model membranes strongly affects the character of intermolecular interactions between phosphoethanolamine (PE) and phosphoglycerol (PG) which is due to appearance of competitive electrostatic attraction between oppositely charged EPOPC and PG. Furthermore, the investigations proved that the addition of cationic lipid reduces stability and increases permeability of the model membranes.

**Acknowledgements** This project was financed by the National Science Centre, Poland (no. 2016/21/B/ST5/00266).

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# The influence of 2-hydroxyoleic acid on the properties of artificial lipid membranes

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Membrane lipids alterations are associated with a wide range of human diseases. The reverse of the pathological state can be achieved by incorporation into membrane specific drugs which pharmacological effect is associated with the regulation of the composition and properties of biomembranes. This in turn may modify the localization and activity of key signaling proteins and hence influence signaling pathways and important cellular functions. These therapeutic approach, termed Membrane Lipid Therapy (MLT), has potential use for the treatment of several illnesses including cancer [1].

This study is focused on 2-hydroxyoleic acid (2OHOA, Minerval) which is MLT drug with anti-tumor activity. Therapeutic effect of this substance is associated with its incorporation into cell membrane and modification of the membrane-lipid composition [2]. Previous results indicate that 2OHOA can inhibit cell proliferation or induce the programmed cell death of tumor cells [3]. Taking into account great therapeutic potential of 2OHOA and the fact that its molecular mechanism of action is still not fully elucidated, providing any new insights into its mode of action seems to be of the utmost importance.

The aim of this study was to investigate the influence of 2OHOA on stability, fluidity and molecular organization of artificial lipid membranes in the context of its membrane-related anticancer properties. The experiments were performed for model membranes of the lipids composition mimicking lipid rafts structure.

The received findings reveal that incorporation of the investigated drug into artificial lipid membranes leads to serious alterations in the properties of the systems. It was found that 2OHOA provokes the increase in membrane fluidity, firmly influence its stability and permeability.

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# Magnetic water treatment

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Water is the most common and important substance in nature. Therefore our life, as well as agriculture and industry, cannot function without water. However, hard water and damage caused by scale formation is a problem which prevails in many industries and households. Equipment damage and decrease in flow rates is a source of financial loss and therefore methods to prevent or remove scale formation have considerable financial impact. One of method to prevent scaling is use of magnetic fields. Unlike chemical water softening, magnetic treatment should have no direct effect on water chemistry, if the magnets are not in contact with water. This type of physical treatment helps to prevent the use of chemicals such as polyphosphates or corrosive substances that are expensive and can be harmful for human life or disruptive to the environment. Although application of external MF in flow systems greatly effects calcium carbonate precipitation and it was extensively studied in recent years the magnetic treatment has remained a controversial process for industrial and domestic water treatment [1-5]. Independent review of the performance of the magnetic treatment has been highly controversial, while the number of commercial magnetic treatment devices might seem to be an indicator of the effectiveness of magnetic fields in the water processing. There have been a lot of conducted studies on the mechanism dealing with how magnetic treatment influences solutes or substances in water, especially in aspect of antiscaling and crystallisation. Only a few works focus on the change of water properties itself. But as a matter of fact, the magnetic treatment also has an impact on water molecules themselves, among others affecting the hydrogen bondings. The aim of our study is to investigate the influence of static magnetic field acting at kinetic condition on the hydrogen bonds structure of water molecules. For this purpose changes in the macroscopic properties of water, i.e.: conductivity, boiling point, kinetics and enthalpy of evaporation, surface tension, the infrared spectrum of absorption were measured.

**Acknowledgements** This project was financed by The National Science Centre based on the decision number DEC-2016/21/B/ST4/00987.

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# Interactions of foam with thin and thick porous materials

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In a number of applications foaming liquids are mixtures of surfactants and polymers. These mixtures frequently show a non-Newtonian power law shear thinning behaviour [1-3]. Surprisingly drainage of foams built up by non-Newtonian liquids does not attract enough attention in spite of wide use of such foams. In a number of applications foams are deposited on porous substrates: hair, skin, textile, sponges and so on, however even the basics of the interaction of Newtonian and non-Newtonian foams with porous materials have never been thoroughly investigated: there is only one publication in the area where a complex interaction of foams with porous substrates was investigated [4]. The current state of drainage of foams built up by non-Newtonian liquids and the studies on drainage kinetics will be presented. It was found [4] that the kinetics of foam drainage on a porous substrate in the case of foam built up by a Newtonian liquid depends on three dimensionless numbers related to the properties of both foam and a porous substrate, and initial liquid volume fraction inside the foam. The result showed that there are three different regimes of the drainage process from foam [4]: (a) rate of imbibition into the porous substrate is faster than the rate of drainage from the foam; (b) a comparable rate of drainage and imbibition; (c) rate of imbibition is slower as compared with the rate of drainage. In the latter case the liquid volume fraction at foam/porous substrate interface reaches maximum limiting value at the moment  $t_m$  and a free liquid layer starts to form on the surface of the porous substrate. However, in the end, the free liquid layer is sucked by a porous substrate and it completely disappears at the moment  $t_M$ . After that moment again all liquid coming from the foam goes directly into the porous substrate and the liquid volume fraction decreases to its equilibrium value determined by properties of both foam and porous substrate.

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# Kinetics of isothermal crystallization of water droplets in water-in-crude oil concentrated emulsions

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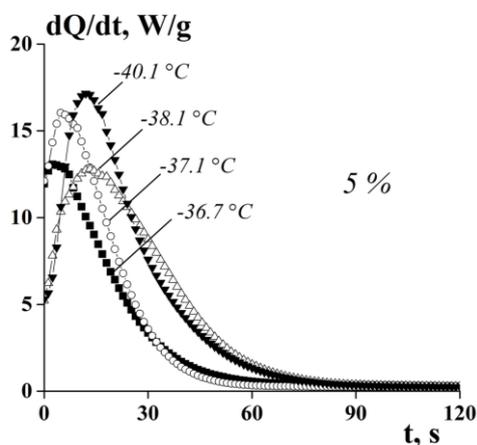
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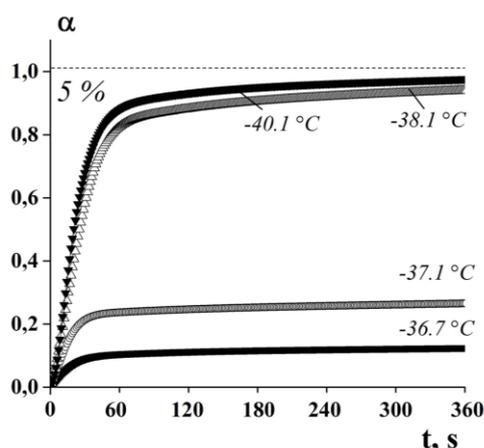
Inverse (water-in-crude oil) emulsion characterization is an essential analytical focus area within the petroleum industry. The objective of the current report is to investigate isothermal crystallization of water droplets containing to water-in-crude oil emulsions ( $\varphi_{\text{water}}=1\div 30\%$ ). Isothermal crystallization was carried out in the temperature range from  $-36$  to  $-41$  °C. The kinetic data for one concentration of water ( $\varphi=5\%$ ) in emulsions are presented in Figure 1 where temperature of crystallization is marked at curves.

The experimental data presented in Figure 1 show that crystallization of water in inverse emulsions can occur only at temperatures below  $-36$  °C and is very slow and incomplete close to this limit. The rate of crystallinity ( $\alpha$ ) monotonously grows in decreasing temperature to  $-41$  °C and at lower temperatures crystallization happens with very high rate. The integral kinetic curves related to these temperatures are presented in Figure 2.

The analytical approximation of the kinetic curves has been made. The correlation between isothermal results and experimental data related to the non-isothermal crystallization obtained in the scanning temperature mode have been presented and discussed in our paper [1].



**Figure 1** Kinetic data of isothermal crystallization of water droplets in water-in-crude oil emulsions.



**Figure 2** Integral kinetic curves. Change in the crystallinity ( $\alpha$ ) of water droplets in time.

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# Probing and Optimising Sponge

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Synthetic sponges are based on the primitive aquatic species, natural sponges, which have adapted to living submerged underwater on sea reefs and whose existence relies on their ability to retain fluid. Like many naturally occurring phenomena, this quality is specifically mimicked by humans, and sponges are manufactured according to varying specifications depending on the purpose at hand. Properties such as porosity, permeability and elastic moduli[1] are investigated and compared in terms of job efficacy, lifetime and hygiene for different types of synthetic sponge. By probing the microstructure using various imaging techniques including confocal microscopy, pore networks can be viewed and better understood as well as produce ways to optimise sponge efficiency. The applications for this research are wide spread from car cleaning to cosmetic purposes, where the sponge properties vary drastically but the fundamental concepts remain the same. The way liquid foams interact with sponges is extremely important; understanding these interactions in the presence of external forces like compression, and deformation reveals an understanding of the mechanisms which allow these sponges to carry out their jobs so effectively, and consequently allows them to be developed further.

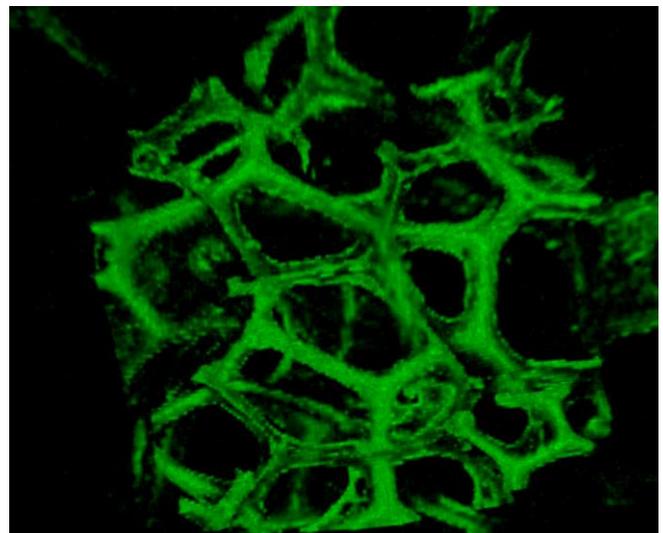
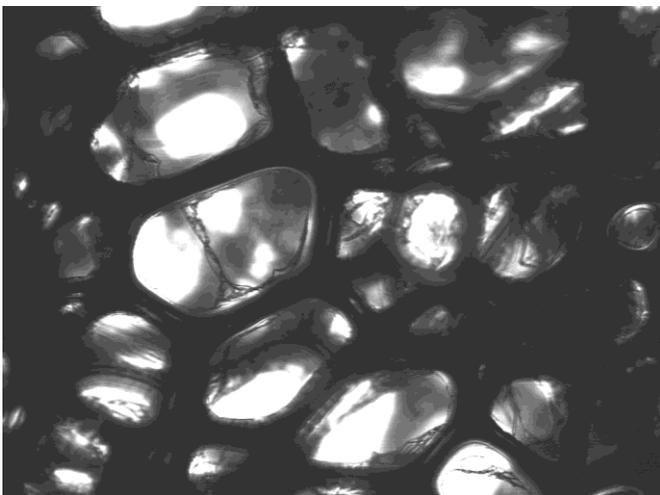


Figure 1: Confocal microscopy images of the pores inside a sponge; (left) 2D and (right) 3D micrographs of sponge dyed with fluorescent material.

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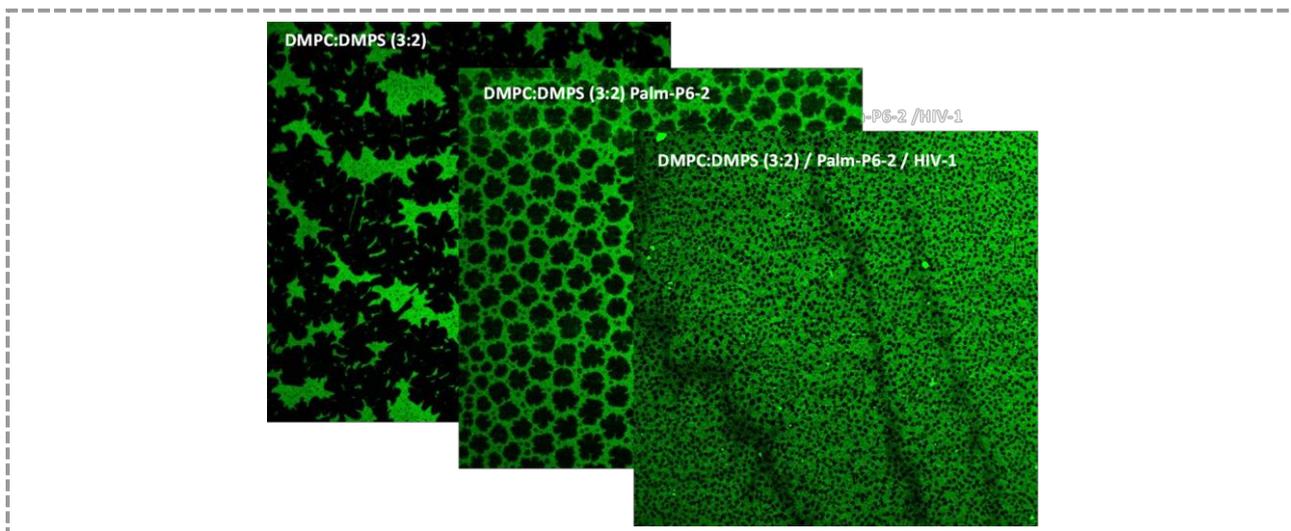
# Effect of Palm-P6-2, an E2-GBV-C derived peptide, on phosphatidylcholine/ phosphatidylserine model membranes

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The human immunodeficiency virus type 1 (HIV-1) is an enveloped viruses that must overcome membrane barriers to deliver the viral nucleocapsid into the cytoplasm. It is the causative agent of the acquired immunodeficiency syndrome (AIDS). A key step in the virus entry is the fusion with host membranes mediated with a fusion peptide (HIV 1-FP). In recent years, many synthetic peptides have been assayed as possible HIV-1 FP inhibitors [1]. The E2 (45-64) synthetic peptide (P6-2) of GBV-C (Acetyl-LCDCPNGPWVWVPAVCQAVG) showed the highest potency in HIV replication trials performed on TZM-bl cells (2) so it has been selected as start point for biophysical studies. To improve its hydrophobicity properties it has been modified changing the acetyl group by a palmitoyl group to obtain Palm-LCDCPNGPWVWVPAVCQAVG derived peptide (Palm-P6-2). In this work, the interactions of this peptide with model membrane composed of 1,2-Dimiristoil-*sn*-glycero-3-phosphocholine and 1,2-Dimiristoil-*sn*-glycero-3-phospho-L-serine: DMPC/DMPS (3:2, mol/mol) or 1,2-Dipalmitoyl-*sn*-glycero-3-phosphocholine and 1,2-dipalmitoyl-*sn*-glycero-3-phospho-L-serine: DPPC/DPPS (3:2, mol/mol) (3) was studied. LUVs were used for binding, quenching, dipole potential and anisotropy studies by fluorescence spectroscopy (4). Penetration kinetics were performed using Langmuir monolayers and Langmuir-Blodgett films for fluorescence microscopy. Figure 1 shows results obtained for DMPC/DMPS (3:2) in absence and presence of Palm-P6-2.



**Figure 1** Effect of Palm-P6-2 on the topography of DMPC/DMPS (3:2) Langmuir-Blodgett films at 24 mNm<sup>-1</sup>. Lipid/peptide ratio (9:1)

**Acknowledgements** This work was supported by Grants CTQ2012-37589-C02-01/02 from the *Ministerio de Economía y Competitividad* and 2014 SGR 216 from the *Generalitat de Catalunya*

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# Effect on the surface tension of bovine serum albumin and lipase from porcine pancreas in the presence of water soluble sulfonated resorcin[4]arenes

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Sulfonated resorcinarenes were synthesized by reacting C-tetra(ethyl) resorcinarene and C-tetra(propyl) resorcinarene with formaldehyde in the presence of sodium sulfite. The cavity formed by the resorcin [4] arenes, is of great interest for the study of the host-guest phenomenon and the different interactions that occur in solution. The resorcin[4]arenes are macrocycles that has been used as host in supramolecular chemistry. In this study the surface tension at the air/water interface of two water-soluble resorcin[4]arenes as a function of concentration were measured using the Wilhelmy method. The results show the presence of aggregation concentration, C<sub>agg</sub>. The effect of these macrocycle, at concentrations after and before the C<sub>agg</sub>, on the stability of Bovine Serum Albumin and lipase from porcine pancreas was studied by dynamic surface tension in aqueous solution.

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# Immobilization of enzymes by overcoating using an atmospheric pressure plasma-deposited polyethylene-like film

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Enzymes are natural catalysts that are ubiquitous in plants, animals, and microorganisms. They accelerate many biochemical and chemical reactions that are vital to living organisms. Enzyme extraction and purification at high grade purity allow their application in industrial, analytical or biotechnological field. However, all these applications are often hampered by lack of long-term operational stability and shelf-storage life of enzymes and by their cumbersome recovery and re-use.

One of the most successful methods proposed to overcome these limitations is the use of an immobilization strategy. Immobilization is a technical process in which enzymes are fixed to or within solid supports. No single method and support is the best for all enzymes and their various applications. This is because of the widely different chemical characteristics and composition of enzymes, the different properties of their substrates and products and the various uses of the product [1]. Moreover, all of the immobilization methods may present a number of advantages and drawbacks. Adsorption is simple, cheap and effective but frequently reversible; covalent attachment is effective and durable, but expensive and easily worsening the enzyme performance; diffusional problems are inherent in confinement or encapsulation. An alternative strategy can be the coupling of enzyme adsorption on a support and its overcoating by a polymer layer. The enzyme is expected to be entrapped under the polymer layer that should protect the enzyme from leaching while should allow access to substrate and product molecules.

Polymerization induced by Plasma Enhanced Chemical Vapor deposition (PECVD) at atmospheric pressure is a powerful way to deposit films of polymer materials that can be realized in mild conditions (moderate temperature, dry state, reduced ion bombardment), allowing the immobilization of enzymes. In PECVD polymerization is initiated by the plasma and reactive fragments from the precursor molecules form a layer network [2].

In this contribution we report preliminary results obtained with a two-step immobilization procedure in which the enzyme is adsorbed on a support and then overcoated by a polyethylene-like coating deposited by PECVD at atmospheric pressure.

Two different enzymes have been evaluated after their immobilization. The coating permeability to Horseradish Peroxidase (HRP) and to a small molecule (fluorescein) has been spectrophotometrically followed. Scanning electron microscopy analysis has been also performed to visualize the uniformity of the deposits on HRP. The kinetic constants ( $K_m$  and  $V_{max}$ ) of Mushroom Tyrosinase have been determined before and after the immobilization with the same polyethylene-like coating, in order to evaluate possible effects of plasma exposition on enzyme functionality.

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# Modified ion-exchange membranes: correlation between porous structure characteristics and electrotransport properties

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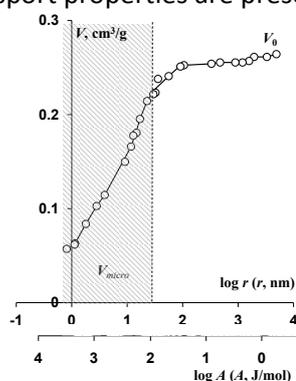
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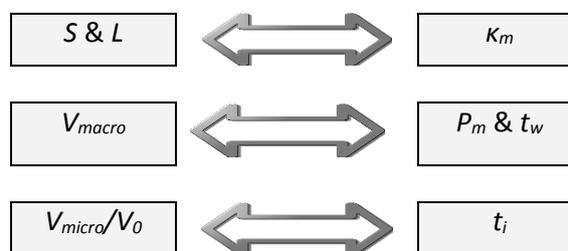
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The results of investigation of the porous structure characteristics and electrotransport properties of ion-exchange membranes are reviewed. The method of standard contact porosimetry [1] was used to determine pore volume distribution versus pore radius or water binding energy in ion-exchange membranes. The maximum value of porosity ( $V_0$ ), the specific internal surface area ( $S$ ), the distance between the neighboring fixed groups ( $L$ ) at the internal interface, the degree of membrane heterogeneity as volume of macropores ( $V_{macro}$ ) and ionic selectivity as fraction of the practically ideal selective micro- and mesopores volume in a total volume of water in the membrane ( $V_{micro}/V_0$ ) can be calculated from porosimetric curves (Fig. 1).

Membrane conductivity ( $\kappa_m$ ), diffusion permeability ( $P_m$ ), transport number of counter-ions ( $t_i$ ) and water transport number ( $t_w$ ) were measured according to [2] in order to find the correlation between structural and electrotransport characteristics of ion-exchange membranes. Perfluorinated MF-4SK (Russia) and Nafion 115 (USA) membranes modified by the organic and mineral additions were used as research subjects. Polyaniline, silica, hydrogen zirconium phosphate and platinum dispersion were used as modifiers. The results of a comparative analysis of structural characteristics found from porosimetric curves and electrotransport properties are presented schematically in Fig. 2.



**Figure 1.** Integral function of water distribution on the binding energy and the effective pore radii for the Nafion 115 membrane.



**Figure 2.** Correlation between porous structure characteristics and electrotransport properties of ion-exchange membranes.

The correlation between porous structure characteristics and electrotransport properties of the modified perfluorinated membranes was established and the role of nature of modifying components and method of membrane modification was revealed. It allows one to present an idea about the localization of the modifier in membrane structure.

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# Investigation of selectivity and structure of hydrate complex fixed ion – counter ion of modified perfluorinated membranes

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Nowadays, modification is one of the approaches to obtain ion-exchange materials with improved characteristics. Selectivity is the most important characteristic of membranes that has great influence on their applying in electromembrane processes. The experimental estimation of electromigration transport numbers of counter ions is associated with considerable difficulties so various theoretic approaches are used to evaluate them [1]. The effects of hydration including the structure of the hydrated complex fixed ion-counter ion is also important for using membranes in various electromembrane devices. The purpose of this reserche was to evaluate selectivity and hydrate properties of modified membranes.

Perfluorinated MF-4SK and Nafion membranes were the objects of the study. Polyaniline (PANI) and hydrated silica (SiO<sub>2</sub>) were used as modifiers. The modification by PANI was carried out by the method of successive diffusion of polymerizing solutions through the MF-4SK membrane to water [2]. The intercalation of the SiO<sub>2</sub> into the matrix of the Nafion membrane was carried out by ~~NH~~ siturimethod [3].

Concentration dependences of potentiometric transport numbers of counter ions ( $t_{+app}$ ) and water transport numbers ( $t_w$ ) in NaCl and HCl solutions were obtained and used to calculate the electromigration transport numbers of counter ions ( $t_{+}^*$ ) by the Scatchard equation:

$$t_{+}^* = t_{+app} + Mm_{\pm} 10^{-3} t_w,$$

where M is the the molar mass of solvent, 18 g/mol;  $m_H$  is the average molality of external solution. The selectivity of investigated membranes is higher in HCl solutions than in NaCl because of the specific selectivity of perfluorinated membrane to H<sup>+</sup>.

The model describing the electroosmotic properties of ion-exchange membranes as two-phase systems was used to estimate the distribution of water in the hydrated complex fixed ion-counter ion in investigated membranes. The division of structural elements of the swollen membrane into two pseudophases (gel phase and intergel solution) is carried out by the mechanism of conductivity and allows to estimate the total flow of water as flows through the phases of membrane. The values of hydration numbers of the fixed ion and counter ion were calculated taking into account the correlation between  $t_w$  and the hydrate capacity of the gel phase determined experimentally. The obtained results are consistent with the NMR data: the hydration number of the sulfo group is in the range of 1 to 3. It was shown that the intercalation of hydrated silica into the Nafion membrane leads to a more equivalent distribution of water near the fixed ion and counter ion both in NaCl and HCl solutions.

**Acknowledgements** The present work was supported by the Russian Foundation for Basic Research (project № 08-01117-15)

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# Bacterial adhesion on dental surfaces

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Bacterial adhesion on tooth and dental restorative material surfaces can lead to unhealthy complications. The objective of this study is to investigate the influence of surface roughness, surface charge and hydrophobicity on the degree of bacterial adhesion. The experiments were made with *Streptococcus mutans*. The roughness, morphology and texture of the dental surfaces were measured and evaluated by profilometry [1,2]. Surface hydrophobicity was determined by contact angle measurement whereas the surface potential was estimated from streaming potential measurements. The adhered cells are stained and detected spectrophotometrically and consequently compared with the results obtained by scanning electron microscopy [1,2]. Preliminary results indicate that the bacterial adhesion extent depends mainly on the surface roughness and surface hydrophobicity.

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# DOUBLE LAYER ELECTROSTATICS OF HETEROGENEOUS SURFACES WITH CIRCLE PHASE CONTOURS

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A system composed of two semi-infinite bulk phases (air/electrolyte solution) divided by a flat charged surface is studied. The particular considered surface is modelled as a Langmuir type monolayer consisting of two surface sub-phases, divided by a circle contact line (see Fig.1). The charge distribution in the liquid phase ( $g_B$ ) as well as on the surface ( $g_S$ ) is assumed within the framework of the Gouy-Chapman theory. The gas phase is supposed electro neutral. This system defines a non-trivial 3D-2D-1D boundary value problem, formulated and solved for a straight line (1D) phase elsewhere [1,2]. The novel element here is that the line phase is a charged circle (rim). The rim curvature effect includes the appearance of additional potential difference inside/outside the circle. Basic analytical relations are obtained and evaluated for the surface potential. The role of the potential is discussed with respect to the bio-membrane pore permeability. Another effect, the so-called Maxwell stress is analyzed. Special attention is paid on its radial component at the rim. Aside of the mentioned above effects, some electrical parameters, specific for 2D, 1D phases, are discussed. Such parameters are the respective surface dielectric constants,  $\epsilon_s$  (2D) and  $\epsilon_L$  (1D). Formally defined within the generalized Maxwell equations, they are evaluated and shortly discussed as excess quantities (within the framework of *Gibbs* theory).

Fig.1 A sketch of the studied system, with all substantial physical parameters.

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# Droplets in emulsion gels: from fillers to networks

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Because of their ability to strongly adsorb at oil/water interfaces and to stabilise oil droplets by steric and electrostatic repulsion, water-soluble proteins are widely used as efficient emulsifiers. At low pH, proteins can aggregate and also form gels, either of protein molecules in solution or of protein-covered droplets. The soft materials formed from protein-stabilised emulsions are referred to as emulsion gels, however, this designation is not precise enough to reflect the variety of composition of these materials. It is thus important to take into account the ratio between adsorbed and suspended proteins in solution before gelation, as during emulsification not all the proteins in solution adsorb at the interface. If the ratio is low, i.e. most of the protein is suspended, the system can be seen as a matrix of protein gel with the oil droplets acting as fillers, as in polymeric materials. At a higher ratio the emulsion gel is more of a composite formed of both a protein and a droplet network.

Our objective is to study in detail the protein-stabilised emulsion gels considering the full range of their composition. A first step is to characterise separately the gelation of purified suspensions of protein-stabilised droplets, and of suspensions of pure proteins. These components are then combined, resulting in emulsion gels of well-characterised compositions, thus allowing a rigorous approach to these systems.

We use sodium caseinate as a case-study for the protein because of its outstanding properties as a surface-active agent and stabiliser, and because of its well-known ability to form gels. Sodium caseinate-stabilised emulsions are produced using a high-pressure homogeniser, the resulting droplet size is close to the size of naturally occurring caseinate assemblies, i.e. 100-200 nm. We combine rheological and microscopic approaches to characterise the behaviour of the gels, in order to develop our understanding of how the separate networks of droplets and proteins develop and contribute to the overall properties.

Figure 1: Storage moduli of gels composed of: only droplets (g), only proteins (■), and a mixture of proteins and droplets (X, color indicates the value of the ratio  $\frac{\text{protein}}{\text{protein} + \text{droplets}}$ ) as a function of the total volume fraction  $\frac{\text{protein} + \text{droplets}}{\text{total volume}}$ .

# New applications of Imaging Ellipsometry at the liquid/gas and liquid/liquid interface.

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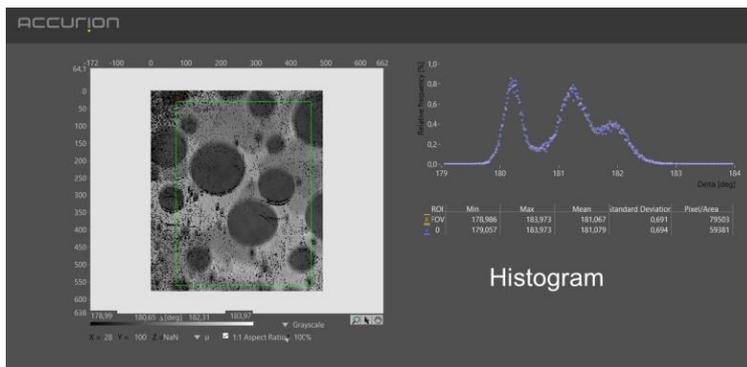
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In case of imaging nanofilms at the air/water interface Brewster angle microscopy (BAM) is state of the art. BAM can be seen as a subunit of the imaging ellipsometry – an imaging can also act as a Brewster angle microscope – and imaging ellipsometry is the more general approach that offers more quantitative results. Ellipsometry is based on the ellipsometric angles Delta and Psi or in case of imaging ellipsometry on microscopic maps of Delta and Psi. The ellipsometric angles will be transferred by optical modelling into thickness maps or the refractive index of the layers.

From the point of view of data acquisition, microscopic mapping at the air/water interface needs a fast recording method and from the point of view of the experimental setup, a very efficient vibration isolation concept is needed.

For applications at the liquid/liquid interface (like a droplet) in variable distances to a solid interface or analog air/liquid interface (like a bubble in a liquid environment) with variable distance to a solid interface a new sample holder concepts are required.

We will report the latest progress in microscopic mapping at the air/water interface (Fig. 1) and new cell concepts for the characterization of droplets or bubbles with variable distance to a solid surface (Fig. 2) that enable as well the view through a prism as in transmission through the windows of the cuvette.



**Figure 1** Microscopic Delta map and histogram of the resulting data of Ethylstearate at the air/water interface.



**Figure 2** New sample holder concept with an under surface lift (USL).



# Interfacial Rheology for the Design of Core/Shell Capsules: Coacervate/Polyurea Membranes at the Oil/Water Interface

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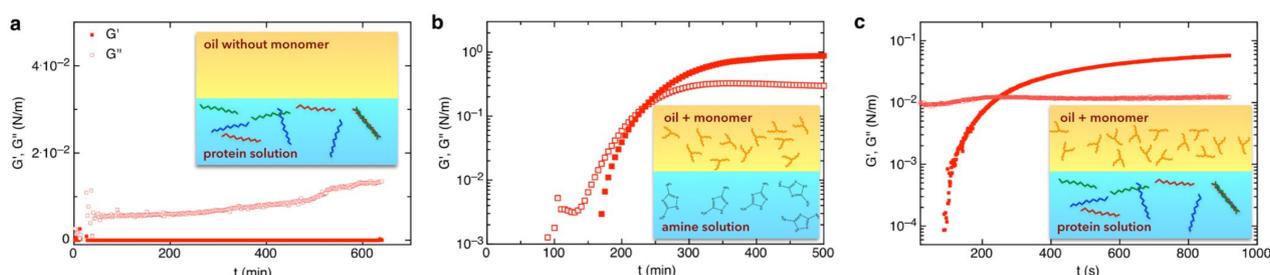
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In this contribution, we investigate composite coacervate/polyurea membranes formed by associative phase separation of a protein and weak polyanion, followed by subsequent interfacial polymerization to form polyurea at the oil/coacervate interface[1]. We demonstrate how linear and nonlinear interfacial shear rheology[2] allow to both track the synthesis of those composite interfaces *in-situ*, and to obtain the viscoelastic profile of the resulting composite membranes. In particular, we show how the interfacial rheological behavior can be controlled by coupling associative biopolymer phase separation with interfacial polymerization, allowing to design core/shell capsules for the encapsulation of oil drops with dense, highly stable and cross-linked interfacial layers with excellent barrier properties.

We elucidate the mechanisms of interfacial polymerization by screening the role of the different components (protein, polyanion, polyurea oligomeric precursors) participating in the interfacial membrane formation; these experiments are complemented by a detailed analysis of the barrier properties and chemical composition of the resulting composite membranes.

In addition to obtaining quantitative information on the interfacial polymerization kinetics and mechanisms, we investigate the linear and nonlinear interfacial viscoelastic behavior of the resulting membranes both on flat interfaces studied in an interfacial rheometry setup, and on spherical membranes of the actual capsules *in-situ* using nanoindentation testing. This combination of methods allows us to link the in-plane interfacial rheological properties with the macroscopic mechanical behavior of the core/shell capsules.

Finally, we point out general learnings for the interfacial rheology and three-phase wetting phenomena in coacervate-based core/shell systems, focusing on the interfacial energy balance in systems involving coacervate/water, oil/water, and coacervate/oil interfaces, and we describe the interplay between interfacial physics and formation of core/shell capsule systems.



**Figure 1** – Model experiments to elucidate interfacial polymerization of polyurea/coacervate composite membranes at the oil/water interface tracked by oscillatory interfacial rheology ( $G'$ ,  $G''$ : elastic and viscous interfacial shear moduli). Complex coacervates are formed by associative phase separation of a protein and a weak polyanion. (a) Monomer-free reference case (interfacial viscous modulus dominates): the protein component only adsorbing at the interface between water and the neat oil; (b) reference polyurea layer polymerized between an aqueous monomer solution and an oil phase containing oligoisocyanate precursor; (c) interface between the oil phase containing oligoisocyanate and a model protein solution.

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# Voltammetric studies at polarized ionic liquid membranes: Reaction of biguanide drugs with methylglyoxal

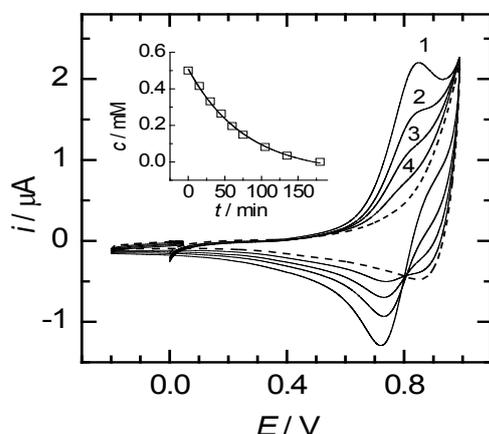
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Simple electroanalytical approach is used to get an insight into scavenging kinetics and mechanism of the methylglyoxal (MG) reaction with biguanides metformin (MFH<sup>+</sup>), phenformin and 1-phenylbiguanide under the physiological conditions (pH 7.41 and 37 °C). The approach is based on monitoring of the concentration profiles of protonated biguanides by ion-transfer voltammetry (ITV) at the polarizable room-temperature ionic liquid membrane [1]. Effects of the reactant's concentrations and pH lead to the proposition of mechanism which includes an acid-base reaction of biguanide and which separates the parallel reactions of the protonated and deprotonated biguanide with methylglyoxal. Reaction rate increases considerably in the sequence metformin < phenformin < 1-phenylbiguanide. Kinetic data confirm the previous finding that scavenging of methylglyoxal by metformin is a relatively slow reaction. Optimization of the background electrolyte enables to detect both the protonated biguanide and the MG anion in the reaction mixture by capillary electrophoresis (CE). CE analysis yields the mole-to-mole ratios of the reacted biguanides to methylglyoxal between 0.6 and 0.7 pointing to the simultaneous formation of a 1:1 and a 1:2 reaction products [2].



**Figure 1.** CVs ( $10 \text{ mV s}^{-1}$ ) of the aqueous mixture containing  $0.5 \text{ mM MFH}^+$  and  $5 \text{ mM MG}$  in  $3.9 \text{ mM}$  phosphate buffer (pH 7.41) measured at  $37 \text{ °C}$  after (1) 0 min, (2) 30 min, (3) 60 min and (4) 105 min from mixing MF and MG; the background current is shown by the dashed line. Inset: time profile of the MF concentration evaluated from the positive peak current on CV.

**Acknowledgements.** This work was supported by grant no. 15-03139S from Grant Agency of the Czech Republic.

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# Ion Pairing and Adsorption of Sunset Yellow/CTAB Mixtures at the Air-Water Interface

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Since air/liquid interfaces are ubiquitous within aqueous foam, it is particularly important to study their properties on a molecular scale in order to understand the effects of molecular building blocks on the stability of foam. For removal of azo dyes from aqueous systems, particularly foam fractionation is also of great interest.

In this contribution, macroscopic foam properties of aqueous Sunset Yellow (6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate, SSY) – CTAB (hexadecyltrimethylammonium bromide) mixtures were investigated and correlated with molecular properties of the corresponding air/water interfaces. In particular, interfacial sensitive methods such as vibrational sum-frequency generation (SFG) and tensiometry, as well as bulk sensitive UV/VIS spectroscopy, were used to deduce structure-property relations from the interface to the macroscopic foam.

By adding CTAB to aqueous SSY solutions, changes in optical extinction spectra due to strong electrostatic interactions between the oppositely charged azo dye and the surfactant were observed. The SSY / CTAB – complexes which were already formed in the bulk solution are found to be highly surface active, while the unmodified azo dye has no measurable surface activity. Time-resolved vibrational SFG spectra revealed the adsorption kinetics of different molecular species at the interface: Initially, the air/water interfaces are covered within <1 s by free CTAB surfactants while at a later stage SSY/CTAB complexes start to replace the positively charged free CTAB at the interface. As a result, the strength of the interfacial electric field decreases which is confirmed by the decreasing O-H stretching bands around 3200 and 3450 cm<sup>-1</sup> in our SFG spectra. The adsorption of SSY/CTAB complexes is enhanced remarkably by adding higher amounts of Sunset Yellow which results in 1:2 dye-surfactant ion pairs. This conclusion is consistent with negligible O-H stretching intensities at a SSY/CTAB molar ratio of 1:2, because this observation is indicative for air/water-interface with zero net charge [1-3]. Obviously, this also consistent with the azo dye / surfactant – complex being electrically neutral at the interface. The decrease in O-H stretching intensity and thus interfacial charging is accompanied on a macroscopic level by a similar decrease in foam stability.

For that reason, we conclude that Sunset Yellow / CTAB foams are mainly stabilized by electrostatic repulsion forces, as the loss of net charge at the interface at higher dye concentrations leads to lower foam stabilities and larger bubble sizes. This fulfills the classical DLVO picture of foam film stabilization via the electrostatic disjoining pressure and is different from our previous work which showed that for macromolecules like proteins [1-2] and polyelectrolytes [3], macroscopic foam stability is enhanced by uncharged aggregates which reduce coalescence and drainage.

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# Formation, physiochemical and interfacial study of carbamate surfactants

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Switchable surfactants have grown in interest over the last two decades since they respond to external stimuli and induce changes in the macroscopic behavior of systems. The use of gases to control the behavior has been appealing and a popular system is CO<sub>2</sub> in combination with an inert gas such as nitrogen or argon, as it can be used as pH regulator while avoiding the problem of salt built-up upon cycling.<sup>1</sup> Yet, another aspect of interest is the use of CO<sub>2</sub> as a building block covalently linked to a surfactant bearing an amine group namely alkyl carbamate.

We have studied three alkyl primary amines in presence of CO<sub>2</sub>. The three different amines are presented in figure 1. Octyl and dodecylamine have been chosen in order to evaluate the effect of the alkyl chain, while the N,N-di(propylamino)dodecylamine (Y12-amine) presents two primary amine susceptible of reacting with CO<sub>2</sub>. We discuss how these variations in structures influence the anionic carbamate formation and its reversibility, and report the physiochemical and self-assembly properties of the different system in bulk and at the gas-water interface. Among the three amines investigated only Y12-amine formed water soluble carbamate surfactant. Furthermore Y12-carbamate was also studied at the gas-water interface using the pendant drop technique with a sealed chamber where the gas composition surrounding the drop could be controlled. We could demonstrate that the interfacial carbamate formation under a CO<sub>2</sub> stream induced a decrease of the surface activity of the Y12-amine. Moreover, we could also demonstrate the applicability of such systems for suspensions of hydrophobic particles.

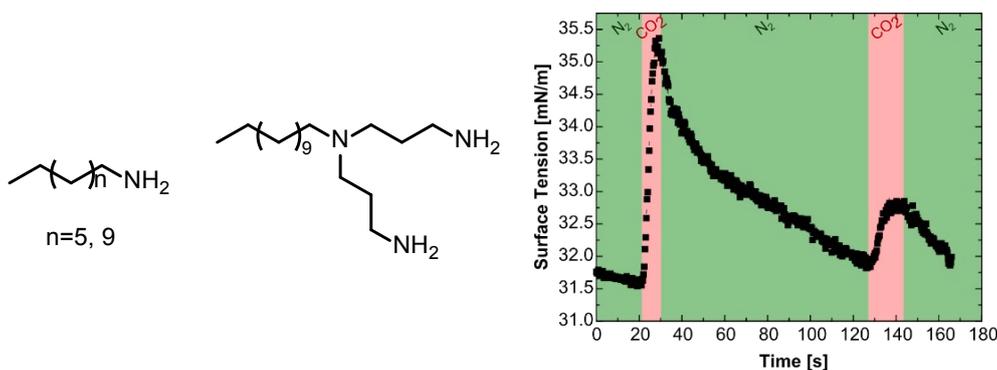


Figure 1a) octylamine, dodecylamine, and Y12-amine. 1b) interfacial response to CO<sub>2</sub>/N<sub>2</sub> cycling at 100 x CMC.

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# Neutron Reflectometry Reveals Structural Aspects of Blood Protein Adsorption to Polymer Brushes

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Protein adsorption to biomedical surfaces, for example of implants, is a major issue because it can lead to harmful foreign body reactions. Surface functionalization with hydrophilic polymer brushes is a common strategy to suppress undesired protein adsorption. However, numerous cases where this approach failed are reported and further investigation of the molecular mechanisms is required. Here, we use neutron reflectometry (NR) to characterize the adsorption of blood proteins to poly(ethylene glycol) (PEG) brushes grafted to planar phospholipid surfaces. The unique structural insights provided by NR allow distinguishing between different adsorption modes<sup>1,2</sup>. For whole human blood serum the reflectivity curves reveal significant primary adsorption into the lipid head group region and suggest the presence of ternary adsorption at the brush periphery. In context with the commonly neglected antigenicity of PEG we systematically characterize the structural aspects of antibody binding to polymer brushes with various chain lengths and grafting densities. To this end we obtained qualitatively different results for antibodies specific to the PEG end points and to the backbone.

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# Solvent/water solubilized by ethanol: the anomalous re-entrant emulsification effect observed with moderate centrifugal fields revisited

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*Initially immiscible Solvent-water combinations can be co-solubilized by co-solvents. Some of them behave as hydrotropes<sup>1</sup>. Hydrotropes show a preferential adsorption/desorption around solute. Whenever preferential solvation occurs around a molecule or around an ultra-flexible microemulsion “droplet”, the classical buoyancy term introduced by Svedberg has to be generalized in order to take into account the modification of the model ratio of the layers “around” the solute considered: a simple general intuitive expression has been given by R. Piazza a few years ago<sup>2</sup>.*

*We show here that the enhanced gradients observed near critical points in binary as well as ternary mixtures in the vicinity of critical points in the phase diagram can be understood via MD simulations. In the case of ternary solutions containing “pre-ouzo” aggregates (alias UFME) stabilized by an accumulation in an “emerging” interface<sup>3</sup> can even be at the origin of the “anomalous” double meniscus described since the seventies in some regions where spontaneous emulsification occurs. We establish the following results:*

- steep equilibrium concentration gradients with noticeable accumulation of ethanol at the bottom of the centrifuge cell are noticed near critical points in binary solutions of ethanol and dodecane. These are steeper close to the critical point.*
- the phenomenon is even enhanced in the domain of concentration where UFME exist, i.e. “pre-ouzo” aggregates that were observed and understood by solvation-competition: at speeds as low as 3000 rpm, significant gradients of weakly bound aggregates are observed*
- at slightly higher speeds, a re-entrant “anomalous” phase separation occurs: a defined region of the concentration gradient in the test-tube crosses the phase boundary towards a two phase system observable via a defined turbid zone. In those cases, the top and bottom of the tube under moderate centrifuge fields are w/o and o/w in organized nanostructures, while the middle of the tube only stabilizes as a spontaneous emulsification “ouzo effect” triggered by moderate centrifugal field.*

*We are not aware of any earlier predictive theory of the sedimentation coefficients observed. In these types of moderate centrifugation speed experiments, sedimentation equilibria as obtained will be rationalized via the general theory of UFME<sup>4</sup>.*

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# Influence of oils on the efficiency of surfactants used in fire-fighting foam formulations

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The known theory underpinning the use of fire-fighting foams remains primitive and empirically based; few attempts [1–3] have been made to model or investigate the behaviour of foam formulations from a chemical perspective. For this reason, a sound understanding of the physical and chemical processes that take place during the extinguishment of a flammable liquid will not only potentially hasten the development processes, but allow more environmentally-responsive low-F or hydrocarbon analogues to replace the existing F-carbon surfactants.

This work will present some new advances and understanding about the properties and colloidal science of fire-fighting foam formulations. The predominant material used in the formulations to give the desired interfacial properties are partially fluorinated surfactants, which as expected provide very low surface tensions. In initial work, a typical fire-fighting foam formulation has been broken down into its constituent parts so that the individual fluorinated surfactants can be well understood and characterised. By understanding how these different materials work both individually and as mixed systems, it will be possible to start to appreciate at a more profound level the processes that are occurring during the extinguishment of flammable liquids. Here, experiments have been carried out to determine how the presence of oil, a model close to practical applications, affects the stability of a fire-fighting foam formulation. These studies have been carried out on the formulation components both individually and as mixed systems in mimics of a real fire-fighting formulation. Foam lifetime studies have shown that all F-surfactants exhibit both good foamability and foam stability, as one might assume, but adverse effects are observed when an oil is incorporated into the system. Additional discussions will be made on how small-angle neutron scattering (SANS) has provided direct information on how the presence of oil is impacting on the self-assembled structures of the surfactants used in the fire-fighting foam formulation.

**Acknowledgements:** The financial support of Angus Fire LTD, United Kingdom

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# Surfactants at the Design Limit

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Generally speaking, molecules can be broken down into being either polar or non-polar (examples being water and oil respectively). These two classifications of molecules display individual, and often opposite chemical properties and hence for example, do not mix well. Surfactants help overcome these limitations of immiscibility because they are amphiphilic (dual-natured) molecules, possessing both hydrophilic and hydrophobic groups. Due to the dual nature, they are associated with many useful interfacial phenomena, and as such are key components for diverse industrial processes including – detergents, cosmetics, paints, herbicides, medicine and oil recovery. The most heavily investigated interfacial phenomena of surfactants is their ability to significantly alter surface tension ( $\gamma$ ).

Fluorocarbon surfactants display the most effective reduction of surface tension. Unfortunately, this has important environmental consequences because of the persistence, bioaccumulation and toxicity of fluorocarbons.<sup>1</sup> One alternative is to use hydrocarbon surfactants. However, typically, these are unable to reduce the surface tension to significantly low values compared to fluorocarbon analogues.

Recently a series of novel low-surface energy hydrocarbon surfactants has been introduced, with highly branched chains.<sup>2</sup> These so called “hedgehog“ surfactants have achieved low surface tensions which match those of fluorocarbon analogues. A recent review proposed that the limiting surface tension at the CMC ( $\gamma_{cmc}$ ) is dependent on efficient surface packing at the air-water interface, hence excluding air/vacuum from the film.<sup>3</sup> These highly branched chain “hedgehog“ surfactants give rise to efficient packing and space filling in surface monolayers, yielding very low values for hydrocarbon surfactants (the lowest published value being  $\gamma_{cmc} = 23.8 \text{ mN m}^{-1}$ ).<sup>4</sup> By mixing “hedgehog“ surfactants and manipulating the architectural structure of the tail or headgroup, even lower aqueous surface tensions have been achieved. The research presented here describes some of the novel ways hydrocarbon surfactants have been developed, and their special properties.

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# Simultaneous stress and weight measurements for particulate films made from capillary suspensions

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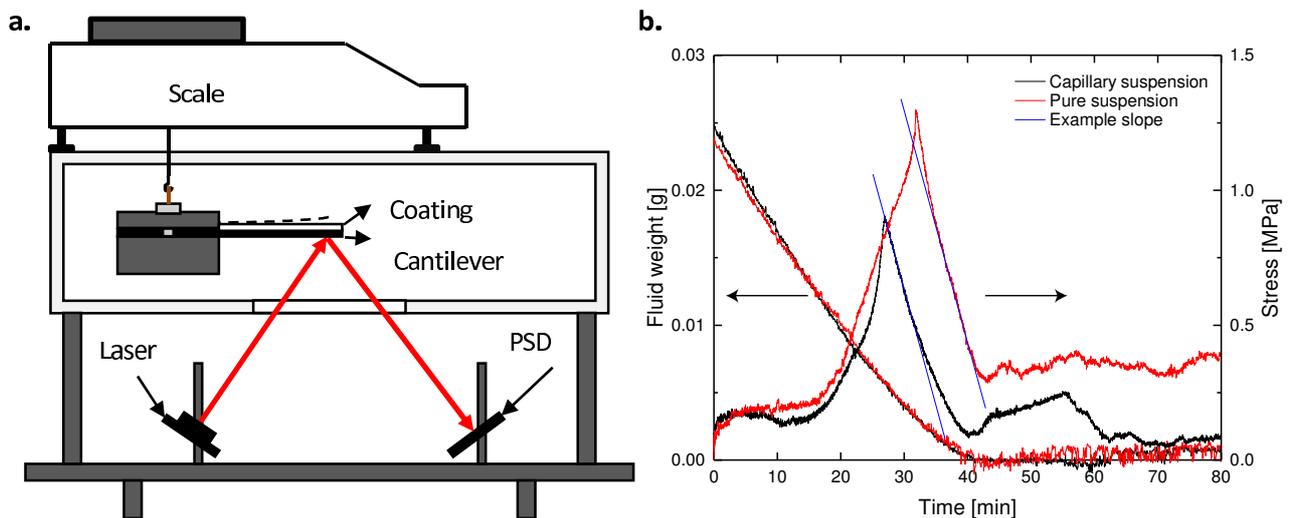
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Cracking and particle mobility are a significant problem in the drying of films from hard sphere suspensions. One pathway to avoid these problems is by using capillary suspensions [1]. In the pendular state, the preferentially wetting secondary fluid forms capillary bridges between the particles. The capillary forces from such bridges induce the formation of a sample-spanning particle network [2, 3], which limits the direction of particle motion during film drying and the capillary force of the bridges counters the capillary force within pores generated by evaporation. Crack-free films can be produced at thicknesses much greater than the critical cracking thickness for a suspension without capillary interactions, and even persists after sintering. This method is applicable to a broad range of materials and can be easily implemented using well-established industrial methods.

An in situ weight and stress measurement of a drying film allows direct relation of dynamic changes in stress with its corresponding drying rate. The overall stress of a film can be measured using the cantilever deflection method [4] as the film dries in a temperature and humidity controlled chamber as shown in Figure 1a. Capillary suspensions, with a higher shear modulus, can lower the overall stress in the film while drying, as shown in Figure 1b. Even though no visible cracks occur in either film, a characteristic increase and then relaxation occurs. Capillary suspensions change the shape of the stress profile as a function of drying time where similar slopes are present at different stages of the stress relaxation. Variation with drying temperature and humidity are also discussed.



**Figure 1** a. In situ stress and weight measurement apparatus with controlled drying chamber. b. Stress development and weight loss data of a pure suspension compared to a capillary suspension showing lower peak stress as well as a variation in peak shape.

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# Linking interfacial properties to emulsion microstructure: Understanding the relationship between molecular structure of polymeric emulsifiers and emulsion stability

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Controlling the microstructure of emulsions is essential for the design of emulsion based products and for their product properties. However, this is a challenging task due to several instability phenomena that can lead to change in emulsion microstructure either directly after production or during the emulsion shelf-life. One of the most important instability phenomena in this respect is the coalescence of dispersed phase droplets.

Coalescence occurs due to droplet collisions in the outlet of the emulsification device which can cause rupture of the interfacial film separating two droplets. Over the shelf-life of emulsions, dispersed phase droplets are closely packed and in contact with each other. Again, rupture of the interfacial film can occur and can lead to droplet coalescence and coarsening of the emulsion microstructure.

It is assumed that all of the above mentioned phenomena can be controlled by controlling the rheological properties of the interfacial film. These properties in turn depend on the molecular properties of the used emulsifiers. While there is some knowledge on how the interfacial properties depend on the molecular characteristics for low molecular weight surfactants, there is still a lack of thorough understanding when polymeric emulsifiers are used as sole emulsifying substances. More importantly, a reliable correlation between interfacial properties and emulsion microstructure is generally missing.

Therefore, the aim of this contribution is to highlight the advances of our group concerning the relationship between the molecular structure of polymeric emulsifiers and the stability of single and multiple emulsions against coalescence [1]. The focus lies on single droplet experiments that link information gained from dilational rheological measurements to droplet size distributions of the actual emulsions. For this purpose, a novel measurement device – the Diffusion and Coalescence Time Analyzer (DCTA) – will be presented [2]. With this device, it is possible to quantify the resistance of the interfacial film against coalescence by visualizing the coalescence process. Ultimately, the goal of this research is to bridge the gap between the molecular structure of the emulsifier and the microstructure of the emulsion to allow for a targeted choice of polymeric emulsifiers.

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# Detailed Balance in Polar Fluids

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In the theoretical treatment of hydrodynamics the balance equation for the angular momentum is often ignored (limit of zero moment of inertia), and one only accounts for the Navier-Stokes Equation (force balance equation). This usually implies that the anti-symmetric part of the stress tensor vanishes. Hence, when considering hydrodynamic fluctuations that conserve detailed balance, the stress tensor noise correlation function is taken to be symmetric. Although for isotropic fluids symmetry ensures symmetric noise correlation, this is not in general the case for anisotropic fluids such as nematic or polar fluids.

We have derived the inertial dynamic equations for polar liquid crystals (including the angular momentum equation) and with the use of stochastic field theory the entropy production rate was calculated. It has been found that the inclusion of an antisymmetric stress tensor noise is crucial to ensure detailed balance in the inertial case. Therefore, one cannot ignore the balance equation for the angular momentum and the limit of vanishing moment of inertia should be taken carefully. Taking this limit for polar fluids we find the (unusual) form of the noise in the hydrodynamic equation for the polar order parameter, while recovering the Navier-Stokes equation with symmetric stress noise. This result have various implications on the treatment (both analytically and in simulations) of fluctuating hydrodynamics for all fluids that can exert torques on the system boundaries.

# Conformational behavior of graft copolymers in selective solvents and their sorption on lyophobic surface

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Conformational behavior of graft copolymers and their sorption at surfaces interacting selectively with the backbone is a result of a number of synergic and antagonistic effects. The conformations are affected not only by the interactions of grafts and backbone with the solvent, but also by interactions of the copolymer with the surface. We performed an extensive series of coarse-grained computer simulations. We used dissipative particle dynamics (DPD) and studied copolymers differing in grafting density and in the lengths of grafts and varied solvent quality for the backbone. The attractive interaction of the surface with the backbone and repulsive interaction with grafts were kept constant in all simulations.

Results of systematic simulations allowed us to construct phase diagrams which show regions (combinations of solvent selectivity and the lengths of grafts) where the copolymers are strongly or weakly adsorbed, or fully dissolved in bulk solvent. The description of the behavior is supplemented by conformations typical for individual regions. The complexity of the behavior is mainly due to the competition of following factors: (i) Poor quality of the solvent for the backbone lowers the overall copolymer solubility and promotes the adsorption, (ii) but it simultaneously causes the contraction of the backbone and lowers the probability of backbone-surface contacts. During the lecture, the behavior will be discussed in detail and important conclusions concerning the experimental chromatography of copolymers and other separation techniques will be also presented.

New pieces of information provided by simulations are not only interesting from the theoretical point of view, but they facilitate the prediction and tuning the adhesion in technological applications of graft copolymers. Last, but not least, they help to interpret results of modern chromatographic methods used for the characterization of copolymers which combine the separation mechanisms of size-exclusion chromatography with different variants of interaction chromatography.

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# Emulsifying properties of Chitosan/Sodium lauryl ether sulfate system

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Chitosan is cationic biopolymer that has many potential applications in the food, cosmetics, and pharmaceutical industries, because of its unique nutritional and physiochemical properties [1, 2]. Many of these applications depend on the interactions between chitosan and anionic surface active substances, which results in chitosan/surfactant complexes formation [3]. These complexes can alter the adsorption layer around the oil droplets, thus affecting emulsion stability [4]. For these reasons, the main goal of this study was to investigate interfacial properties of chitosan/sodium lauryl ether sulfate (SLES) complexes.

In order to understand the stabilization mechanism, interface of oil/water systems that contained mixtures of chitosan and SLES, was studied by measuring the interfacial tension. Considering the fact that the properties of the oil phase influences the adsorption process, three different types of oil were investigated: medium-chain triglycerides - Saboderm TCC, a semi-synthetic oil, paraffin oil, a mineral oil, and natural oil obtained from the grape seed.

The surface tension measurements at the oil/water interface, for pure chitosan water solutions, indicate to a poor surface activity of this biopolymer. Addition of SLES to chitosan solution causes a significant decrease in interfacial tension for all investigated oils. Based on the results of the measurements of interfacial tension, system Saboderm TCC/water was selected, for obtaining of 20% oil-in-water emulsions. Emulsions were stabilized by mixture chitosan/SLES, in mass ratios that correspond to different regions of their interactions. The emulsions characteristics (stability, size and size distribution, zeta potential) were investigated.

Results of this study are important for understanding the influence of polymer-surfactant interaction on the properties of solution and stability of dispersed system. Also, they provide information about optimal chitosan/SLES mass ratio suitable for use as wall material for the microencapsulation of hydrophobic active molecules in cosmetics.

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# Release profiles of esculin-loaded hydrogel microcapsules covered with polyelectrolyte shells

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Polymer-based microparticles appear to be a promising candidate for a targeted delivery system for esculin – a phyto-constituent widely used in the pharmaceutical area as a health promoting agent [1]. However, due to its poor bioavailability its therapeutic application is limited, thus a development of an efficient oral transportation system is required. Therefore, esculin was encapsulated in negatively charged calcium alginate cores by means an ionic gelation technique [1] and then oppositely charged polyelectrolyte shells were deposited by the electrostatic adsorption using a compatible polycation: a polysaccharide - chitosan, a protein – gelatin, or the pair of synthetic polyelectrolytes poly(allylamine hydrochloride)/poly(4-styrenesulfonate) (PAH/PSS). The glycoside encapsulation efficiency was obtained from UV-Vis measurements. The structure and morphology of the hydrogel microcapsules were visualized using scanning electron microscopy (SEM). The thickness of the layers was measured by ellipsometry [2] and their masses and viscoelastic properties were analyzed by quartz crystal microbalance with dissipation monitoring (QCM-D) [2,3]. Coatings characterization was complemented with their zeta potential values determined by the streaming potential measurements [3]. Additionally, release of esculin from the fabricated microcapsules was measured *in vitro* in simulated gastric and intestinal fluids, in order to investigate the influence of the type of polymer used for the microparticles shell formation on their cargo liberation abilities.

The glycoside was successfully loaded (EE>50%) into the microcapsules with sizes in the range of 824 – 993  $\mu\text{m}$ . The kinetic measurements revealed that the esculin release behavior of the microparticles depends on the type of polymer adsorbed onto the alginate core and can be related to the thickness, mass and the zeta potential of the polyelectrolyte membranes and different esculin release mechanisms were noticed. Nevertheless, our results indicate that the fabricated polymeric microcapsules seem to be applicable as promising internal carrier systems for the plant derived therapeutic agents.

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# Lyotropic behaviour of a poly(ethylene oxide)-*graft*-poly(vinyl acetate) copolymer in polar and nonpolar media

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Polymeric surfactants represent a very interesting class of tunable amphiphilic macromolecules [1] with potential applications in many industrial fields, such as nanotechnology, pharmacology, consumer goods and cosmetics. Indeed, thanks to the possibility of customizing their molecular structures in a task-oriented fashion, these high-molecular weight amphiphiles can be used for the encapsulation and delivery of a plethora of substances with diverse physical-chemical properties. They can serve, for example, as emulsion stabilizers [2], or as carriers for drugs [3] and active ingredients through the formation of nanoparticles [4] and nanostructured colloidal systems. In the present work, we report on a poly(ethylene oxide)-*graft*-poly(vinyl acetate) copolymer of industrial interest [5] due to its simple molecular architecture and its ability to form a wide range of lyotropic assemblies in water and in oils. We investigate the phase behaviour of this polymer in aqueous medium and in the presence of common perfume and surfactant molecules. The nanoscale structure of these systems is here elucidated using optical and confocal microscopies, as well as dynamic light- and small-angle x-ray scattering.

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# Sugar and pH responsive nano-assemblies based on boronic acid-containing polyelectrolytes

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Boronic acid-containing polyelectrolytes represent a new class of stimuli-responsive polymers with potential applications as self-regulated drug-delivery systems and chemical sensors for biologically important polyols like glucose and other saccharides. Phenylboronic acids (PBA) in aqueous solutions exist in two forms which are in equilibrium; neutral • trigonal and anionic • tetragonal form. Tetragonal forms of PBA bind covalently with compounds containing cis-1,2- and 1,3-diol groups through reversible boronate formation (Figure 1b) [1]. Stimuli-responsive polymers are very important for medicine because of their ability to undergo self-assembly in response to variations in the local environment [2]. Boronic acid-containing polymers were prepared via quaternization of poly(4-vinylpyridine) (P4VP) by [2-(bromomethyl)phenyl]boronic acid with the high level of modification (Figure 1a). Obtained polyelectrolytes were characterized in aqueous solutions in the wide range of pH by static, dynamic and electrophoretic light scattering. The interactions of QP4VP-PBA with saccharides were studied via fluorescent measurements.

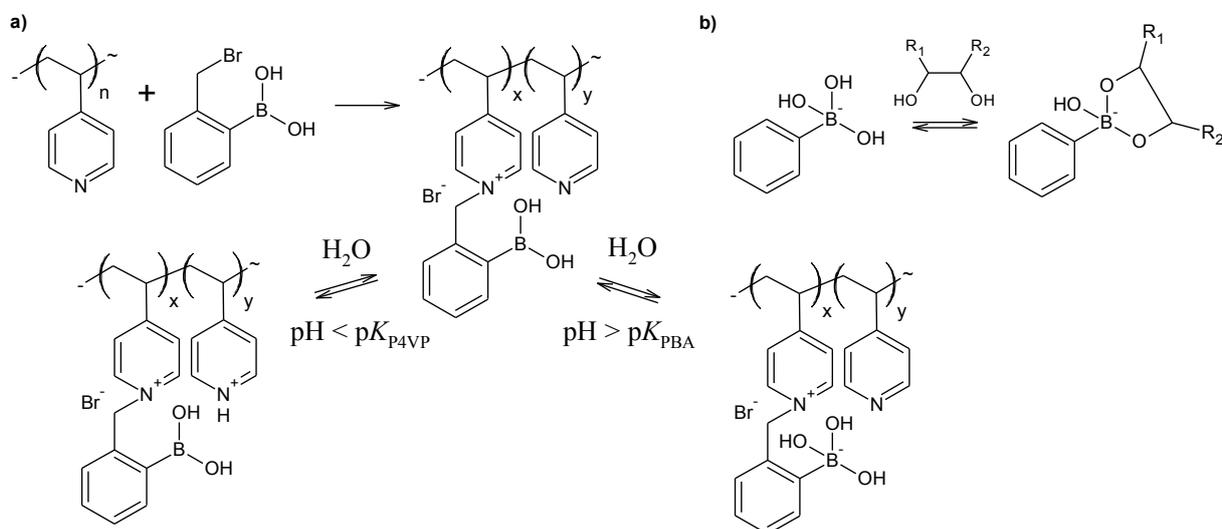


Figure 1: a) preparation of QP4VP-PBA polyelectrolytes, b) reaction of PBA with diols

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# Flocculating activity of *Rhodococcus opacus* FCL-1069

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Bacteria are diverse group of microorganisms, which can produce secondary metabolites with potential biotechnological applications, among them are extracellular polymeric substances (EPS). The physicochemical properties of EPS (coagulating, thickening, gelling, stabilizing, water-binding) and biological activities (antitumor, antiviral, antibacterial activity) are commonly apply in chemical, pharmaceutical, and food industry [1]. Their synthetic analogues have been reported as polymers causing of health and environmental problems. For example, polyaluminium chloride and polyacrylamide have neurotoxic and carcinogenic impact on human cells. However, these substances are still applied in wastewater treatment due to their low-cost production and high efficiency [2]. On the contrary, exopolymers are eco-friendly, biodegradable and what is important some of them can be obtained from agro-industrial wastes, which makes them highly advantageous alternative of the synthetic polymers. The main purpose in microbial exopolymers application, is to select new bacterial strains that are able to growth on low-cost substrates what consequently lowers costs [3]. The acquisition of novel exopolymers and identifications of all their properties can indicate new directions of their application.

In the present study, the bacterial strain *Rhodococcus opacus* FCL-1069 was tested due to its flocculating activity. The strain was incubated on liquid medium for 14 days; during that time the samples of culture broth were collected and investigated based on the series of spectrophotometric measurements. The flocculating activity was determined in the presence of kaolin suspension with addition of Ca<sup>2+</sup>. Additionally, the surface morphology of *Rhodococcus opacus* was observed by scanning electron microscope (SEM).

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# Physicochemical characteristic of bioflocculant from *Rhodococcus rhodochrous*

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Nowadays, water pollution and other ecological damages had become fundamental problems. The progress of industrial processes has a negative impact on human and another health. Particularly harmful is the release of toxic heavy metals from mining to water ecosystems [1]. Several technologies have been applied to remove these contaminations such as activated carbon adsorption, ion exchange, chemical precipitation, coagulation, flocculation, membrane filtration, and reverse osmosis [2]. Following the trend of eco-friendly methods, the bioflocculation is used as an effective technique in wastewater treatment, which enable to remove particles like colloids, dyes, suspended and dissolved solids, and other chemical impurities with low molecular weight. Therefore, many microorganisms had been isolated, which secrete flocculating products known as bioflocculants. The chemical components and physical properties of bioflocculants are usually determinants of their flocculating abilities and the mechanism of flocculation process [3]. Therefore, establishing of these two aspects would highly improve the knowledge about the flocculation mechanism.

In the present study, the bioflocculant was isolated from culture broth of *Rhodococcus rhodochrous* by ethanol extraction. The kaolin suspension method was used for the flocculating activity of studied product determination. The bioflocculant's chemical composition was estimated by the series of spectrophotometric measurements including the uronic acid, amino sugars, reducing sugars and *N*-acetylated amino sugars presence. The total sugar content was determined using the phenol-sulphuric acid method and the total protein content was tested by Bradford method with bovine serum albumin as a standard. Moreover, the bioflocculant was analysed by the Fourier transformation infrared spectra and the X-ray photoelectron spectroscopy.

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# Dynamical and structural properties of a polymer confined in nanoscopic droplets

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Polymer water mixtures serve as an ideal model system to resemble the complex interplay between water and proteins. Besides structural information, i.e. protein conformation, dynamical aspects can be also important for biological functionality. However, investigating dynamics in confinement, especially in soft confinement, is a difficult task, because polymer dynamics have to be separate from the movement of the confinement itself. A powerful technique allowing for these investigations is quasielastic neutron scattering. Using an appropriate deuteration scheme of the system under investigation polymer and confinement dynamics can be addressed selectively.

The soft confinement is provided by an AOT based water in oil (octane) microemulsion. The droplet radius, i.e. the size of the confinement, can be varied precisely by the composition of the microemulsion up to 5 nm. As a model polymer the water soluble polyethylene glycol (PEG) with a molecular weight of 1500 g/mol is chosen. Its radius of gyration was determined by small angle scattering to be 1.4 nm. The dynamics of polymer in bulk solution, bare microemulsion droplet and polymer in confinement are investigated with neutron spin echo spectroscopy (NSE). For the investigation of confinement properties the microemulsion system was composed of deuterated water, deuterated octane and protonated AOT leading to a sharp contrast on the surfactant shell surrounding the droplet. In case of polymer studies the AOT was also deuterated and only the PEG was left protonated.

In the investigated range of scattering vectors  $q$  and Fourier times  $\tau$  the polymer in bulk solution only shows diffusional dynamics. Internal dynamics like Zimm modes could not be observed. The bare microemulsion droplets also show diffusion but exhibit additional shell fluctuations, due to a bending rigidity of the surfactant shell in the order of  $k_b T$ .<sup>[1,2]</sup> These fluctuations can significantly be tuned by the addition of PEG into the microemulsion droplets, leading to either a decrease or increase of the bending rigidity depending on confinement size.<sup>[3]</sup> For the confined polymer dynamics separate on two length scales. At small scattering vectors, corresponding to a length scale larger than the droplet size, diffusion comparable to the droplet dynamics is found. At large scattering vectors, thus on length scales smaller than the confinement size, dynamics become diffusive again, but on a much faster level. These faster dynamics may be understood as superposition of droplet and segment diffusion.

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# Design of materials based on marine biopolymers to culture muscle-cells

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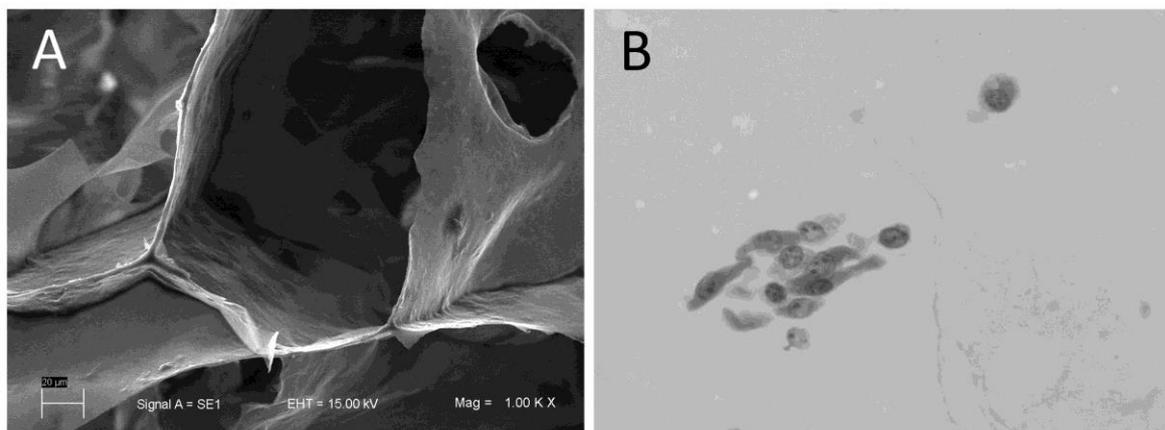
Biomaterials as hydrogels and polymer-scaffolds are used to culture cells. Currently, these materials are prepared with mammalian polymers as bovine-gelatin, collagen, hyaluronic acid, fibrin, and other. The main application to culture muscle-cells into scaffolds is for medical uses, but novel industrial technologies as *in-vitro* meat also need to use these materials.

A polyelectrolyte complex was made blending cationic fish-gelatin and sodium alginate. The fish-gelatin was prepared using the method described by Enrione et al [1]. To obtain a stable hydrogel solution without precipitation of the ionic components, a gelling agent (agarose) was used. Then, to create a porous interface, the hydrogels were frozen (-80°C) and subsequently freeze-dried to sublime the water.

The design of the material was based on a formulation approach, using as variable the gelatin/alginate ratio. Physical and thermophysical characterization of the material were done using DVS (dynamic vapor sorption), DSC (differential scanning calorimetry) and SEM (scanning electron microscopy). The Figure 1A shows the microstructure of the material obtained by using SEM.

The biocompatibility of the microstructured material was studied seeding muscle-cells (C2C12 cell line). The Figure 1B shows cells growing into the material after one week of seeding. The cells were studied using histochemical techniques as described by Acevedo et al [2]. The material is biocompatible and allows the proliferation of viable muscle-cells.

The conclusion of this work is that marine biopolymers allow the preparation of suitable materials to culture muscle cells.



**Figure 1** Microstructure of the material (A) and muscle-cells growing into the pores (B)

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# Methacrylate hydrogels for biomedical applications

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In this work, two well-known biocompatible methacrylate polymers (polyethylene glycol methyl ether methacrylate (PEGMEM) and 2-(dimethylamino) ethyl methacrylate (DMAEM)) have been polymerized to get a new copolymer hydrogel using the free radical polymerization reaction and different concentrations of the cross-linker. The hydrogel has been characterized by <sup>1</sup>H-NMR that confirmed the composition of the hydrogel of equal ratios of both monomers. The DSC analysis revealed the decomposition temperature and the water content as a function of the cross-linker concentration. The swelling behavior for the different hydrogels has been evaluated too.

The hydrogel has been utilized for the preparation of a new biomaterial mineralized with calcium phosphate using the reaction diffusion method. The shape of the calcium phosphate crystals was tuned changing the cross-linker concentration [Figure 1]. The performed selected area electron diffraction revealed the composition of the microcrystals to be mainly Brushite (CaHPO<sub>4</sub>·2H<sub>2</sub>O) [1]. This biocomposite is intended for tissue regeneration and scaffolds applications.

The same copolymer was used for the preparation of pH-responsive microgels using concentrated emulsion polymerization method [Figure 2]. The size of the microgels was controlled by changing the surfactant and the cross-linker concentrations. Swelling of the microgels was triggered by lowering the pH of the medium. The microgels were loaded with glucose oxidase enzyme, then the enzyme activity and the swelling behavior was evaluated in the presence of glucose. The enzyme triggered responsive microgels are of a potential interest as smart drug delivery system.

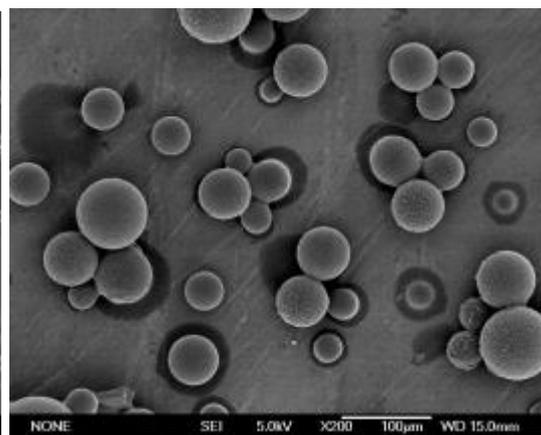
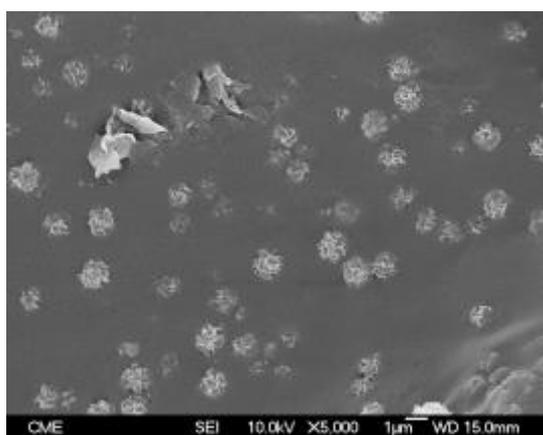


Figure 1 Calcium Phosphate microcrystals embedded within the hydrogel structure

Figure 2 SEM micrograph of the microgels.

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# Electrochemical Properties of Poly(Azure A) films synthesized in sodium dodecyl sulfate solution

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The electrodeposition of thin films of conducting polymers onto the surface of screen printed electrodes is one of the most extensive chemical platforms to design modified electrodes. In the present communication, a new strategy for the electrochemical preparation of conducting polymers based on Azure A in the presence of SDS micellar solution is presented. Radicalization of Azure A monomers was carried out by cyclic voltammetry onto screen printed carbon electrodes (SPCEs). To characterize them, electrochemical techniques and SEM have been employed. Furthermore, the  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  redox probe was used to characterize the electroactive area of the PAA(DS)-modified electrodes. Results point to the PAA(DS) electrochemical mechanism involving anion transfer and proton transfer, where the anion transfer is probably slower than the proton transfer.

The modified electrode was used as a sensor for reduced nicotinamide adenine dinucleotide (NADH) determination. To demonstrate that the sensor has a good catalytic response, we compared the current response of the sensor towards NADH with different PAA films synthesized in the presence of other inorganic anions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ), under identical experimental conditions. PAA(DS)-SPCEs clearly displayed the greatest sensitivity to NADH. These results indicate that the SDS anions inserted into the macromolecular structure of the PAA polymers confer PAA(DS) films with very interesting properties, such as high conductivity and reactivity towards analytes. This opens up the possibility of using SDS in further applications as new electrochemical sensing platforms with enhanced capabilities.

The results of this work have been recently published in *Journal of The Electrochemical Society* [1].

## Acknowledgements

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# Poly(N-Isopropylacrylamide)s with dodecyl and carboxyl terminal groups in aqueous solution: Influence of electrostatic interactions on thermoresponsive behavior

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Poly(N-isopropyl acrylamide) (PNIPAm) synthesized by RAFT polymerization using S-1-dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid)trithiocarbonate as a chain transfer agent forms micelles in aqueous solutions with the core of hydrophobic terminal dodecyl groups and the corona of PNIPAm chains with carboxylic groups at the periphery, the ionization of which prevents the micelles from phase separation above the lower critical solution temperature of PNIPAm in water [1].

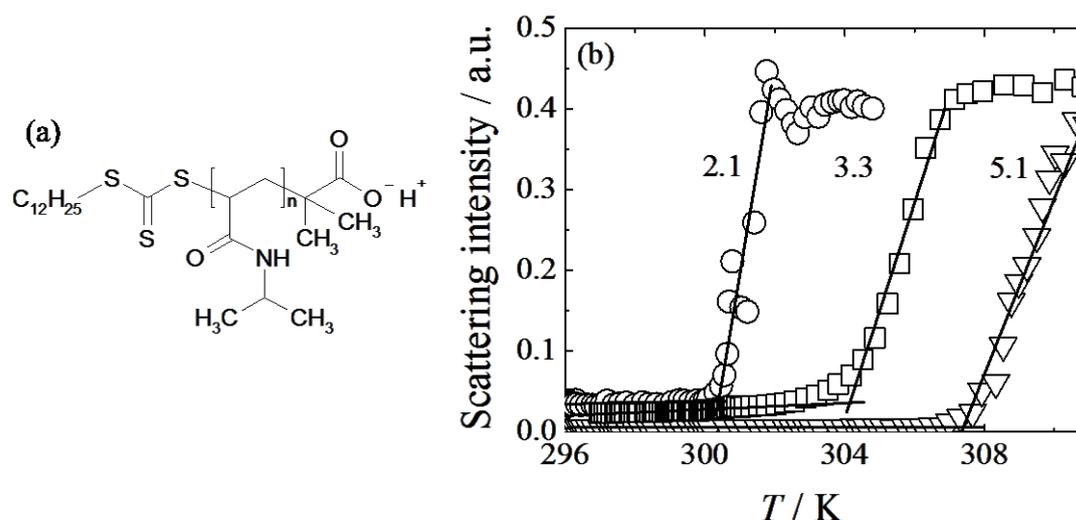


Fig. 1. (a) Structure of HOOC-PNIPAm-C12. (b) (a) Scattering intensity vs. temperature for HOOC-PNIPAm-C12 aqueous solutions at various pH (indicated at the individual curves).

In this communication, we report on the aggregation behavior of HOOC-PNIPAm-C12 (Fig. 1a) in aqueous solutions using static and dynamic light scattering, SAXS, isothermal titration calorimetry and fluorescence spectroscopy with N-(dodecanoyl)aminofluorescein as an amphiphilic fluorescent probe. We show that the cloud point temperature (CPT) of HOOC-PNIPAm-C12 can be shifted by adjusting the surface charge of HOOC-PNIPAm-C12 micelles [2] either by changing pH of the solution (Fig. 1b) or by commicellization of HOOC-PNIPAm-C12 with surfactants of the opposite (N-dodecylpyridinium chloride, DPCI) and like (sodium dodecyl sulfate, SDS) charge. Kinetic measurements indicate that the aggregation of HOOC-PNIPAm-C12 above the CPT is efficiently accelerated by screening electrostatic repulsion between PNIPAm micelles by changing ionic strength of the solution.

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# Gels, Can They Handle the Heat? – The Temperature Dependence of Colloid-Polymer Gel Collapse.

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Using temperature as an external stimulus, the delayed collapse of a model colloid-polymer gel with a weak, long range attraction has been studied.

The delayed collapse of colloid-polymer gels has been studied extensively due to their use in many formulated products, including: paints, personal care products and agrochemicals. Whilst temperature cycling has been used for many years as an industrial test for formulation stability, relatively little is known on the effect of temperature on a gel's stability [1]. During the initial delay time ( $\tau_d$ ) before collapse, the gel undergoes structural rearrangement caused by thermal fluctuations, this is due to the weak attractive forces between the particles being of order  $k_B T$ , leading to a gradual coarsening of the gel structure [2]. Eventually these structural rearrangements cause the gel to macroscopically collapse, as the particle network can no longer support the weight of the gel.

Here we present data on the measured delay time ( $\tau_d$ ) of a PDMS and xanthan depletion gel between 25 °C and 60 °C, in which a distinct 2 regime dependence becomes apparent, with  $\tau_d$  at high temperatures becoming almost temperature independent. This macroscopic delay time was compared to the calculated Kramer's escape time ( $\tau_{esc}$ ), the timescale over which individual particle bonds break within the gel structure. The ratio between  $\tau_d$  and  $\tau_{esc}$  was found to be comparable for all compositions at each temperature. We also present rheological data over the same wide temperature range, showing how various rheological properties of the gel, solvent system and xanthan are affected by temperature.

**Acknowledgements** The financial support of the Engineering and Physical Sciences Research Council, and Syngenta AG.

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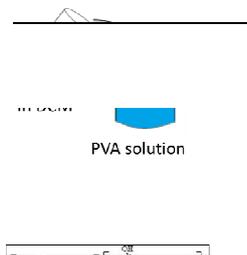


# Chitosan-based dual-drug delivery thermo-responsive wound healing applications

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Wound healing is a complex process where tissue layers are replaced. Chronic wounds often involve proteases, pro-inflammatory cytokines, and persistent infection, which hinder the healing process [1]. In the present work, we are exploring the potential use of chitosan-based hydrogels in wound dressing. These hydrogels can incorporate antioxidants and anti-inflammatory agents, which are beneficial for wound healing. The hydrogels are designed to be thermo-responsive, meaning they can transition from a liquid state to a solid state upon heating, allowing them to adhere to the wound and release drugs as needed.

Hydrogels were fabricated by mixing a chitosan solution and a PVA solution at 4°C. Subsequently, the mixture was incubated at 37°C. At this pH, the repulsion between  $-NH_3^+$  groups is reduced, and the intermolecular hydrogen bonding leads to the formation of a thermo- and pH-responsive hydrogel. The final concentration of 5 mg/mL was achieved by adjusting the initial concentrations at 4°C. For the incorporation of drugs, microparticles were fabricated by solvent evaporation. Dichloromethane was poured on a chitosan/PVA hydrogel, and upon the evaporation of the organic solvent, the microparticles were formed. The morphology of the microparticles was studied by scanning electron microscopy (SEM), and the encapsulation efficiency was determined via UV-VIS spectroscopy.



**Figure 1.** Schematic representation of the hydrogel fabrication process.

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# Single microgels in core/shell equilibrium: A novel method for limited volume studies

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By inventing a method for introducing limited amounts of surfactant or protein in single micro gels held in a small aqueous volume, investigating core/shell formations in equilibrium is now possible in a way not previously explored. Dodecyltrimethylammoniumbromide (DTAB) and cytochrome c has been used with results in line with theoretical predictions [1]. The simplicity makes experiments quick and opens up for studying expensive or hard-to-obtain substances due to the small amounts of material required. Further experimentation has been done with mixed solutions showing partition between a surfactant rich phase in the outer shell and a protein rich core at certain charge ratios and relative surfactant/protein amounts.

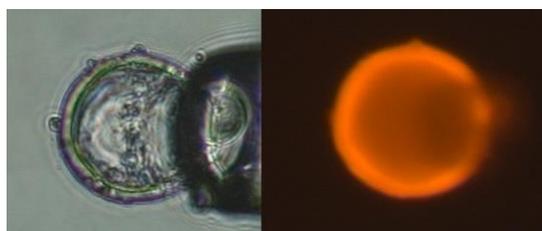


Figure 1. DTAB with Rhodamin B fluorescence marker absorbed into a single microgel displaying a stable core/shell formation after 24 hours.

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# Upper Critical Solution Temperature (UCST)-type thermoresponsive polymers from acrylamide-based monomers

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UCST-type thermoresponsive polymers that phase separate from solution upon cooling present a tremendous potential not only in aqueous media where they can be used in drug delivery, diagnostic and microfluidic applications [1], but also in water/alcohol mixtures, where they can be used for instance in sensing systems for alcohol-soluble drugs [2]. However, only a few thermoresponsive polymers have been reported in ethanol.<sup>[1,2]</sup> In this context, acrylamide-based monomers can be very useful building blocks for designing novel UCST-type polymers because of their hydrophilic nature (with the right side chain) and propensity to form hydrogen bonds.

We want to present our latest results on the copolymer poly(acrylamide-*co*-acrylonitrile) (P(AAm-*co*-AN)) that present a UCST in water [3,4] as well as on two homopolymers based on an acrylamide derivative of 2,6-diaminopyridine, namely poly(*N*-(6-aminopyridin-2-yl)acrylamide) (PNAPAAm) and poly(*N*-(6-acetamidopyridin-2-yl)acrylamide) (PNAcAPAAm) that show UCST-type thermoresponsiveness in water/alcohol mixtures [5].

Our focus for P(AAm-*co*-AN) is its aggregation behaviour above and below its phase transition temperature as the size of thermoresponsive polymeric systems is of prime importance for biomedical applications (as size dependent processes take place in the body) and is linked to the optical properties of a material that matter in materials science.

In the case of PNAPAAm and PNAcAPAAm, we focused on the co-solvency/co-non solvency effect on the phase transition temperature in water/alcohol mixture. Indeed, polymers with UCST behavior below 60°C

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# Dynamics of polymer brushes and adsorbed microgel particles near solid planar surfaces

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The physical properties of stimuli-responsive polymer systems still attract great interest in basic research. Systems that undergo a temperature-induced phase transition are one prominent example. The formation of polymer brushes and the adsorption of microgel particles at solid surfaces (e.g. silicon single crystal surfaces) lead to changes in the physicochemical properties in comparison with the properties in bulk. Such findings raise the question how the interactions with the solid surface affect the inner structure and dynamics of the polymer system.

Surface sensitive scattering techniques like neutron reflectometry, small angle neutron scattering (GISANS) and neutron spin echo spectroscopy under grazing incidence (GINSES) are well-suited to investigate these aspects [1].

We report on scattering experiments on the near surface structure and the inner dynamics in adsorbed microgel particles and polymer brushes using these techniques. First results of the combination of analysis of the experimental data with numerical simulations of the experiment in the framework of the Distorted Born Wave Approximation [2] are presented and discussed.

The investigated systems were for the first time studied by GINSES which uses evanescently scattered neutrons and therefore probes the near-surface dynamics in the adsorbed microgel films. The reported experiments demonstrate the feasibility of these surface sensitive measurements. Apart from that the results indicate a slowing down of the inner dynamics in the vicinity of the substrate. At increasing distance from the substrate, the relaxation is comparable to the bulk [3].

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# Rheology of cellulose microfibril networks dispersed in media of low dielectric contrast

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Cellulose microfibrils are a unique class of nature-based nanomaterials with their width typically about 40-140 nm and length spanning a few microns.<sup>[1]</sup> Attributed to their abundance and specific properties, cellulose in the form of microfibrils find a plethora of applications in diverse areas ranging from food products to high-strength composites. Previous research has shown that these shape anisotropic particles form an interesting colloidal system to study owing to their attractive interactions forming an extended network when dispersed in water.<sup>[2]</sup> In this work, the microfibrils were dispersed in dimethyl sulfoxide instead of water in order to reduce the effective Hamaker constant and hence lowering the attractive van der Waals interactions. The resulting non-linear rheological properties of these dispersions were studied. With an objective to investigate the effect of the network micro-structure and inter-fibril interactions on the mechanics, we present some interesting rheological properties of these systems.

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# Structure, thermodynamic and kinetic signatures of a model synthetic polyelectrolyte coacervating system

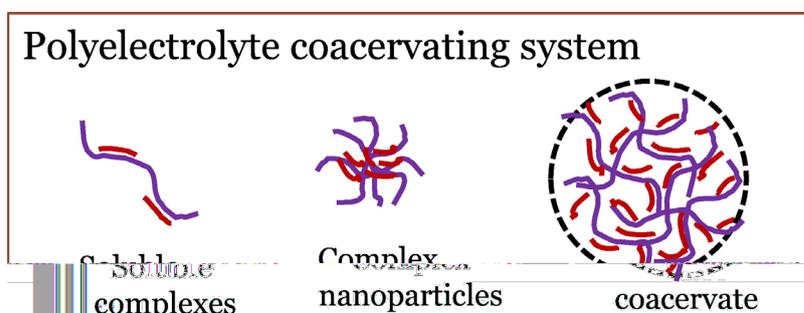
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Polyelectrolyte complexes (PECs) are the association complexes formed between oppositely charged macromolecules. A large body of work has been devoted to the preparation, morphology characterizations and performances of PECs. Much less attention was paid on the microscopic structures and microsecond range kinetics of such strongly interacting systems. The very short reaction time associated to the strength of electrostatic interaction and steric hindrance of the polyion often favors the formation of frozen structures. In such conditions, the mixing time which is related to the way the polyions are coming into intimate contact has a marked influence on the structure and stability of PECs as reported by many authors. In this work we have studied a fully synthetic coacervating system made of polyacrylic acid (PAA) and poly(diallyldimethylammonium chloride) (PDADMAC) oppositely charged polyelectrolytes at pH 10, where PAA chains are fully deprotonated. The structure, thermodynamic and kinetic signatures of various complex structures formed according to the initial molar charge ratio were discussed. Fast mixing was achieved with the help of a Stopped-Flow device although dialysis was chosen to monitor the assembly under pseudo-equilibrium conditions. Among the main points of interest, we can highlight (i) The presence of **true** soluble PECs existing in a defined range of physicochemical conditions (ii) The presence of PEC nanoparticles likely precursors of coacervation on both sides of the stoichiometry which can disproportionate to some extent into larger micron size coacervate droplets (iii) The distinctive kinetic signature of coacervation close to stoichiometry evidenced by a bell-shaped peak in light scattering at very short times ( $\sim 100$  ms) (iv) The presence of a 'nematic' correlation peak in the dense coacervate phase (SANS). (v) The structures formed are at equilibrium owing to a relatively low binding energy between PAA and PDADMAC independent of the mixing time and mixing pathway. Some of these results can be rationalized on the basis of weak interaction unfolding between oppositely charged PEs as revealed by microcalorimetry measurements.



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# The influence of biosurfactant film on adhesion of water to hydrophobic solids

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Adhesion of water to the solid surface is very important in such processes as coating, printing, cleaning and others [1]. The liquid adhesion work to the solid surface can be determined based on the Young-Dupre equation [1,2] from which it results that the liquid surface tension and contact angle are decisive for its values. For a given liquid it is possible to change the conditions of this process changing the properties of solid by covering its surface for example by a surfactant film. Recently there has been observed a special interest in biosurfactants which are produced by microorganisms such as bacteria, moulds and yeasts [3]. These surfactants exhibit not only high surface activity but they are also biodegradable and non-toxic. Additionally, biosurfactants can change the interfacial tension at the interface and protect various kinds of surfaces against adhesion of bacteria to them which is of significant importance in medicine [4]. The properties of the solid surface/biosurfactants film depend on the film thickness and the orientation of surfactants molecules in the formed layer. On the other hand, this phenomenon affects adhesion of the surfactant layer to the hydrophobic solids surface and it changes the hydrophilic-hydrophobic balance of such solids as well as the adhesion of water to solid surfaces. The adhesion of the surfactant layer to the solid surface can be determined if the component and parameters of the tail and head of surfactants surface tension as well as those of solid surface tension are known. However, the adhesion of water to the hydrophobic solid and the solid covered by the surfactant layer apart from the Young-Dupre equation can be deduced also based on the components and parameters of the surface tension of solid, surfactant layer and water. Thus the purpose of this study was to establish the surface tension of the hydrophobic solids such as polytetrafluoroethylene (PTFE) and polyethylene (PE) and their surfaces covered by rhamnolipid and surfactin layer. The parameters and components of the surface tension of the surfactant layer were determined by the measurements of water, formamide and diiodomethane contact angle based on the van Oss et al. theory [5].

**Acknowledgements: The financial support from National Science Centre in Poland, Project No. 2014/15/B/ST4/05086 is gratefully acknowledged.**

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# Rhamnose and sucrose as a model of hydrophilic part of some natural surfactants

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Van Oss and Constanzo [1] stated that surface tension of surfactants depends on the way of their molecules orientation toward the air phase. If they are oriented by hydrophobic parts, then surfactants surface tension results only from the Lifshitz-van der Waals intermolecular interactions. However, when the surfactants molecules are oriented by the hydrophilic parts toward the air, then their surface tension results from the Lifshitz-van der Waals and from the Lewis acid-base intermolecular interactions. Knowledge of the components and parameters of hydrophobic and hydrophilic parts of surfactants allows to predict the Gibbs free energy of interactions of surfactant molecules through the water phase. On the basis of this energy and contactable area of surfactant molecules it is possible to predict critical micelle concentration (CMC) of surfactants [2]. The surface tension of hydrophobic part of surfactant molecules can be established at the first approximation on the basis of the surface tension of hydrocarbon from which this part was formed. In the case of hydrophilic part of surfactants molecules, it is more complicated to determine components and parameters of its surface tension. Commonly these components and parameters are determined by the contact angle measurements of the model liquids on the thick layer of surfactants formed from the surfactant solution at its concentration much higher than CMC. So far, in the literature it is difficult to find values of components and parameters of the biosurfactants and sugar surfactants surface tension. Therefore the purpose of our studies was to determine the components and parameters of hydrophilic parts of rhamnolipid (RL) and n-octyl- $\beta$ -D-glucopyranoside (OGP) and compare them to those of rhamnose and sucrose. These substrates were chosen as model ones of the hydrophilic part of RL and OGP. These components and parameters were calculated from the contact angle values measured for water, formamide and diiodomethane on the thick layer of RL and OGP as well as rhamnose and sucrose formed on the apolar and monopolar polymers. The obtained results indicate that the values of the Lifshitz-van der Waals component and electron-acceptor and electron-donor parameters of rhamnose surface tension are comparable to those of hydrophilic part of RL and those of sucrose to the hydrophilic part of OGP. Based on the comparison it was concluded that rhamnose is a proper model for determination of hydrophilic parts of rhamnolipids and sucrose is that for OGP.

**Acknowledgements: The financial support from National Science Centre in Poland, Project No. 2014/15/B/ST4/05086 is gratefully acknowledged.**

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# Prediction of apolar and monopolar polymers wetting by aqueous solution of some surfactants

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Wettability of solids which plays a very important role in practice depends on the difference between the work of liquid adhesion to the solid surface and work of liquid cohesion. The visual measure of the wetting process is the contact angle [1]. According to the Young equation the value of the contact angle of a given liquid or solution depends on its surface tension, surface tension of solids and solid-liquid (solution) interface tension [1]. To solve the Young equation against the cosine of the contact angle the dependence between the solid-liquid or solid-solution and the surface tension of liquid or solution as well as the solid surface tension must be known. In the literature there are many approaches to the solid-liquid interface tension but that of van Oss et al. seems to be the most useful for prediction of some solid wetting [2]. According to the van Oss et al. approach [2] the cosine of the contact angle of liquid or solution on the apolar solids depends only on its surface tension, surface tension of liquid and the Lifshitz-van der Waals component of liquid surface tension. In the case of monopolar solids the dependence of cosine of contact angle and components as well as parameters of the solid and liquid surface tension is more complicated because the electron-acceptor and electron donor parameters of acid-base component of liquids or solution must be taken into account. During the contact angle calculations of the aqueous solution on the apolar and monopolar polymers, it occurred that using the value of the Lifshitz van der Waals component of water surface tension determined by Fowkes [1] from the water-*n*-alkane tension and equal 21.8 mN/m, the calculated values are different than those measured. Therefore the purpose of the studies was to analyze the values of components and parameters of water surface tension based on the contact angle of water on the polytetrafluoroethylene surface. Based on this analysis the different values of these parameters were established [3-5]. It proved that using these new values it was possible to predict the values of the contact angle of aqueous solutions of many anionic, cationic and nonionic surfactants including biosurfactants and sugar surfactants on the polytetrafluoroethylene (PTFE), polyethylene (PE), polymethyl methacrylate (PMMA) and polyamide (nylon 6) surfaces. Moreover, from these calculations the discrepancy between the critical surface tension of polymers wetting and their surface tension could be explained.

**Acknowledgements: The financial support from National Science Centre in Poland, Project No. 2014/15/B/ST4/05086 is gratefully acknowledged.**

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# Usefulness of different kinds of approaches to the interface tension for some surfactant films properties determination

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The interface tension is equal to the sum of surface tension of the phases being in the contact diminished by adhesion work of phase 1 to phase 2. To solve the Young equation against the surface tension of solid the relationship between the adhesion work of liquid to the solid surface and the solid and liquid surface tension should be known. In the literature there are two main approaches to this relationship. Fowkes [1] as the first stated that the surface tension of solid and liquid can be divided into many parts resulting from the different intermolecular interactions. However, from the practical point of view the surface tension was divided into dispersion and polar components. In consequence the adhesion work of liquid to liquid and to solid can be divided into two parts: one resulting from the dispersion interactions between two phases and the other from polar ones. Fowkes expressed the dispersion part of adhesion work by the geometric mean from the dispersion components of surface tension of the phases being in contact. In turn, Owens and Wendt [2] expressed also the polar part of adhesion work by the geometric mean of polar components of the surface tension of two phases in contact. Wu [3] stated that adhesion work can be expressed by the harmonic mean from dispersion and polar components of solid and liquid surface tension. Van Oss et al. [4] claimed that the adhesion work of liquid to liquid and to solid can be expressed by the geometric mean from the Lifshitz-van der Waals components of phases 1 and 2 and the geometric mean from the electron-acceptor and electron-donor parameters of phases 1 and 2 and vice versa of the acid-base components of surface tension of these phases. In contrast to Fowkes, Owens, Wendt, and van Oss et al. [1-4] Neumann et al. [5] proposed that the work of the adhesion of liquid to solid can be expressed by the geometric mean from the surface tension of solid and liquid corrected by the parameter of the intermolecular interactions between the liquid and solid which is a linear function of solid-liquid interface tension. The purpose of the studies was to examine usefulness of the above mentioned approaches to the interface tension for determination of the surface properties of the surface layer formed on the PTFE (polytetrafluoroethylene) and PMMA (polymethyl methacrylate) surface by rhamnolipid and n-octyl- $\beta$ -D-glucopyranoside. On the basis of the calculations it was concluded that the approaches based on the partition of the surface tension of liquid and solid surface tension on the components and parameters provide more information about the properties of the layers if these components are used consequently. It means that a given approach would give reasonable values of the layer surface tension if the components and parameters of the liquids surface tension were determined by the same approach.

**Acknowledgements: The financial support from National Science Centre in Poland, Project No. 2014/15/B/ST4/05086 is gratefully acknowledged.**

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# Dependence between kind of solids and properties of natural surfactant films

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The hydrophobic and hydrophilic balance of the solids surface can be changed by the surfactants film formation. These changes depend on the values of components and parameters of the solid surface tension as well as the hydrophobic and hydrophilic parts of surfactants. This means that the orientation of the surfactants molecules in the surface layer decides about its hydrophilic and hydrophobic properties. In turn, the orientation of surfactants molecules depends on the components and parameters of the solid surface tension. In the literature it is difficult to find the considerations dealing with the hydrophilic and hydrophobic balance change of different kinds of polymers, particularly those applied as an implant by natural surfactants film. Among the polymers applied as implants the polytetrafluoroethylene (PTFE), polyethylene (PE), polymethyl methacrylate (PMMA) and polyamide (nylon 6) play a very important role. Thus the purpose of our studies was the determination of the surface properties of these polymers by the contact angle measurements of water, formamide and diiodomethane on the layers of RL (Rhamnolipid) and sugar surfactants formed on these solids from the solutions at different concentrations. The obtained results were analyzed based on the surfactants molecules orientation in the surface layers and their contactable area of hydrophobic and hydrophilic parts. The changes in the orientation of surfactants molecules were reflected in the changes of the components and the parameters of the solid surface covered by the surfactants layer. This reflection was established by using different approaches to the interface tension in the Young equation [1-5]. It was found that in any case the orientation of surfactants toward the air phase by the hydrophobic parts of their molecules was not detected. However, at the proper concentration of the surfactants in the aqueous solution applied to the layers formed on the studied solids surface, the parallel orientation of surfactants molecules was observed. It also appeared that for the layers obtained from the solution of surfactants of the concentrations higher than their CMC (critical micelle concentration), the values of the contact angle for water, formamide and diiodomethane were almost the same, independently of the kind of the polymer on which the layers were formed. From this fact it was concluded that in such a layer at the layer-air interface the surfactants molecules are oriented by hydrophilic parts toward the air.

**Acknowledgements: The financial support from National Science Centre in Poland, Project No. 2014/15/B/ST4/05086 is gratefully acknowledged.**

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- [4] C.J. van Oss, R.J. Good and M.K. Chaudhury, *Langmuir*, 1988, **4**, 884.
- [5] D. Li and A.W. Neumann, *Adv. Colloid Interface Sci.*, 1992, **39**, 299.

# Extraordinarily Rapid Rise of Tiny Bubbles Sliding beneath Superhydrophobic Surfaces

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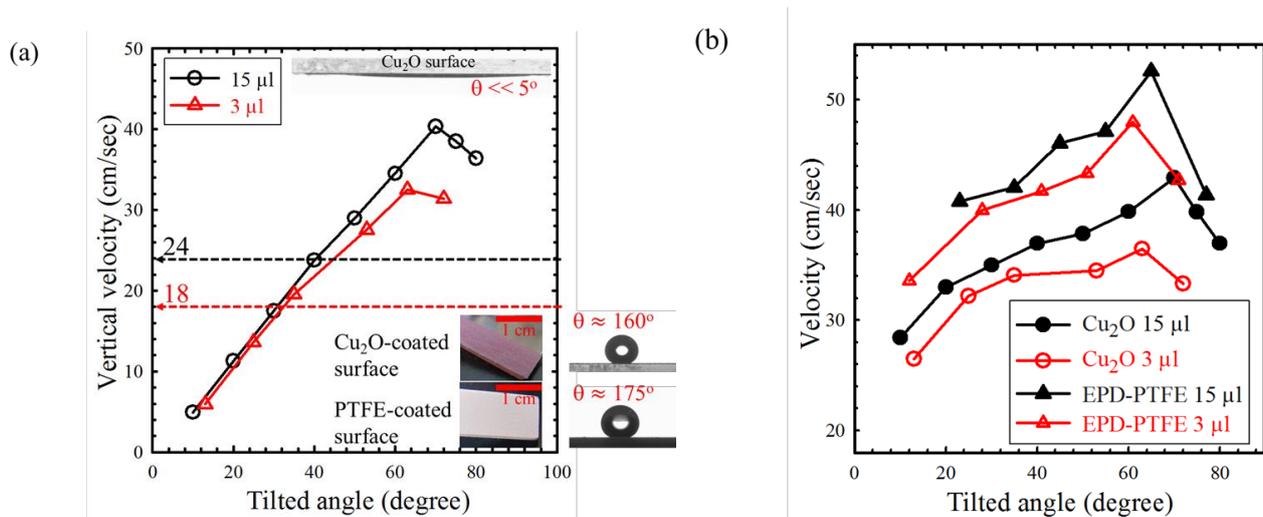
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Tiny bubbles readily stick onto substrates and remain static due to contact angle hysteresis (CAH). Nevertheless, tiny bubbles can slide slowly on a tilted surface with ultralow CAH since capillarity is overcome by buoyancy. It is surprising to observe experimentally that bubbles of 3~15  $\mu\text{l}$  (diameter 1.79~3.06 mm) slide beneath a tilted superhydrophobic surface at a vertical ascent rate faster than freely rising ones of high Reynold numbers  $\sim O(10^2)$  (Figure 1). As the tilted angle increases, the drag coefficient remains essentially the same as that of a freely rising bubble but the frontal area of the flat bubble rises monotonically. Nonetheless, the frontal area of the sliding bubble always stays much smaller than that of a freely rising bubble. Consequently, the small drag force associated with sliding bubbles is attributed to their substantially small frontal areas on superhydrophobic surfaces. [1]



**Figure 1.** (a) Variation of the vertical velocity of a bubble with the tilted angle beneath superhydrophobic Cu<sub>2</sub>O-coated glass surfaces for two bubble volumes. The inset are the photos and contact angles for Cu<sub>2</sub>O-coated and PTFE-coated surfaces, respectively. (b) Variation of the sliding velocity of a bubble with tilted angle beneath superhydrophobic Cu<sub>2</sub>O-coated and PTFE-coated surfaces for two bubble volumes.

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# Meniscus Shape and Wetting Competition of a Drop between a Cone and a Plane

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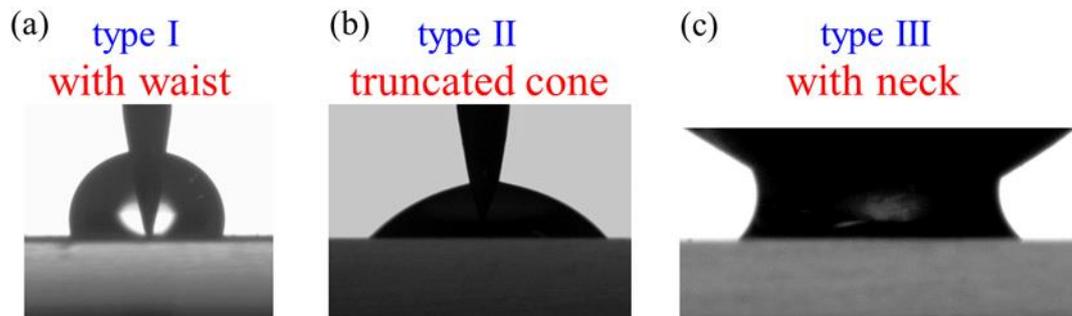
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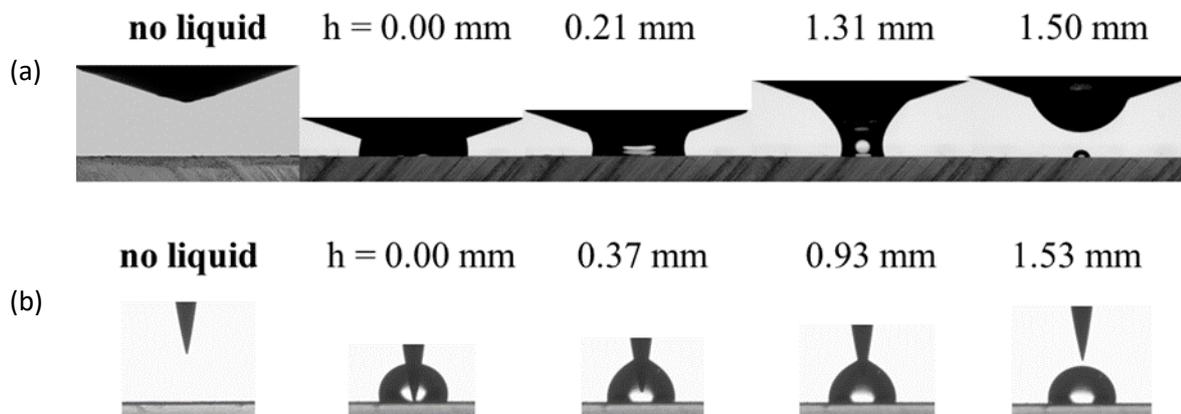
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The formation of liquid bridge between a cone and a plane is related to dip-pen nanolithography. The meniscus shape and rupture process of a liquid meniscus between a cone and a plane are investigated by Surface Evolver, many-body dissipative particle dynamics, and macroscopic experiments. Dependent on the cone geometry, cone-plane separation, and wetting properties of cone and plane, three types of menisci can be observed before rupture (Figure 1) and two types of wetting competition outcomes (Figure 2) are seen after breakup. It is interesting to find that after rupture, the bulk of the liquid bridge volume is not necessarily retained by the cone which is more wettable. In fact, a sharp hydrophilic cone often loses wetting competition to a hydrophobic plane. To explain our findings, the “apparent” contact angle of the cone is introduced and the behavior of drop-on-cone/plane system is analogous to that of liquid bridge between two parallel planes based on this concept.[1]



**Figure 1.** Meniscus shapes of a drop between a cone and a plane: (a) with waist, (b) truncated cone, and (c) with neck can be identified based on experiments and SE simulations.



**Figure 2.** Experimental observations of wetting competition. (a) water drop ( $V = 5.0 \mu\text{l}$ ) between a metal cone with  $2\alpha = 137^\circ$  and a polycarbonate sheet. (b) water drop ( $V = 5.0 \mu\text{l}$ ) between the tip of a pin with  $2\alpha = 16^\circ$  and a paraffin film.

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# Modeling contact angle of a liquid droplet sitting on a cosine wave-like square-array pattern surface with different surface roughnesses

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A liquid droplet sitting on a cosine wave-like square-array patterned surface in the Wenzel state is simulated by using the Surface Evolver to determine the contact angle. For a fixed drop volume, both hydrophilic (with an intrinsic contact angle of 70°) and hydrophobic surface (with an intrinsic contact angle of 120°) show multiple metastable states at a given surface roughness [1]. The maximum and minimum contact angles among the multiple metastable states at a fixed viewing angle correspond to the advancing and the receding contact angles, respectively. The contact angle of minimum energy among the multiple metastable states is defined as the most stable (equilibrium) contact angle. The equilibrium contact angle will change with surface roughness. For hydrophobic surfaces, the equilibrium contact angle increases along with surface roughness. On the other hand, the equilibrium contact angle decreases along with an increase in surface roughness for hydrophilic surfaces.

For hydrophobic surfaces, the Cassie–Wenzel wetting transition of a liquid droplet sitting on a cosine wave-like square-array patterned surface is also simulated by using the Surface Evolver. All the metastable states of a liquid drop with a fixed drop volume on the model surface are determined at different surface roughnesses. It is interesting to find out that when the surface roughness is slightly smaller than the transition roughness (between the Wenzel and Cassie states) the drop under the condition of the advancing and receding contact angle would exhibit the Cassie and Wenzel state, respectively [2]. An increase in the surface roughness may induce the wetting transition from the Wenzel state to the Cassie state to occur.

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# Antifouling amphiphobic coatings for protection in sea environment

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A relatively young field achieving growing interest as innovative solution is represented by highly hydro and oleophobic (amphiphobic) [1] materials dedicated to the marine environment.

Taking into account the limitations imposed by international laws in terms of environmental protection, technological and ecological aspects allow to be merged, also for the absence of release of chemicals like heavy metals or organometal compounds. In this work different mixed organic-inorganic coatings dedicated to the marine environment, showing highly water and oleo repellence, have been compared for applications and characterized and tested both in laboratory and field conditions. Investigations in real seawater have to be considered as crucial to evaluate the behaviour of such surfaces in complex environments not reproducible in laboratory[2].

Preliminary tests for wearing, thermal stress and durability have been also carried out in order to study amphiphobic systems for other applications related to the marine environment, like power or desalination plants.

## Acknowledgements:

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# Surface adhesion enhancement on superhydrophobic surfaces.

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Superhydrophobic surfaces, have intrigued the scientific community with respect to the surface patterns and their characteristic wetting states. The lotus leaf and the rose petals are two such extensively studied naturally occurring superhydrophobic surfaces that differ in terms of surface adhesion, that is the lotus leaf exhibits self-cleaning whereas rose petal is high adhesive. These surfaces find a potential application in bio-implants as the self-cleaning properties of the surface help keep the surface bacteria and pathogens free<sup>1</sup>, and the adhesion properties help in desired attachments of the cells to the surface. An effort has been made in the present study to create a superhydrophobic surface with hierarchical wrinkle structures which can demonstrate an increase in the adhesive property of the surface. A patterned wrinkled surface was first created using Sylgard 184 (PDMS, 10:1 base to cross linker ratio) film by applying a mechanical strain and subjecting the film to a step of consecutive heating and cooling. The created surface demonstrated an increase in the surface adhesion (measured using a custom built device)<sup>2</sup> to up to 40% of that of the unwrinkled PDMS surface. Similarly, adhesion tests were then repeated on rose petal replicas, created using fresh rose petals as moulds<sup>3</sup>, and on rose petal replicas with hierarchical wrinkled patterns. Figure 1 is a comparison between the adhesion force of a normal PDMS surface without any patterns, a rose petal replica, a rose petal replica with hierarchical wrinkled structures (hierarchical patterned surface) and a normal PDMS surface. It was observed that the hierarchical patterned surface shows an increase in the adhesion of the surface as compared to a simple rose petal replica.

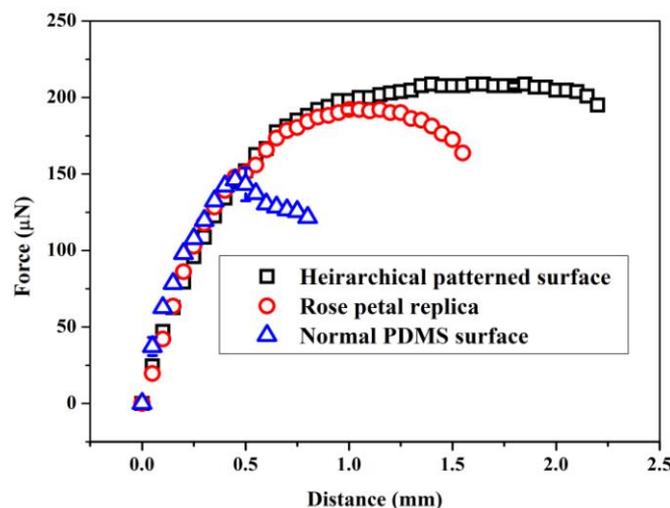


Figure 1: Comparison of the adhesive forces of PDMS surface, rose petal replica and rose petal replica with hierarchical wrinkled surface.

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# Tunable Aqueous Polymer Phase Impregnated Resins: Contact angle as prediction parameter for impregnation

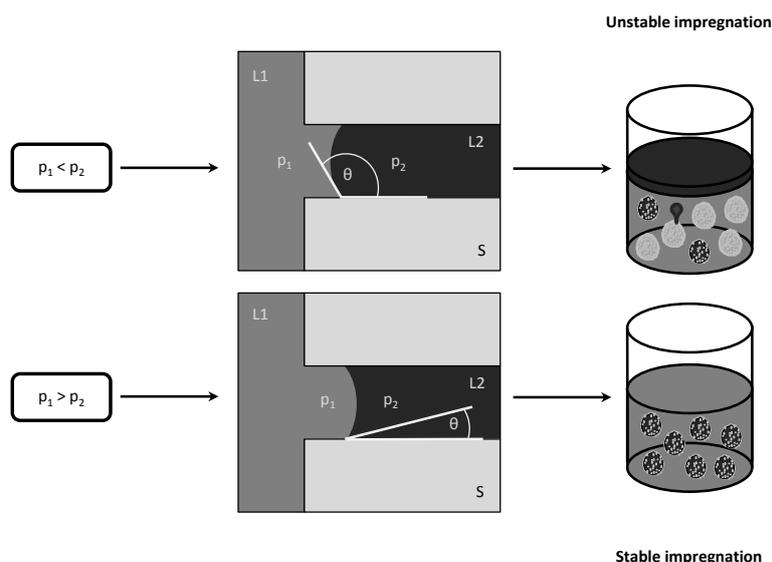
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Aqueous Two-Phase Extraction (ATPE) is known to be a gentle separation technique for biotechnological products due to the high water content of the aqueous two-phase system (ATPS) used. However, the phases' physicochemical properties like low interfacial tension, high viscosities and small density difference enable an intense emulsification and thus can lead to long phase separation times. This major drawback renders classical ATPE uneconomical for industrial application as additional equipment and energy is needed to promote faster phase separation. Our approach to enhance phase separation during ATPE, is the Tunable Aqueous Polymer Phase Impregnated Resins (TAPPIR<sup>®</sup>)-Technology, where one phase of the ATPS used is immobilized inside porous solids, which are then dispersed in the other aqueous phase. A stable impregnation of the immobilized phase is the basis to make the TAPPIR<sup>®</sup>-Technology competitive to classical ATPE and other protein recovery techniques. Thus, the aim of this study is to investigate the impregnation stability describing parameter.

In this context the influences of the physicochemical properties of the ATPS namely density, viscosity and interfacial tension and the parameters of the solid namely material type and pore size on the impregnation stability were analysed. The process parameter can influence both the parameters of the ATPS and the solids, so the impact of the temperature and the pH value on the impregnation behaviour were investigated. As the interaction between the ATPS and the solids is affected by a complex competition of molecular interaction forces, it is elaborate and time-consuming to determine the impregnation stability. The contact angle was proposed to describe the impregnability and the impregnation stability (see Fig.1). To validate if the contact angle can be used as fast determination method, the impact of additives namely proteins, displacement salts and surfactants on the impregnation stability was examined. The three-phase contact angle was found to predict the impregnation stability and to promote a faster design of a TAPPIR<sup>®</sup> separation system.



**Figure 1** Interaction of the impregnated polymer phase, the salt phase and porous solid described by the contact angle for a stable and unstable impregnation in an ideally cylindrical pore.

# Colloid chemistry approaches for enhancing the anti-icing potential of superhydrophobic coatings

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In recent decades, considerable efforts were made by researchers to attain a more detailed understanding of the physicochemical phenomena governing the icing processes and to develop more efficient systems for the prevention of icing and/or mitigation of its consequences. The approaches, that are currently most popular for de-icing and icing prevention, such as mechanical, chemical (including “nonfreezing liquids”) and electrothermal methods, are generally power-consuming, and are not always sufficiently efficient and environmentally safe. Furthermore, all of these methods require the permanent active involvement of personnel.

In last years, there has been increasing interest in icing reduction by means of passive protection using icephobic surfaces. Icephobic surfaces are such surfaces that, due to their physicochemical properties, facilitate a decrease in ice, snow and freezing drizzle accumulation on materials operating under atmospheric conditions and regularly contacting atmospheric precipitates. One of the most promising approaches to the creation of icephobic surfaces involves development and preparation of mechanically and chemically stable superhydrophobic coatings on the surfaces of materials being protected.

Our studies have shown that atmospheric icing, in essence, is governed by surface phenomena. In this presentation, we will formulate the basic physicochemical mechanisms determining the anti-icing performance of superhydrophobic surfaces. We will show the advantages of superhydrophobic coatings as effective means for protection against atmospheric icing and snow accumulation and will discuss new colloid chemistry approaches for enhancing the anti-icing potential of superhydrophobic coatings. The results indicating the role of surfactants, surface charge density and specific ion effect in the anti-icing performance of superhydrophobic coatings will be presented.

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# Three-dimensional numerical study on droplet dynamic characteristics during oblique impacting onto super-hydrophobic Spherical surfaces

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The impact of droplets on objects is widely encountered in a variety of industrial processes, nature and agricultural production, such as spray droplets impacting onto the horizontal tube wall in seawater desalination device, rain impacting on the ground and the wing in the nature, and the pesticide ejected by spraying device impacting on crops, and so on. The morphology of droplet impacting onto surface has effect on heat exchange between the droplets and surface, so it has important theoretical and engineering significance to research the process of droplet impacting on surface.

Coupled Level Set and Volume of Fluid (CLSVOF) method was applied to carry out three dimension numerical simulations to analyze droplet dynamic characteristics during oblique impacting onto super-hydrophobic spherical surface, and the air entrainment and breakup phenomenon are mainly studied. Results show that when droplet impacting onto super hydrophobic spherical surface with contact angle  $160^\circ$ , under different impact angles ( $0^\circ$ ,  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$  and  $60^\circ$ ), all the droplets spread out and recoil and rebound. When the impact angle are  $0^\circ$  and  $15^\circ$ , the change difference of droplet spreading coefficient over dimensionless time is smaller. With the increase of impact angle, droplet maximum dimensionless spreading coefficient decreasing, and dimensionless time to reach maximum spreading coefficient is nearly the same.

Under different impact angles, with the increase of impact Angle, the maximum atmospheric film diameter and height are both decreasing, and the time to reach maximum atmospheric film is increasing. When the impact Angle is  $15^\circ$ , entrainment maximum bubble diameter and height before liquid film fracture is minimal. When the impact Angle is  $30^\circ \sim 60^\circ$ , with the increase of impact angle, entrainment maximum bubble diameter before liquid film fracture decreases and entrainment maximum bubble height before liquid film fracture increases firstly and then decreases.

When droplet impacting onto super hydrophobic spherical surface with contact angle  $160^\circ$ , the breakup number of droplet decreasing with the increase of impact angle. Moreover, the critical conditions of droplet spreading, rebound (no break), rebound (breakup) and crushing are given out under different impact angles ( $0^\circ \sim 30^\circ$ ).

**Keywords:** impact angle, super hydrophobic spherical surface, bubble entrainment, breakup, critical condition

# Mimicking a lotus leaf ultra hydrophobicity at home: a facile method to prepare mechanically durable superhydrophobic titanium

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Inspired by the Lotus leaf, superhydrophobic surfaces (SHS), on which the water contact angle is greater than  $150^\circ$  and the sliding angle is lower than  $10^\circ$ , are of tremendous interest in recent years due to its potential applications in both the industry and basic research. The superhydrophobicity depends not only on the surface energy of the material but also on its surface morphology. Two main approaches have been developed to prepare superhydrophobic surfaces: increasing the roughness of the hydrophobic substrate or formation of the rough coating followed by modification with the low free energy chemicals. Many efforts have been made to obtain artificial non-wetting surfaces; however, complex synthesis, inability to scale up the production processes and, generally, the fragility of the hierarchical micro-nano features limits their practical applications.

Titanium and its alloys are the material of choice in a large variety of applications due to its high chemical stability, low specific gravity, high melting point, mechanical strength, and biocompatibility. Here, we developed a facile, fast, inexpensive and scalable method to fabricate mechanically durable superhydrophobic titanium (SHS Ti) surfaces with hierarchical nano- and microstructures. The hierarchical morphology was prepared by electrochemical anodization of Ti alloys in aqueous solutions. The intrinsically superhydrophilic titanium oxide layer was further functionalized by a low-surface-energy self-assembly monolayer based on the phosphate chemistry. After modification with the perfluoroalkyl-bearing phosphate, the coating shows ultrahigh self-cleaning properties with a water contact angle of  $180^\circ$  and a sliding angle of  $0^\circ$  demonstrating the perfect Cassi-Baxter wetting state. Using facile laboratory devices, samples of  $20 \times 30$  cm area with uniform superhydrophobicity were produced. Our SHS Ti surfaces preserve their non-wetting characteristics not only under laminar and turbulent flow but also under direct impact of hard and heavy particles such as Yttria-stabilized-Zirconia. Moreover, the SHS Ti surfaces show superior resistance to complex liquids such as blood and repel attachment of marine bio-foulers such as green algae and mussels under static and dynamic conditions. A facile and inexpensive instrumentation, environmentally friendly and reusable aqueous anodization solutions and phosphate-based surface functionalization compounds, which are few orders of magnitude cheaper than widely used silane-based chemicals, and the fact that there is no need for pre- and post-anodization surface treatments makes it possible to produce superhydrophobic titanium at home conditions. Furthermore, economic analysis of our surface treatment method shows that the additional expenses to convert bare Ti to the SHS Ti are negligible concerning the cost of titanium itself.

# Exploiting the stability of slippery polyaniline rough surface impregnated with fluorinated oil

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There are two classical models that describe the relation between interfacial tension and contact angle for rough surfaces, the Wenzel [1] and the Cassie-Baxter models [2].

Self-cleaning surfaces such as ones found on lotus leaves combine chemical composition and hierarchical structure to minimize interaction between water and the surface [3] leading to a superhydrophobic effect. Aiming to mimic that effect this work presents an electropolymerized polyaniline surface prepared onto stainless steel that showed a highly rough topography with hierarchical structures which was functionalized with perfluorocarbon chains, leading to a superhydrophobic surface with a pronounced Cassie-Baxter effect, with contact angles tending to 180°.

This superhydrophobic effect is stable under mild contact conditions, as low pressure or non continuous contact for long time of exposure. Nonetheless, sinking the functionalized electropolymerized polyaniline surface in water enabled to observe that after some time the Cassie-Baxter contact condition starts to dismiss while a Wenzel contact condition takes place on the surface. In the first minutes after been sunken, it was visible a cape of air lying between the surface and the water, granting a non wetting property to the surface. Notwithstanding, after a while, this film of air started to escape through the liquid phase and some sites of the surfaces became wetted. In less than an hour all surface became wetted and the well pronounced Cassie-Baxter contact has changed completely into a Wenzel condition.

Impregnating the functionalized polyaniline surface with a fluorinated oil and sinking it in water, even under magnetic stirring, results in a stable surface. While the air film completely escapes before an hour for non impregnated surfaces, the fluorinated oil remains intact over the four hours that test was conducted. Water is able to expel the air trapped on the surface and wet it, but is not able to do the same with the fluorinated oil, since it is better stabilized by the fluorocarbon chain present onto the polyaniline surface by the functionalization.

Thereby, is concluded that superhydrophobic surfaces that lies on Cassie-Baxter phenomena are not enough to be employed in circumstances that it have to be in direct water contact for long periods, such as inorganic scaling or corrosion prevention. In the other hand, an oil impregnated surface, like the slippery liquid infused porous surfaces (SLIPS), made by Wong et al. [4], shows to be promise at under water applications that are needed to last longer.

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# Engineering of interfaces in the nanostructured materials based on polyurethane and multi-walled carbon nanotubes with surface functionalization

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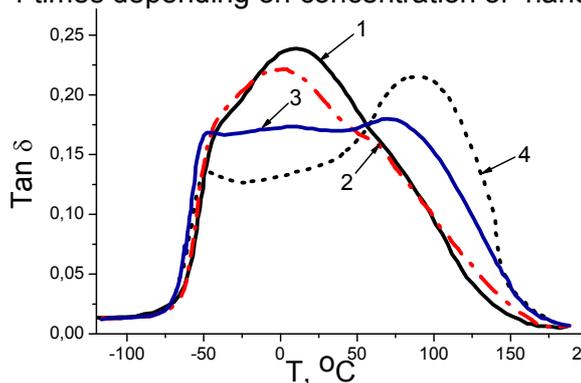
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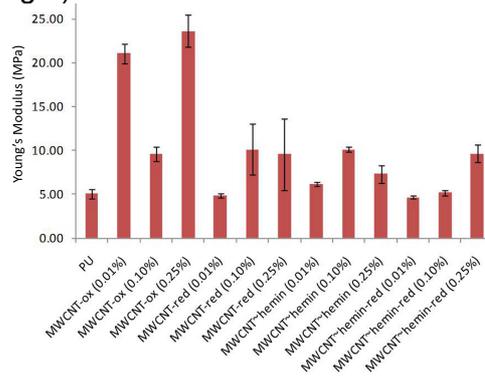
Via acid oxidation and reduction chemical procedures, carboxyl, phenol, lactone functional groups to be used as cross-linking sites to the matrix were generated on the MWCNT surface. The functional groups were attached to the MWCNT surface either directly through covalent bonding or by van der Waals forces only. The nanocomposites based on thermosetting polyurethane matrix and MWCNT with different functional groups on the surface were prepared and investigated. SEM and TEM analyses revealed that a good nanotube dispersion and distribution in the PU matrix were observed for the nanocomposites with ultralow contents of functionalized MWCNTs (up to 0.1%) whereas both individually separated nanotubes and their small agglomerates were presented in the matrix at higher content of nanofiller.

The pronounced dynamic heterogeneity within the PU glass transition was registered by dynamic mechanical analysis (Fig.1) and creep rate spectroscopy especially at direct covalent bonding between MWCNT surface and matrix in the nanocomposites. The results were treated in the framework of chemical inhomogeneity, constrained dynamics effects and different motional cooperativities. Due to the cardinal changes in the interactions at the interface two- or threefold enhancement in mechanical properties compared with neat PU matrix, was attained in the case of MWCNTs with covalently attached functional groups.

The mechanical properties testing indicated that small amount of MWCNTs (0.01%) could significantly improve the mechanical performance of the matrix. The tensile strength was increased from 2.0 MPa to 4.0 MPa. The best results were obtained for nanocomposites containing MWCNTs which covalently bounded to the matrix: the Young's Modulus increased by 2–4 times depending on concentration of nanotubes (Fig.2).



**Figure 1** Temperature dependence of  $\text{Tan } \delta$  in DMA measurements for neat PU(1) and nanocomposites with 0,01% (2), 0,10% (3) and 0,25% of MWCNT-ox.



**Figure 2** Comparative effects of Young's Modulus (MPa) of PU containing MWCNT-ox, MWCNT-red, MWCNT~hemin and MWCNT~hemin-red for each filler content of 0.01, 0.10 and 0.25 wt%.

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# Effect of nanoparticle morphology on the strength of fractal aggregates

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In this work we investigate the impact of core-shell nanoparticle morphology, in particular thickness and softness of the shell on the strength of the formed fractal aggregates. At the model system we used nanoparticles (NPs) composed of poly methyl methacrylate (PMMA) and butyl acrylate (BuAc). To cover broad range of conditions we prepare NPs with different shell thickness covering range from 5 to 15 nm composed of the mixture PMMA and BuAc. This allowed us to modulate T<sub>g</sub> of the shell from approximately 5 C up to 25 C. Aggregate strength was measured by aggregating the NPs under fully destabilized conditions in the presence of shear. Size and fractal dimension of formed aggregates was determined by the static light scattering. To minimize the impact of aggregation on the steady state aggregate size aggregation was performed under very dilute conditions with a NPs volume fraction equal to  $1 \cdot 10^{-6}$ . To investigate the impact of shell properties on the aggregate strength the temperature of the experiment was selected such to cover the range below as well as above the T<sub>g</sub> of NPs shell material. Strength of aggregates was determined from the scaling of aggregate size as a function of applied shear rate.

It was found that when temperature was below the T<sub>g</sub> of NPs shell material the aggregates strength follows the theoretical prediction derived for fractal aggregates composed of hard primary particles interacting through the van der Waals forces. In contrast, for temperatures above the T<sub>g</sub> of NPs shell material aggregates strength was substantially higher illustrated by the absolute aggregate size as well as by the increased slope of the scaling of aggregate size as function of applied shear rate. Furthermore, there was observed increased compactness of the prepared aggregates as documented by an increase of fractal dimension. This data clearly indicates that additional interaction, i.e. particle adhesion and plastic deformation, becomes important as observed on the macroscopic properties of the formed aggregates. This can be efficiently induced by the temperature increase during aggregation experiment. On the other hand, by increasing the applied shear rate it was found that above certain point the measured scaling starts to deviate that measured at lower shear rates and becomes similar to that derived for hard spheres interacting through van der Waals forces. This observation is explained by the interplay between various mechanisms, aggregation, plastic deformation and breakup, which all have different time scales. Application of the observed phenomena can find application in the improvement of the porous material properties simply by tuning the temperature of the process.

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# Antimicrobial lipid nanocarriers loaded with organoselenium compounds: Fabrication, physical stability and biological evaluation

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Over last few decades organoselenium compounds, among them benzeneselenazol-3(2H)-ones, have been extensively investigated as potential pharmaceuticals. Ebselen (2-phenylbenzeneselenazol-3(2H)-one) and its analogues have received particular attention as glutathione peroxidase mimics, antioxidant and anti-inflammatory agents [1-3]. Furthermore, a number of organoselenium compounds have been selected as promising anticancer, antiviral and antimicrobial agents [4-6]. Although these compounds have a great potential as new perspective pharmaceuticals their practical use is still limited due to low solubility in water. Thus, the purpose of our study was to develop an effective nanocarrying system for selected organoselenium compounds.

Lipid nanoparticles are made from physiological compounds, i.e., biodegradable lipids and natural surfactants, and existing in the nano-size range have attracted increasing attention in recent years [7-8]. In the present work we have provided properties of two different types of lipid nanocarriers, i.e., solid lipid nanoparticles (SLNs) and nanostructured lipid carriers (NLCs) prepared via high pressure homogenization method which is the most reliable and powerful technique to the production of small particles with a low polydispersity index. The sizes of the studied nanosystems along with the size distribution were determined by dynamic light scattering (DLS), while shape and morphology – by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The physical state of the studied nanoparticles was characterized by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The biological evaluation of organoselenium compounds and delivery systems containing organoselenium cargo was carried out towards gram-positive bacterial species (*Staphylococcus* spp., *Enterococcus* spp.) and yeasts (*Candida* spp.).

The obtained nanocarriers have desirable chemical and colloidal stability, making them useful for therapeutic or combination antimicrobial therapies. Owing to the optimized encapsulation methodologies, the organoselenium therapeutics can improve treatment many diseases. Results of our studies provide guidelines for design of new lipid-based systems for bioactive organoselenium compounds delivery.

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# The incorporation of magnetite nanoparticles into model biological membranes

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Iron oxide nanoparticles (maghemite and magnetite nanoparticles) are a special class of the nanomaterials. The magnetite nanoparticles (MNPs) possess specific properties important for biomedicine such as a small size, strong chemical affinity and superparamagnetism. Their potential arises also from MNPs transport within tissue using magnetic field gradient as a driving force and their ability to generate heat upon an external magnetic field. These features makes the MNPs candidates for an application in magnetic resonance imaging, targeted drug delivery and hyperthermia.

Previously, numerous types of nanoparticles for medical application were synthesized, but only a few of them are actually introduced on the market. One of the reasons behind it is limited understanding of interaction between MNPs and biological systems. Our research is an attempt to systematize and expand knowledge in the area of functionalized MNPs behavior in contact with model membranes. Native membranes are composed of various lipids with embedded proteins, whereas the model membranes can be formed by one type of phospholipids at the gas/liquid interface. Such system allows simultaneously control many chemical and physical parameters such as membrane packing density and permeability.

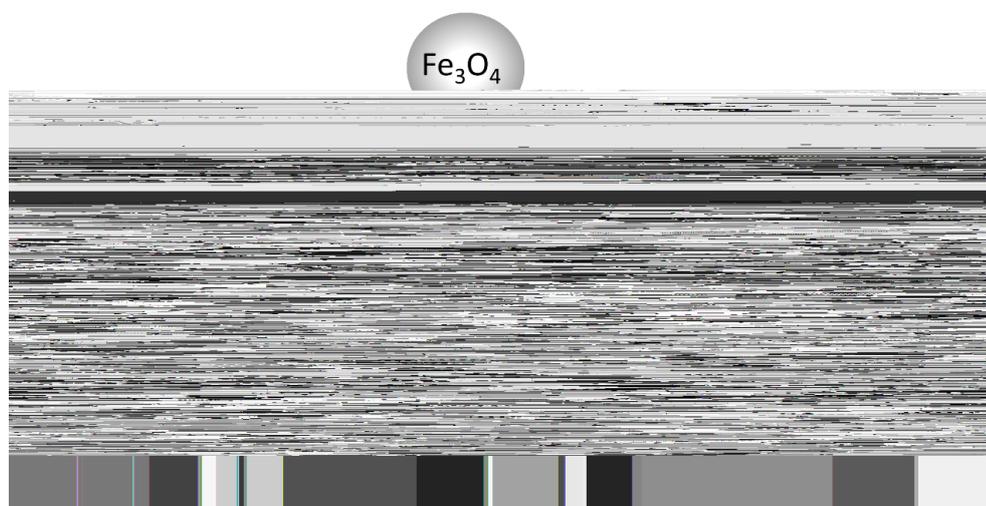


Figure 1. The graphical illustration of our research purpose

The biological membrane models were created using Langmuir technique. The thermodynamic properties of mixed films of the MNPs and phospholipids as well as adsorption of the MNPs from the subphase into the previously compressed phospholipid monolayers were analyzed based on the compression isotherms. The textures of the Langmuir films were investigated *in situ* using Brewster angle microscope. It delivered information about structure and molecular organization in monolayers as well as miscibility of the components. The Langmuir films were transferred onto mica and Si wafers. The films topography and the magnetic domains distribution was imaged in nanometer scale by atomic and magnetic force microscopy.

## Acknowledgements

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# Perylene derivatives in polymer matrixes as active layers for organic light emitting diodes

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Application of small-molecule dyes as well as polymers in organic light emitting diodes (OLEDs) allows for production of flat, thin and flexible devices by low-cost solution processing methods. However, polymer based devices has limited performance reproducibility due to batch-to-batch variations of the molecular weight, regioregularity, purity and dispersivity. Better understanding of molecular structure-device performance offer phosphorescent and fluorescent dyes thanks to reproducibility and simplicity of their synthesis. The wide range of available low-molecular-weight dyes, especially porphyrin and perylene derivatives, create possibility of further improvement of already commercialized OLEDs parameters such as efficiency, colour purity, lifetime and stability [1]. Unfortunately, the dyes have a strong tendency to aggregate, what reduces luminescence quantum yield (QY) [2] and can restrain their application.

Here, we present studies on the active layers of p-type (Pn) and n-type (PCIn) perylene derivatives with four lateral alkyl chains composed of n carbon atoms in polymer matrix of poly(methyl methacrylate) (PMMA) and poly-(N-vinyl carbazole) (PVK) obtained by spin-coating technique. In the bay positions of the perylene core of PCIn molecules were attached four chlorine atoms, what causes twisting of the perylene skeleton and thus reduces the strength of intermolecular interaction leading to aggregation [1,3,4]. The absorption and fluorescence spectra delivered information on types of aggregates formed by the Pn and PCIn dyes in polymer matrixes. Furthermore, the thin layer films QY was determined using integrating sphere method [2]. Our research show that perylene dyes exhibit variety aggregation forms depending on their concentration in polymer matrix. The QY value changes from 10–20 % for purePn films up to near 100 % for 0.1wt% of the dye in the matrix, while in the case of PCIn QY value remains in the range of 20–35% independent from dyes concentration. The electrooptical characterization of OLEDs with P4 and PCl4 dyes in the active layers was also performed.

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# Layer by layer self-assembled of synthetic/natural polyelectrolytes multilayers on maghemite nanoparticles

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In this work we have obtained functionalized magnetic nanoparticles (MNPs) by using the layer by layer self-assembly polyelectrolyte technique (LbL) [1]. The magnetic nanoparticles were synthesized by coprecipitation method [2]. The TEM images shown spherical nanoparticles with an average particle size about 8.53 nm. The X-ray diffraction analysis indicated iron oxides such as maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). The surface charge of the nanoparticles was modified with the polystyrene sulfonate (PSS)/polyallylamine hydrochloride (PAH), and the sodium carboxymethyl cellulose (CMC)/chitosan (CHI) using the LbL technique, which lead to reversal in the sign of  $\zeta$ -potentials.

We have observed that the magnetization properties decreased little bit when the polyelectrolyte multilayer is adsorbed on the MNPs, also they exhibit a same magnetic behavior with respect to number of layers of PSS/PAH and CMC/CHI. Where the saturation magnetization values of NMPs coated with PAH/PSS multilayers is slightly less than NMPs coated with CMC/CHI [3].

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# In vitro cytotoxic evaluation of the curcumin encapsulated in multilayers of biopolymer-magnetic nanoparticles

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The objective of this work was the synthesis and characterization of magnetic nanoparticles (MPMs) functionalized with biopolymers by Layer by Layer deposition technique (LbL), in order to study its release profile and evaluate their cytotoxic activity in vitro using the human breast tumor cell (MCF-7). MnFe<sub>2</sub>O<sub>4</sub> nanoparticles were obtained by alkaline coprecipitation with subsequent functionalization of their surface by the LbL technique, using chitosan and chondroitin sulfate alternately [1]. To optimize the functionalization was carried out the study of speciation, which showed the optimal pH (5.0) for greater interaction between the surface groups of the biopolymers and MnFe<sub>2</sub>O<sub>4</sub> based on their values of pKa's obtained in potentiometric and conductimetric titrations. The encapsulation of the curcumin in the MNPs coated with polymers, it occurred by the addition of an ethanolic solution of the curcumin (0.3 mg/ml) in chitosan solution fixed at pH 5.0, being deposited alternately in the layers of the polymers [2].

The MNPs coated with polymers showed low PDI, hydrodynamic diameter in the range of 198 nm and zeta potential depending on the pH and polymer added. The interaction between the biopolymers, the curcumin and the MnFe<sub>2</sub>O<sub>4</sub> also was characterized by FTIR, XRD, XPS, ICP-OES, TGA, TEM, and magnetization. The encapsulation efficiency of curcumin was evaluated by fluorescence spectroscopy, obtaining 44.1 ± 5.9, 40.3 ± 6.4 and 49.5 ± 5.2 % in the layers 2, 3 and 4, respectively. The controlled release of the curcumin occurred gradually, by diffusion mechanism. In vitro cytotoxic activity evaluation of the curcumin was determined by the MTT assay [3], observing that free curcumin and nanoencapsulated in layers 2, 3 and 4 of biopolymer-magnetic nanoparticles reduced to (19.2, 26.5, 28.2 and 36.4 %, p < 0.0001, respectively) the viability of the MCF-7 cells in the 96h period.

**Acknowledgements** The financial support of DPP/UnB and FAPDF.

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# Dispersion of polymer nanoparticles using block copolymer dispersant

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Nanoparticles of polycaprolactone are prepared by means of the nanoprecipitation process. Such process consists in dilution with water of a solution of polymer in acetone. Precipitation of the polymer takes place as the amount of water is such that a diphasic region is entered. This yields aqueous dispersions of polymer nanoparticles (diameter ~ 100-200 nm) in the very dilute regime. Colloidal stability requires the addition of a stabilizer (emulsifier) which also builds a hydrophilic shell around particles for increasing biocompatibility in blood stream. Nonionic stabilizers with long hydrophilic polymer parts provide steric stabilization and stealthy character to the nanoparticles.

Thus amphiphilic block copolymer of the poly(caprolactone)-*block*-poly(ethylene glycol) (PCL-*b*-PEG)<sup>1</sup> type were investigated for the stabilization of polycaprolactone (PCL) nanoparticles, both under long term storage conditions and during the preparation by the nanoprecipitation process. Production of nanoparticles indeed requires that they are efficiently stabilized during their fabrication.

A challenge regarding practical applications is reaching high enough concentrations of nanoparticles. The nanoprecipitation process is limited to dilute systems yielding concentrations below 1 wt%. The present work firstly used the classical process in order make physical chemistry clearer. Thereafter increasing the concentration was considered.

The classical preparation in dilute conditions often results in the emulsification of both PCL nanoparticles stabilized by part of the PCL-*b*-PEG and block copolymer micelles coming from the presence of excess PCL-*b*-PEG. The amount of PCL-*b*-PEG micelles was titrated in the suspensions; it could be reduced by decreasing the PCL-*b*-PEG load in the recipe. Unfortunately there always remain free PCL-*b*-PEG micelles coexisting with PCL nanoparticles. As the residual concentration of PCL-*b*-PEG micelles reached lower levels, the stability of PCL nanoparticles was progressively compromised. A recipe that would allow full adsorption of PCL-*b*-PEG to PCL nanoparticles was inferred by extrapolation; but the stability of the suspension was very poor. It turned out that a slight residual concentration of free PCL-*b*-PEG is necessary in the aqueous phase; such free PCL-*b*-PEG compounds self-assemble as micelles. It is devised that failure at the preparation of PCL nanoparticles avoiding excess free PCL-*b*-PEG came from the slow kinetics of adsorption of PCL-*b*-PEG to PCL nanoparticles. Indeed, partial coverage of particles was disclosed by zeta potential measurements. It is required that a high enough concentration of stabilizer is present in order to make adsorption fast enough for successful emulsification.

Increasing the concentration of nanoparticles could be done by reversing the ratio of acetone and water. While the classical process makes use of large water/acetone ratios (typically 3/1 to 5/1), emulsification was performed at low such ratio (below 1/1). Indeed it is just required that a diphasic region of the phase diagram is entered for nanoprecipitation takes place. A large amount of acetone is often detrimental to the stability of classical emulsions; polymer suspensions stabilized by block copolymers resisted such conditions, so that preparations leading to nanoparticles concentrations up to 5 wt% after evaporation of acetone were successful.

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# Development and characterization of an eye-drop liposomal formulation with acetazolamide

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Glaucoma is considered one of the leading causes of irreversible blindness in the world. The main risk factor in glaucoma is the chronic elevated intraocular pressure (IOP). Acetazolamide (ACZ) is one of the most effective drugs for the treatment of ocular hypertension, however its use is limited to oral administration (with important systemic side effects) due to its low ocular bioavailability (poor aqueous solubility and low corneal penetration)[1]. The purpose of this work was to develop an eye-drop liposomal formulation loaded with acetazolamide, included in a polymeric solution, to increase the drug residence time after instillation and by hence its ocular bioavailability. *In vitro* and *in vivo* tolerance studies have been performed to ensure the preservation of the ocular surface.

Liposomes were prepared according to the technique described by Bangham and modified in our research group[2]. The ratio of phosphatidylcholine:Cholesterol:Vit-E:ACZ components in the organic solution was 8:1:0.08:0.3 respectively. The tonicity of the formulation was adjusted to physiological values using erythritol, trehalose and borate buffer. After extrusion, the resulting liposome dispersion was diluted 1:2 with a hydroxypropylmethyl cellulose solution (Final concentration 0.3%).

The size analysis of dispersed ACZ-loaded liposomes showed unimodal distribution ( $160.9 \pm 4.38$  nm) and the ACZ concentration in the formulation resulted 0.7 mg/mL. The proposed formulation was further characterized in terms of pH (values around  $7.00 \pm 0.01$ ) and osmolarity ( $295.5 \pm 1.5$  mOsm/L). Also, the average viscosity and the surface tension values of the formulation measured ( $4.7 \pm 0.1$  mPa·s and  $47.6 \pm 0.5$  mN/m respectively) were both compatible with the physiological tear film. The liposomal formulation and its components resulted not cytotoxic *in vitro* according to standard specifications against cells (J774 mouse macrophages and HeLa cell lines) after 2 hours of exposure. *In vivo* tolerance assay in rabbits after instillations (25  $\mu$ L) showed no signs of discomfort during the study (24h).

In summary, the ACZ-loaded liposomal polymeric formulation proposed in this work resulted well tolerated (in vitro and in vivo), and might be considered as a promising ocular drug delivery system for the treatment of glaucoma. Further studies will be focused on the evaluation of its *in vivo* hypotensive activity.

**Acknowledgements:** Research Group UCM 920415, RETICs (Oftared) RD16/0008, MAT 2013-43127R and FIS PI13/00516

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# Decoration of plasmonic nanoparticles with responsive polymers

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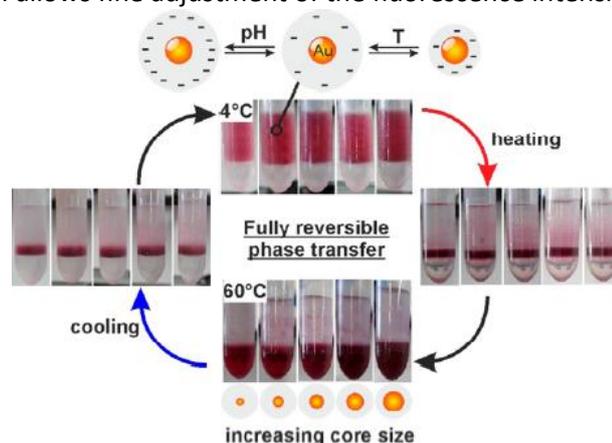
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Gold nanoparticles have been in the focus of research for decades due to their localized surface plasmon resonance (LSPR) in the visible wavelength range. Their unique optical properties make them interesting for many applications including sensing, lasing and metamaterials. For such purposes it is often necessary to modify the nanoparticle surface in order to enhance the colloidal stability, introduce new functionalities and allow for dispersion in different solvents. Ligand exchange with polymeric ligands is often used to increase the stability of the nanoparticles either by steric or electrostatic interactions or to render them hydrophobic to enable phase transfer to non-aqueous media.[1] For a successful ligand exchange the ligands must bear a functional group with a high binding affinity to gold which are in particular amines [1], trithiocarbonates and thiols.[2]

Here, we use  $\alpha$ -trithiocarbonate- $\omega$ -carboxyl-terminated poly(*N*-isopropylacrylamide) (PNIPAM) to stabilize gold nanoparticles and allow for their phase transfer to an organic phase. The success of the ligand exchange is confirmed by light scattering, extinction spectroscopy and transmission electron microscopy. While the trithiocarbonate group is at the surface of the nanoparticles, the terminal carboxyl group is susceptible to changes in pH. Furthermore, PNIPAM shows a thermoresponsive behaviour with a lower critical solution temperature (LCST) of approximately 32°C. With this, interparticle interactions can be regulated. The phase transfer of the polymer-coated gold nanoparticles from water to chloroform is reversibly performed by adjusting the pH below the  $pK_a$  of the carboxyl groups and by increasing the temperature above the LCST (see fig. 1).[2]

In addition to that, the free carboxyl-group allows to add new functionalities to the gold nanoparticles. We demonstrate this by attaching dye molecules to the ligands. This system allows to regulate the distance between the plasmonic nanoparticle and the terminal dye molecules by employing the LCST behavior of the polymer linker. This distance control has a strong influence on the dye emission because of non-radiative energy-transfer between the excited dyes and the gold nanoparticles. [3] Hence our inorganic/organic hybrid system allows fine adjustment of the fluorescence intensity by temperature.



**Figure 1:** Fully reversible phase transfer of PNIPAM-coated gold nanoparticles from water to chloroform. [2]

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# Tuneable optical features of amino acids-stabilized gold nanoparticles and nanoclusters

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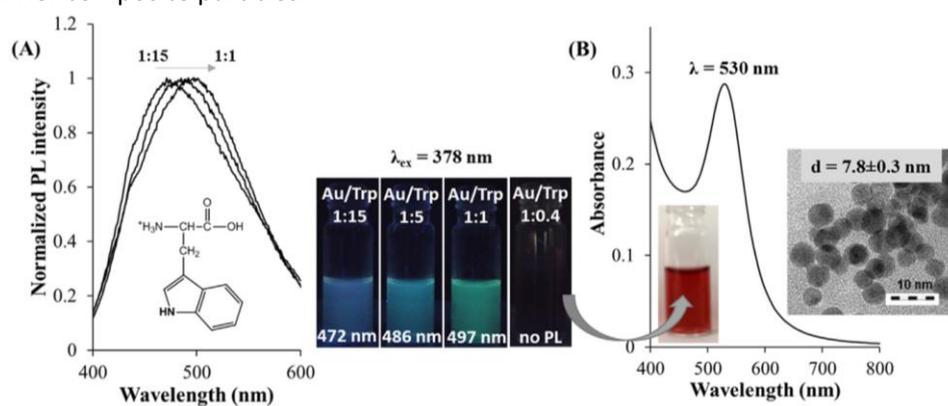
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The biomedical applications (*e.g.*, diagnostic, *in vivo*, *in vitro* imaging, cancer therapy *etc.*) of nanosized gold particles require biocompatible preparation routes. In recent years a simple, one-pot, “green” synthetic routes for the preparation of gold nanoparticles (Au NPs) or nanoclusters (Au NCs) are in focus of interest [1-3].

In this work blue- and green-emitting gold nanohybrid systems have been synthesized by spontaneous interactions of the tetrachloroaurate anions ( $\text{AuCl}_4^-$ ) with *L*-histidine (His) and *L*-tryptophan (Trp) amino acids at 37 °C in aqueous medium. The dominant role of  $\text{AuCl}_4^-$ /amino acid molar ratios as well as the pH in the formation of Au NPs or Au NCs was confirmed by numerous spectroscopic techniques. We demonstrate that without additional reducing agents the His and Trp show different reduction behaviour with  $\text{AuCl}_4^-$  which supports the fact that the unique optical features originate from diverse structures. Because of the pH-dependent complexation and reduction capability of the studied amino acids the dominant presence of polynuclear fluorescent gold(I) complexes (quantum yield (QY%) ~4%) with a well-ordered structure is presumable for His-directed Au system confirmed by mass spectrometry, X-ray diffraction and infrared experiments. The existence of  $d = 8$  nm-sized Au NPs or subnanometer-sized ( $d < 2$  nm) Au NCs ( $\text{Au}_3$ - $\text{Au}_5$ ) that have tuneable blue or green photoluminescence (emission = 470–500 nm) was identified in the samples containing Trp depending on the applied  $\text{AuCl}_4^-$ /Trp ratios. The blue-emitting Au/His nanohybrid system as potential bioimaging agent was used to visualize fluorescently albumin- and chitosan-based drug carrier composite particles.



**Figure 1.** Normalized PL spectra of Au/Trp 1:1; 1:5 and 1:15 systems at acidic pH with the photos of the samples under UV-light (A) and the absorbance spectrum of Au/Trp 1:0.4 at pH = 12.0 with a representative HRTEM image of the Au/Trp NPs (B).

**Acknowledgements:** This work was supported by the Hungarian Research Fund OTKA K116323 and GINOP-2.3.2-15-2016-00038. E. Csapó thanks the financial support of J. Bolyai Research Fellowship.

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# Role of nanocavities in surface enhanced photoluminescence

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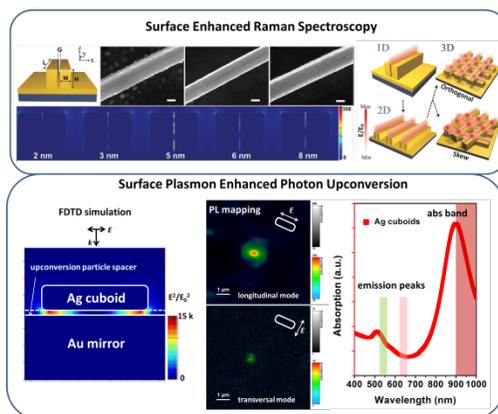
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Surface enhanced spectroscopy has been in the spotlight for decades. The enhancement is usually due to the presence of plasmonic nanostructure that provides “hotspots”. Numerous researches have been conducted but the enhancing mechanisms are yet to be fully understood for various kinds of spectroscopies. We focus here on the contribution of nanocavities in terms of enhancing the corresponding spectroscopy. Vertical and horizontal nanocavities were fabricated by nanoskiving and self-assembly, respectively. The presence of nanocavity confines the incident light down to nanometric scale and hence the near-field electromagnetic field intensity. The unique feature leads to enormous enhancement and also potential alteration of the interaction between plasmonic component and target materials. In this poster we will present separately the contribution of nanocavities particularly in surface enhanced Raman scattering and surface enhanced photon upconversion.



**Figure 1** (upper panel) Constructing line nanocavities via Nanoskiving. (lower panel) Fabrication of nanocavities from nanoparticle self-assembly.

**Acknowledgements** This work is supported by Alexander von Humboldt Foundation and Center for Advancing Electronics Dresden “CfAED”.

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# Colloidal Stability of Aqueous Iron Oxide Nanoparticles with Reversibly Adsorbed Phosphorylated Poly(Ethylene Glycol)

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Aqueous magnetic nanoparticles are being developed for a wide range of applications from biomedicine [1] to magnetic density separation [2]. The particles typically consist of single-domain, superparamagnetic maghemite crystals with a diameter of roughly 10 nm, small enough to prevent cluster formation due to dipole-dipole interactions [3]. In water, charge stabilization may be lost following a change in pH or ionic strength, affecting surface charge or ionic screening. Steric stabilization using an adsorbed surfactant is an option to render the particles more resistant to such changes [4]. Here, we investigate how surface coverage by adsorbed surfactant correlates to colloidal stability.

Iron oxide nanoparticles are synthesized by coprecipitation of Fe(II) and Fe(III) salts as described by Massart [5]. After initial synthesis of magnetite ( $\text{Fe}_3\text{O}_4$ ), the particles are oxidized to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), which is chemically more stable. Sterical stabilization is realized using poly(ethylene glycol), modified with a phosphate head group, which adsorbs onto aqueous iron oxide [4]. We use vibrating sample magnetometry and vibrational infrared spectroscopy to quantify the concentrations of nanoparticles and of free or adsorbed surfactant. We find that desorption of surfactant leads to destabilization of the dispersion, as revealed by the presence of clusters observed by dynamic light scattering and by accelerated sedimentation. Our results demonstrate the value of measuring adsorption isotherms to characterize the ability of surfactants to stabilize aqueous ferrofluids.

**Acknowledgements** This work is part of the research programme *Innovative Magnetic Density Separation for the Optimal Use of Resources and Energy* with project number 14917 which is (partly) financed by the Netherlands Organisation for Scientific Research (NWO).

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# OPTIMIZATION STUDIES OF ASSEMBLING GELATIN NANOPARTICLES OBTAINED BY TWO-STEP DESOLVATION TECHNIQUE

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Gelatin Nanoparticles (GNPs) are promising drug delivery systems due to their biodegradable and biocompatible characteristics [1]. The most employed preparation technique is the two-step desolvation technique (2-SDT) [2]. However, this method has two main drawbacks, the lack of reproducibility and the low production yields. The 2-SDT involves the addition of a desolvating agent (acetone or ethanol) in a first desolvation step to separate the high molecular weight (HMW) fraction of gelatin from the low molecular weight (LMW) fraction. This step allows the isolation of HMW gelatin, needed to perform monodisperse GNPs distribution and reduce the aggregation tendency of the formed GNPs.

The aim of the present work is to optimize the 2-SDT in order to maximize the recovery of HMW and to improve the yield and reproducibility of the technique.

The vials were filled with gelatin type B (250mg) and dissolved in 5 mL of water. Afterwards, HMW gelatin was obtained by desolvation at different temperatures (40-25°C) by adding 5 mL of acetone or ethanol respectively. After precipitation of the HMW, samples were then lyophilized and the amount of HMW gelatin was gravimetrically determined. All of these steps were carried out in triplicate for each solvent and temperature.

The yield percentages obtained with Acetone resulted 17.18%, 14.32%, 10.92% and 10.34% for 25°C, 30°C, 35°C and 40°C respectively resulting lower when using ethanol (9.532%, 7.572%, 4.972% and 4.74%) for the same temperature range respectively.

The recovery of HMW gelatin can be considerably improved by adding acetone as a desolvating agent to a 30°C gelatin type B solution.

**Acknowledgements** The financial support of FEDER-Spanish Ministry of Economy, Industry and Competitiveness MINECO (MAT2013-43127-R). UCM Research Group 920415 and RETICS net (RD12/0034 and RD16/0008).

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# Fundamentals of Nanotoxicity: Interactions between Nanoparticles and Cell Membranes

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Nanoparticles are widely found in modern technologies, ranging from energy conversion to medical applications [1]. However, the cytotoxic effects of nanoparticles are not well understood, stimulating a new research area dubbed '*nanotoxicity*'. Nanotoxicity has been found to depend upon the size, shape and surface chemistry of nanoparticles, and can be imparted via a multitude of toxicity pathways [2]. The most common method for determining the cytotoxic effects of nanoparticles has been through dye-based cytotoxicity assays that can provide information such as cell proliferation, glucose consumption and membrane permeability [3]. However, these assays give little information about the *fundamental interactions* between nanoparticles and cells that lead to cellular entry (endocytosis) and resulting toxicity. An understanding of nanoparticle interactions with membranes is key to understanding endocytosis, membrane fusion and nanotoxicity, as well as improving drug-delivery-vector design. Due to the complex nature of cells, this is difficult to examine *in vitro* and so using membrane models represents a promising and important alternative approach.

This project aims to explore how the physicochemical properties of nanoparticles influence their interactions with various membrane models. Many self-assembled lipid systems have been used previously to model cell membranes, including bilayers, monolayers, and liposomes (or vesicles)[4]. Whilst lipid multilayers have also long been recognised as bearing structural resemblance to cell membranes, they are conventionally prepared by using spincoating from a volatile organic solvent [5], and thus it has been difficult to study the interactions between such lipid multilayers with biomedically relevant nanoparticles often dispersed in aqueous media. We have recently developed a method for preparation of lipid multilayers via dropcasting aqueous DOPC (a common eukaryotic membrane lipid) liposome dispersions on mica substrates that have been characterised using synchrotron X-ray reflectivity (XRR) at the ESRF in Grenoble [6]. So far we have investigated how polyamidoamine (PAMAM) dendritic nanoparticles (dendrimers) of varying size (or generation) and dosage, functionalised with hydrophobic chains, influence *d*-spacing, coherence length ( $L_c$ ) and paracrystalline disorder (*g*) in DOPC lipid multilayers. Interestingly, multilayer structural disorder is promoted not only by the dendrimer size, but also by the method of dendrimer addition in liposome preparation. This is evident from the shift in the Bragg peak positions,  $\Delta Q$ , as well as the peak broadening (*i.e.* widening in the peak full width at half maximum). Co-assembly of the dendrimer with the lipids during the early stage of the liposome formation leads to dendrimer intercalation in the ultimate stacked lipid bilayers, currently being modelled using the ~~AFM~~ *AFM* method [7].

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# Functionalized nanocellulose for epithelial regeneration

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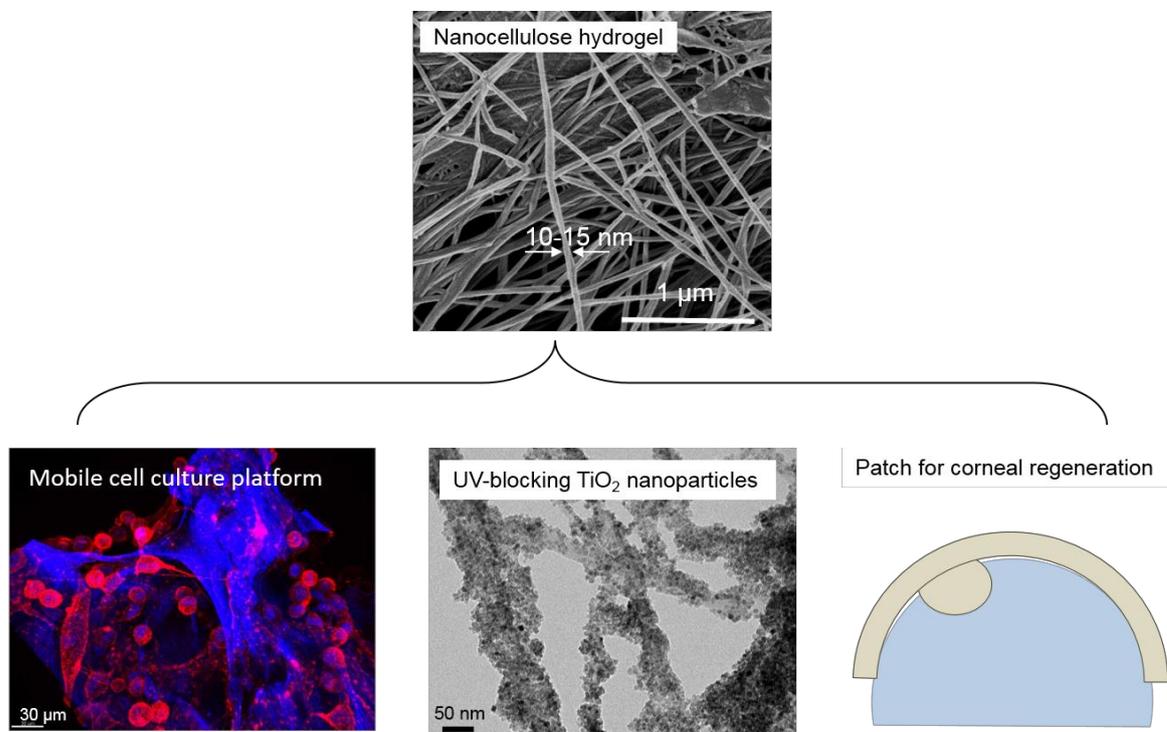
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Nanocellulose is a biopolymer which can be obtained from vegetal or bacterial origin. Nanocellulose of microbial origin is secreted by several bacterial species. This Bacterial Cellulose (BC) forms a stable 3D-network comprised solely of cellulose nanofibres. BC has unique properties that make it a promising candidate material for biomedical applications, especially for tissue regeneration: it has a high liquid holding capacity and demonstrated biocompatibility. It is pure and crystalline and, importantly, its characteristics can be finely tuned during and after its biosynthesis. Thus, our main goal is to exploit BC as a novel biomaterial for epithelial regeneration.

Firstly, we will present biocompatibility studies of bacterial cellulose and the use of BC as a mobile culture platform for adherent mammalian cells. Then, we will describe how bacterial cellulose can be functionalized with TiO<sub>2</sub> nanoparticles. In that way, BC acquires Ultra Violet(UV)-blocking capacity and can be used to protect epithelial tissues from damaging UV-radiation.

Finally, we will show preliminary results on the development of a bacterial cellulose-based patch specifically targeted at regenerating corneal epithelium. Corneal ulcers and wounds are common complications in ophthalmology and normally begin with damage to the outer layer of the cornea: the epithelium. We hypothesize that BC can help in treating corneal defects by means of: providing moisture, reducing the risk of infection and decreasing patient pain. Moreover, in the future, BC could act as well as a drug delivery system.



**Figure 1** Scheme of the possible applications of bacterial nanocellulose in epithelial regeneration

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Conducting polymers (CP) have been extensively studied in recent years due to, inter alia, their electronic properties, suggesting them as new materials exhibiting not only stability under ambient conditions, but also useful in many and varied applications. Among these, polythiophenes (PTH) and their derivatives such as poly(3,4-etylenedioxythiophene) (PEDOT), show interesting properties due to its high conductivity, low band gap, low oxidation potential, high electrochemical stability [1], etc. These properties depend on the electrosynthesis conditions to obtain the polymer, in this case, the systematic study of the effect of different concentrations of a surfactant (SDS) and 1 mM flavin adenine dinucleotide (FAD) used as dopant agents was made, focusing mainly in the study of the oxidation of  $\beta$ -nicotinamide adenine dinucleotide (NADH). Figure 1 shows the cyclic voltammetric response of bare GCE and PEDOT-FAD/GCE in 0.1 M PBS in the absence and presence of 1 mM NADH at a scan rate of  $0.1 \text{ Vs}^{-1}$ . The bare GCE exhibited a broad NADH oxidation wave, with a peak potential in 0.720 V. However, on a PEDOT-FAD modified GCE, the oxidation process starts at  $\sim 0.3 \text{ V}$  and exhibits a sharp oxidation peak at 0.56 V revealed a substantial shift in the peak potential (0.16 V) towards less anodic direction with a three-fold increment in the current signal. The shift in peak potential along with enhanced current signal can be reasoned as catalytic effect through electron transfer mediation. CP are known to behave as electron mediators (PEDOT-FAD film has a rich electron cloud) that promote electron shuttling between the electrode surface and the electrolyte through their redox mediation. PEDOT-FAD polymer is electronically conducting in nature when it is in oxidized state and is selective to cations in the neutral form as reported by Higgins *et al.* [2]. Also the electrocatalytic activity of the polymer film arises from the polarons formation, which has positive charges on the polymer backbone. Therefore, a catalytic activity is revealed from the defined NADH oxidation peak at the PEDOT-FAD/GCE. The catalytic behaviour can also be revealed by the nanoporous networked structure of PEDOT that may facilitate the electron transfer process causing an enhanced current signal and hence the reaction occurs at lower overpotential [3].

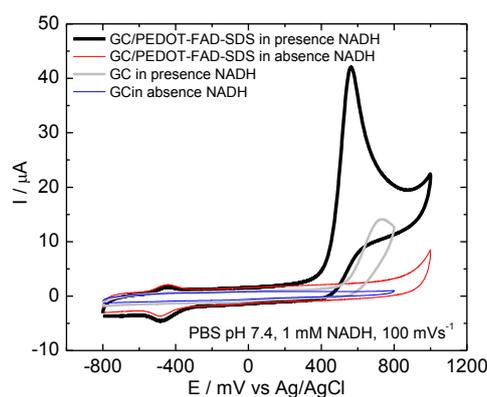


Figure 1. Electrocatalytic oxidation in the absence and presence of 1.0 mM NADH in PBS (pH 7.4) at a scan rate of  $0.1 \text{ V}\cdot\text{s}^{-1}$  on GCE bare and PEDOT-FAD/GCE.

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# Electrochemical sensors based on *in situ* grown bimetallic nanoparticles from recovered inks of spent screen-printed electrodes

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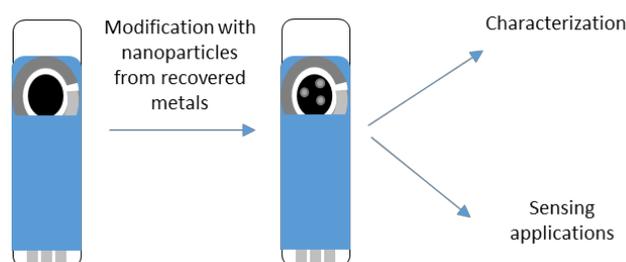
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The need for fast, reliable and accurate analytical information in fields such as environmental processes or industry has driven numerous efforts to investigate the development of sensors [1]. In this sense, screen printing technology is widely used for the production of low-cost disposable electrodes, whose consumption has significantly increased in the last years. As a result, vast amounts of solid waste are being generated, which need to be properly managed [2]. The conductive inks used to manufacture these electrodes contain precious metals that are polluting but also highly valuable. Therefore, the recycling of such metals is convenient, since it can report several environmental benefits [3].

In this work, metallic inks of spent screen-printed electrodes are recovered to be used for the preparation of bimetallic nanoparticles. Different synthetic methods have been studied, using the obtained nanoparticles to modify new screen-printed electrodes for its use as sensors. In addition, characterization of the nanoparticles and modified electrodes has been carried out in order to understand the differences observed in sensing performance between the different electrodes.



**Figure 1** Electrode modification with metallic nanoparticles from recovered inks of spent screen-printed electrodes.

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# Protein-Assisted Plasmonic Nanoclusters as Colloidal SERS Sensors

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We present a novel protein-assisted self-assembly route of small spherical gold or silver NPs (as satellites) with a hydrophilic protein corona onto larger gold NPs (as cores) into three-dimensional nanoassemblies with core/satellite architecture in dispersion. Their interparticle gaps represent hot spots for surface-enhanced Raman scattering (SERS) detection. The highly modular bottom-up fabrication of homo- and heterometallic core/satellite combinations allows for tailored plasmonics. A precise characterization of the morphology in dispersion was achieved using small-angle X-ray scattering (SAXS). By combining the results from SAXS, UV/Vis spectroscopy, and electromagnetic simulations we were able to correlate the structural parameters with the plasmonic coupling within the core/satellite nanoclusters [1].

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# Synthesis and Characterization of Nb<sub>2</sub>O<sub>5</sub> Mesostructures with Tunable Morphology and Their Application in Dye-Sensitized Solar Cells

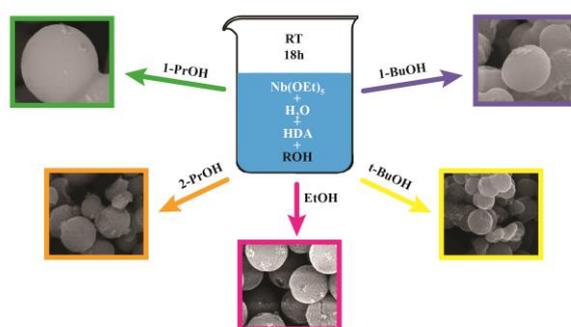
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The relatively low interest of the scientific community for the use of Nb<sub>2</sub>O<sub>5</sub> in DSSCs [1] may be related to the difficulty to prepare it in a form that is thermally stable up to at least 500 °C and which possesses, at the same time, a quite high specific surface area. Different synthetic approaches are present in literature in order to prepare high specific surface area Nb<sub>2</sub>O<sub>5</sub> [2]. Here, mesoporous submicrometric particles of orthorhombic Nb<sub>2</sub>O<sub>5</sub> were prepared by a very simple route consisting in the hydrolysis of niobium ethoxide Nb(OEt)<sub>5</sub> in alcoholic medium containing 1-hexadecylamine as structure-directing agent followed by a hydrothermal treatment. The effects related to the variation of the length of the aliphatic chain of the alcohol solvent (C2 to C4) and the ramification of the alcohol (primary, secondary and tertiary) as well as the reactants to solvent ratio were analyzed in terms of morphology, crystal structure, specific surface area and porosity. The samples were made of orthorhombic [3] Nb<sub>2</sub>O<sub>5</sub> but with different degree of crystallinity, as can be envisaged by the different signal/background ratios. The pore size distribution values indicate that the access of N719 molecules inside the mesopores is allowed, being the diameter of N719 molecule about 1.8 nm [4]. Interesting linear relationships have been found between the total pore volumes and the number of carbon atoms. In primary alcohols for both reactants/solvent ratios and between the maximum values (ranging from 4 to 10 nm) of the pore size distribution and the ramification of the aliphatic chain of the alcohol, i.e. between ethanol (primary), 2-propanol (secondary) and tert-butyl alcohol (tertiary), but in this case only for the highest reactants/solvent ratio. The obtained materials were tested as photoanodes in dye-sensitized solar cells. A remarkable efficiency value of 3.4% under one sun illumination has been achieved by using peanut-shaped particles obtained using 2-propanol as solvent with the lowest used solvent/reactant ratio.



**Figure 1.** By simply modifying the solvent and solvent/reactants ratio, different morphologies can be obtained, from nearly monodisperse beads to peanut-shaped particles, to sintered spheres aggregates, to a mix of different morphologies.

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# Cobalt oxide improves water oxidation and decreases organic dye degradation on silver phosphate as photocatalyst

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In bioinspired photocatalysis involving organic molecules, the lack of physical separation of redox half-reactions adversely affects the product stability. The presence of surface co-catalysts improves chemical stability of organic molecules participating in the redox processes.

Herein, we report the use of silver orthophosphate ( $\text{Ag}_3\text{PO}_4$ ) and  $\text{Ag}_3\text{PO}_4$  functionalized with cobalt oxide ( $\text{Co}_3\text{O}_4$ ) in a comparative study aimed at simultaneous investigation of water photo-oxidation and stability of methylene blue (MB) as a model cofactor. We revealed the increased 'selectivity' of the hybrid material for water resulting in enhanced oxygen evolution and limited dye degradation. We also demonstrated that water photo-oxidation in presence of  $\text{Co}_3\text{O}_4$  was greatly facilitated due to the improved charge transfer kinetics.

Thereby, we showed that  $\text{Co}_3\text{O}_4$  is a promising co-catalyst for the visible light-driven reduction of organic molecules using water as an electron donor.



**Figure 1** Schematic presentation of  $\text{Ag}_3\text{PO}_4$  red-ox potentials revealing its ability to oxidize water under visible-light.<sup>1</sup> Schematic illustration of proposed photocatalytic system showing that  $\text{Ag}_3\text{PO}_4$  surface functionalization with  $\text{Co}_3\text{O}_4$  increases selectivity towards water and decreases affinity for MB resulting in enhanced water oxidation and decreased MB degradation.

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# Bimetallic Colloids: Merging the Advantages of Silver and Gold Nanocrystals

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We present a general approach to achieve the narrow distribution, chemical accessibility, and oxidant stability inherent to gold nanocrystals, while maintaining the advantageous plasmonic properties of silver. To exemplify the combined properties of both metals, we use a cubic morphology enhancing the chemical and plasmonic sensitivity at the corners. This is achieved by consequent control of the growth *via* balancing the reduction potentials and enforcing adequate reaction kinetics (“living conditions”).[1]

The use of gold seeds enables the controlled synthesis of various silver morphologies in aqueous dispersions [1], and therefore, we selected the seed-mediated growth of specific gold colloids to spherical single-crystalline gold nanoparticles. Exploiting these AuNPs as seeds for silver overgrowth via facet-selective capping then enables the preparation of silver nanocubes with sharp edges, a narrow size distribution, and high yield. Finally, we achieved a thin protective gold shell, which ensures oxidant stability, but also facilitates a variety of chemical functionalization protocols in aqueous suspension.[2]

To verify the homogeneity and distribution of the obtained bimetallic nanoparticles we performed a comprehensive characterization by high-angle annular dark field transmission electron microscopy, energy dispersive X-ray mapping and optical spectroscopy.

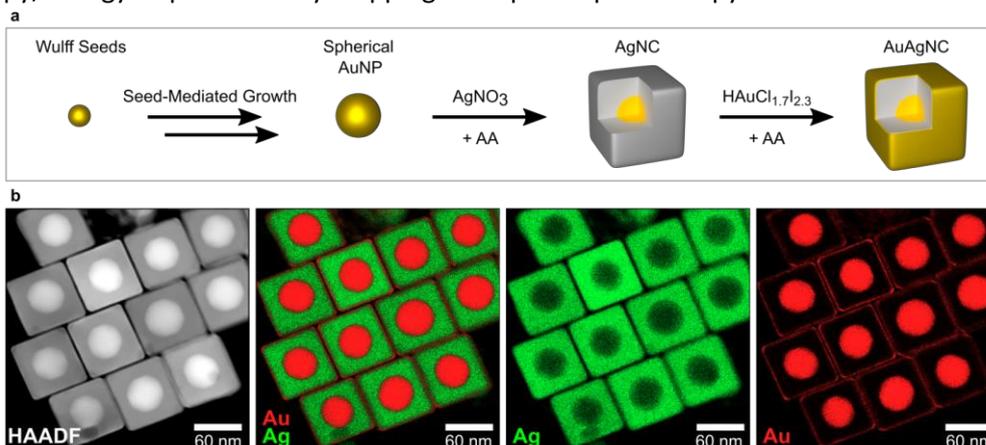


Figure 1: Synthetic Pathway and Elemental Characterization. (a) First, synthesis of spherical single-crystalline AuNPs by seed-mediated growth. Next, facet-selective silver overgrowth to form AgNCs. Finally, gold overgrowth from HAuCl<sub>1.712.3</sub> to yield a sub-skin-depth and homogeneous gold layer (AuAgNCs). (b) HAADF-TEM image and EDX elemental mappings of silver and gold content in the final AuAgNCs revealing a thin and homogeneous gold layer.

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# Synthesis of nanostructured latexes via mini-emulsion polymerisation in aqueous media, leading to water-resistant, hydrophobic films

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Nanostructured latexes synthesized by mini-emulsion polymerization enable the easy preparation of waterproof, hydrophobic films with good mechanical properties [1]. Indeed, they are obtained by water evaporation under ambient conditions without the use of coalescing aids (organic solvent), which might impact the film formation and properties and have environmental consequences. We demonstrate that hydrophobic additives can be encapsulated in the core-shell latexes during their multi-steps synthesis, using UV-filters and bactericide. We then get films with different specificities regarding the entrapped additive. We show that the time and incorporation method of those compounds are critical for their encapsulation and clearly have an impact on the film formation and properties. Finally, it is possible to tune the mechanical behavior of the films by wisely choosing the monomers constituting the core and the shell of the latex and their ratio.

**Acknowledgements** The financial support of LVMH Recherche, Département Innovation Matériaux.

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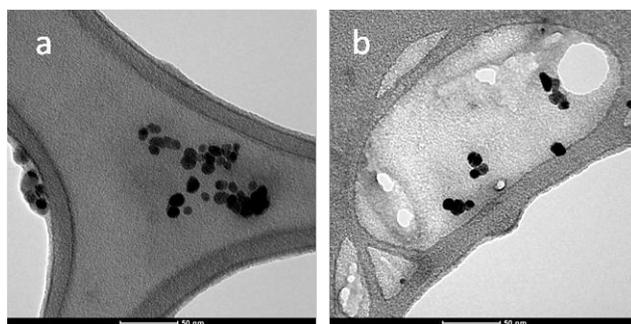
# Preparing Graphene Quantum Dots: effect of the starting material

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Graphene quantum dots (GQDs) are sheets of graphene with lateral dimensions smaller than 100 nm and less than 10 graphene layers. They possess unique physical properties such as strong wavelength-dependent down- and up-conversion photoluminescence which can be tuned for specific applications by controlling their size, shape, or chemical functionality. GQDs can be synthesized by either bottom up or top-down approaches. In a bottom-up approach, GQDs are manufactured from small organic molecules. This methodology is appropriate for controlling the size of GQDs but requires multistep organic reactions and purification at each step. In a top-down method, assemblies of graphene sheets are fragmented into zero-dimensional GQDs with physical, chemical, or electrochemical techniques, including hydrothermal or electrochemical graphene cutting, ultrasonication of graphene – acid solutions, or carbon nanotubes, carbon fibers and graphite. Some of these methods are impractical due to their high complexity, cost and environmental issues. We use a facile one-step wet chemically derived GQDs method from acidic treatment of different starting materials [1]. This methodology has been used for the preparation of GQDs using carbon fibers as starting materials but a systematic study of the effect of the starting material on the properties of the GQDs has not been carried out. With this objective in mind we have synthesized GQDs with the following starting materials: graphite flakes (+100 mesh) and Highly Oriented Pyrolytic Graphite (HOPG) from Sigma-Aldrich. GANF helical-ribbon Carbon Nanofibers none-graphitized and graphene oxide synthesized by a modified Hummer's method [2]. The properties of GQDs have been measured by Transmission Electron Microscopy (TEM), Micro-Raman, FTIR and photoluminescence spectroscopies. Some examples can be seen in the following TEM images.



**Fig. 1** TEM images of GQDs synthesized from: (a) GANF carbon nanofibers and Graphene Oxide (b)

Our results demonstrated that stable GQDs of  $(11 \pm 0.8)$  nm and  $(9.5 \pm 0.2)$  nm were synthesized using GANF and graphene oxide as starting materials, respectively. Stable QDs have not been obtained from different types of graphite as starting material. This may be because the synthesis procedure breaks the graphite sheets into small fragments that do not give rise to stable Quantum Dots. The photoluminescence, FTIR and Micro-Raman spectra depend on the structural properties of GQDs.

**Acknowledgements** . Authors thanks Junta de Castilla y León (SA045U16) and MINECO (CTQ2016-78895-R) for funding the research.

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# High performance electrode materials based on reduced graphene oxide aerogels for application in storage energy devices

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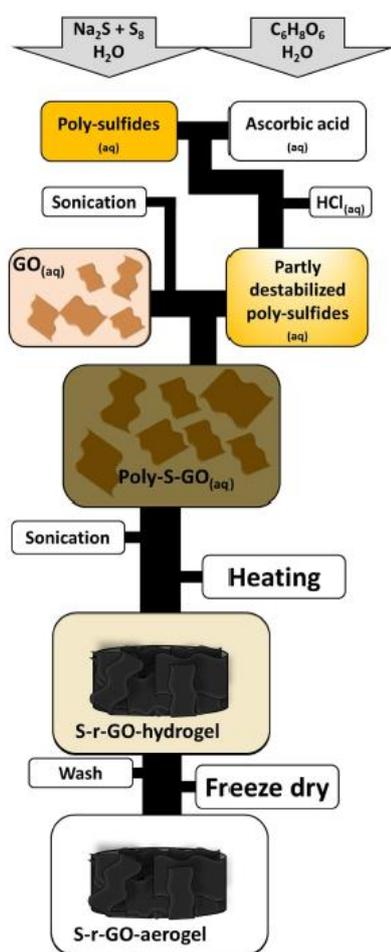
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Graphene is a nanomaterial of interdisciplinary interest, attracts attention of physicists as well as chemists, and engineers [1]. This two-dimensional (2D) sp<sup>2</sup>-hybridized carbon material might be one of the best choices as potential candidate for batteries and supercapacitor materials because its excellent mechanical, electrical,

thermal properties, large surface area, and high chemical stability [2]. Graphene oxide (GO), an oxo-functionalised derivate of graphene, can be prepared on a large scale and mostly single layers with a reasonable size of flakes of several μm are obtained and it can be used as a precursor of graphene [3]. In this work, we present graphene-based aerogels for the use as electrode in energy application, in particular for Li-S batteries. We demonstrate the direct use of a sulphur-containing graphene aerogel as a binder-free cathode in high energy Li-S cells. The sulphur-containing graphene-aerogel is prepared via a new, environmentally benign and straightforward synthesis route starting from graphene oxide (GOx) and polysulfide solution as schematically shown in Fig.1. This synthesis route combine gelling, reduction and sulphur loading in one-pot procedure resulting in a material with very high sulphur loading, which is essential for high energy density sulphur-based battery [4]. By combining the graphene-based aerogel cathode with electrolyte and a lithium metal anode, we demonstrate a Li-S cell with high areal capacity (more than 3mA/cm<sup>2</sup> after 75 cycles), excellent capacity retention over 200 cycles and good sulphur utilization. Based on this performance we estimate that the energy density of this concept-cell can significantly exceed the Department of Energy (DEO) 2020-target set for transport applications.



**Figure 1.** Schematic synthesis procedure of the self-standing reduced graphene oxide based high sulfur loading aerogel monoliths.

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# Removal of organic dyes by magnetic chitosan-alginate beads

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The objective of this work was to develop a magnetic adsorbent prepared from the encapsulation of magnetic nanoparticles (maghemite - Mag) in chitosan (CHI) and alginate (ALG) microspheres. The CHI-Mag and ALG-Mag microspheres were obtained from the addition of 5 mL maghemite (Mag) in a 2% (w/v) CHI solution dissolved in 0.2 mol.L<sup>-1</sup> acetic acid and a solution 3% (m/v) of ALG dissolved in water, respectively. The solutions were dispersed with Ultrasonic Processors 500 and 750 Watt-VCX Series for approximately 2 min at room temperature and 30% amplitude. After the CHI-Mag solution was dripped in a 2% (m/v) solution of sodium tripolyphosphate (TPP) and that of ALG-Mag in a solution 2.0 mol.L<sup>-1</sup> of ClCa<sub>2</sub>, using a peristaltic pump, Ismatéc Reglo model 78016-30. The gelled microspheres were maintained in contact with the TPP and ClCa<sub>2</sub> solutions for 30 min, filtered, washed with water to pH 7.0 and dried at room temperature. By means of the FTIR, TGA, MEV, TEM, optical microscopy, XRD, pore size and saturation magnetization techniques, the efficiency of the method used to prepare the microspheres was proved. The adsorption tests were performed using the dyes; Methylene blue and methyl orange. For this purpose 100 mg of CHI-Mag microspheres were placed in contact with 10 mL of 25 ppm methylene blue and methyl orange solution dissolved in a 0.1 mol.L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>/ NaH<sub>2</sub>PO<sub>4</sub> solution at pH 7.4 and NH<sub>4</sub>OH/NH<sub>4</sub>Cl in pH 9.0. The ALG-Mag microspheres (100 mg) were then contacted with the solutions of the two dyes dissolved in a 0.1 mol.L<sup>-1</sup> solution of HCl/KCl at pH 1.2. At predetermined times the microspheres were magnetically removed and the concentration of dye remaining in solution (*C<sub>eq</sub>*) as measured by UV-Vis spectroscopy. The amount of adsorbed dye (*Q<sub>eq</sub>*) was determined by the mass equilibrium equation and expressed in mmol of dye per g of dry microsphere. The microspheres presented spherical morphology with a dense surface, approximate size of 950 ± 13 μm, pore diameter equal to 3.0 nm and excellent adsorption capacity, removing approximately 95% of the dyes. These characteristics make the CHI-Mag and ALG-Mag microspheres a promising alternative for replacing the conventional adsorbents used for the removal of dyes or heavy metal ions.

**Acknowledgements** The financial support of DPP/UnB and FAPDF.

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# Formation of stable assembly of gold nanoparticles with giant DNA by weak heating

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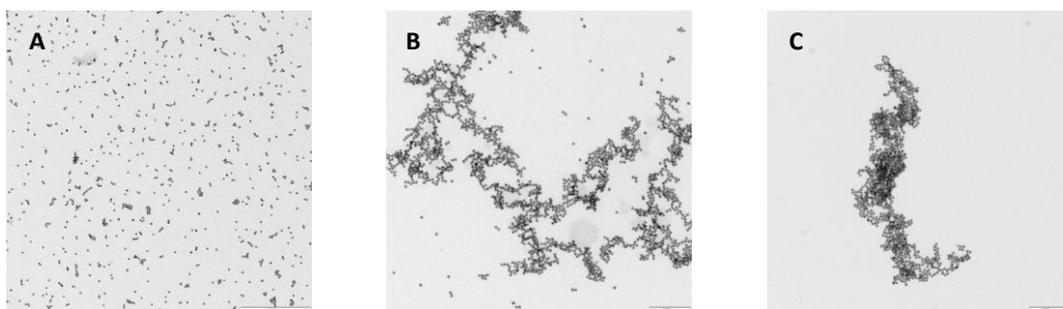
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The improvement of nanoparticles as DNA carriers in target delivery is one of the current challenges in medical research. The requisites for a good gene vector limit the kind of system that can be employed for this purpose, but nanoparticles in particular (due to their size, ease of functionalization and interaction ability) are ideal candidates for gene therapy [1]. Gold nanoparticles (AuNPs) are particularly interesting, since single stranded DNA has a high interaction affinity with the AuNPs surface [2]. Currently, the adsorption of double stranded DNA has been achieved with cationic silica nanoparticles, leading to the formation of histone-like complexes[3]. For gold AuNPs, this strategy is not viable, since cationic colloidal gold is moderately toxic [4].

In the present work, an easy method for the formation of stable anionic AuNPs/t4-DNA assemblies is described, without employing any additional functionalization of the nanoparticles. The key step in the described procedure is the addition of nanoparticles to a mildly heated DNA solution. The structure of the obtained complexes was monitored with fluorescence microscopy, and a histone-like structure, similar to that of silica particles/DNA complexes was observed[3]. TEM images confirm the existence of an interaction between DNA and AuNPs. CD measurements show that the DNA secondary structure is very close to a B-form even after forming the complex. Interestingly, these assemblies stabilize the AuNPs from salt-induced aggregation, in contrast to dispersed nanoparticles; a similar stabilization is also obtained for AuNPs/oligonucleotide complexes [5].



**Figure 1.** A) TEM images of dispersed gold nanoparticles. B) TEM images of nanoparticles in presence of t4-DNA. C) TEM images of nanostructures formed by heating solution.

**Acknowledgements** We thank the Spanish Ministerio de Economía y Competitividad (MinECo), CTQ2016-78703-P (AEI/FEDER, UE) and University de Sevilla for a grant of the V-Plan Propio de investigación (VPPI-US) for their financial support.

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# Enhanced Plasmonic Photothermal Therapy via Intracellular pH-Induced Tip-to-Tip Assembly of Gold Nanorods

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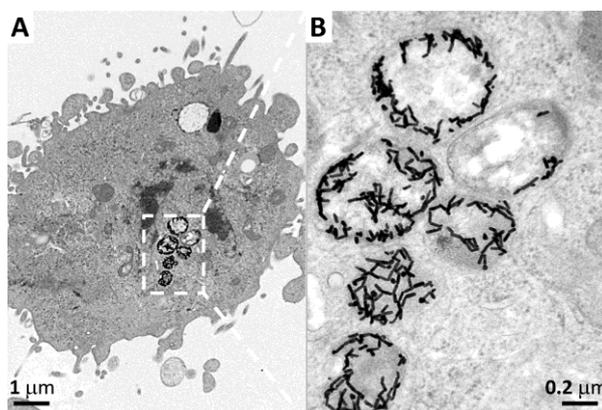
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Plasmonic systems are of great interest for biomedical cancer research and fundamental for photothermal therapy using pulse laser irradiation at the near-infrared (NIR) [1]. The fabrication of plasmonic gold nanostructures which efficiently convert light into heat for cell photothermolysis is an ongoing challenge, with the aim of reducing the applied laser power density to a minimum. We demonstrate that gold nanorods (Au NRs), functionalized at their tips with a pH-sensitive ligand, assemble into oligomers within cell lysosomes through hydrogen-bonding attractive interactions (Figure 1). The formation of hot-spots at the interparticle space allow us to significantly reduce the femtosecond laser power density and Au NR dose, while still achieving excellent cell killing rates. Optimal enhanced plasmonic photothermal therapy was obtained using low-aspect-ratio Au NRs, due to the formation of tip-to-tip oligomers with longitudinal localized surface plasmon resonance bands in resonance with 800 nm Ti:sapphire 90 fs laser pulses [2].



**Figure 1** Representative TEM micrograph (A) and magnification (B) of the lysosome areas of cancer MDA-MB-231 cells after 24 h of incubation with 0.1 nM Au NRs functionalized with lipoic acid.

**Acknowledgements.** A.G.-M. and I.L.-M. acknowledge receipt of Ramón y Cajal Fellowships from the Spanish MINECO. G.G.-R. acknowledges receipt of the FPI Fellowship from the Spanish MINECO.

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# Paraffin-based nanoencapsulated PCM prepared from solvent-assisted emulsions in water

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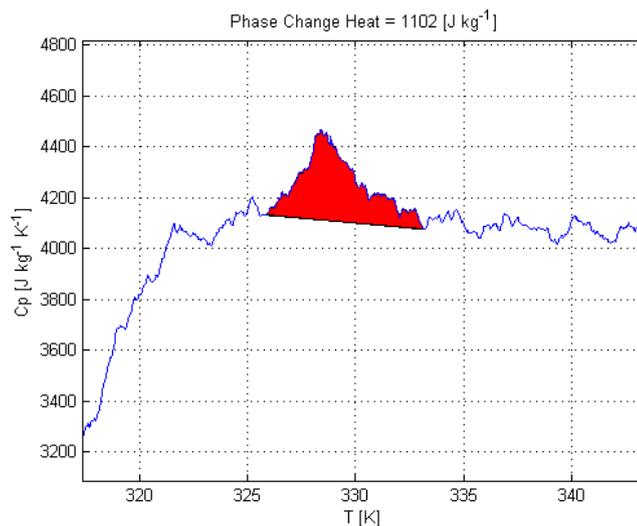
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Phase Change Materials (PCM) as paraffin waxes have attracted much attention due to the possibility of exploiting their latent heat of fusion or solidification for the purpose of heat storage during heating or cooling, in addition to their chemical stability and tunable melting at moderate temperatures [1]. Anyway, due to some drawbacks as the low thermal conductivity and thermal hysteresis of PCM, the scientific community has been pushed to study more complex systems based on paraffin emulsions in water. Emulsions or nano-encapsulated PCM offer the advantage of higher heat transfer due to the presence of water phase and higher surface area of PCM phases. Applications include solar thermal storage [2], waste heat recovery, intelligent building, thermal regulating fabric, etc. [3]. The main problems related to these systems are the colloidal instability of emulsions that can lead to particles settling, creaming, flocculation or coalescence and the effect of supercooling that often arises for nano-sized PCM.

In this work, nano-emulsions of paraffin waxes in water have been produced by a solvent-assisted route. Concentrations as high as 10 wt% have been obtained starting from two commercial paraffin waxes, with nominal melting temperatures of 55 °C and 70 °C respectively.

Thermal properties as the thermal diffusivity of suspensions, temperature and latent heat of melting and solidification of nano-PCM are under investigation. Figure 1 shows preliminary data on calorimetric measurements of specific heat for a 2 wt% of 55 °C melting paraffin. The peak corresponding to the fusion latent heat has a maximum at 55 °C, which is the same fusion temperature of the bulk paraffin sample. The estimate latent heat of fusion is 1.1 J/g, considerably lower with respect the theoretical expected value of 3.4 J/g. Further experiments are under way to complete the thermal characterizations of all samples and to verify the exactness of this value.



**Figure 1** Specific heat and phase change heat measurement for a 2 wt% emulsion of 55 °C melting paraffin.

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# Surface oxidation of Single Wall Carbon Nanohorns for the production of surfactant free water-based colloids

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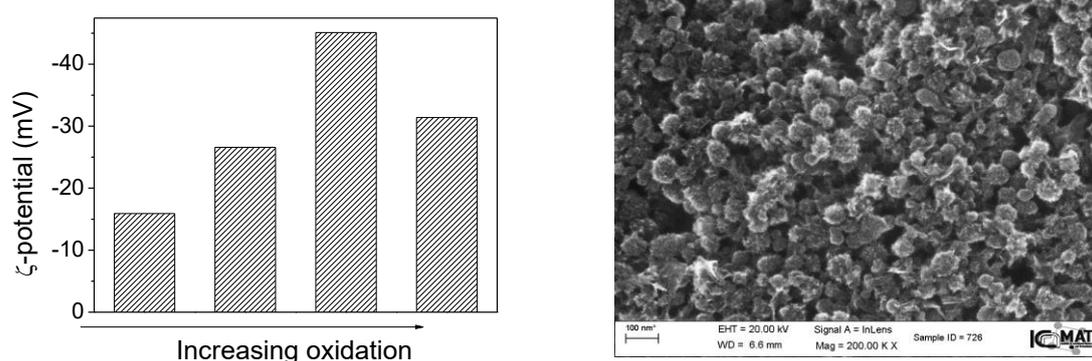
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Stable suspensions of Carbon Nanohorns (CNHs) in water or other polar solvents are useful for several applications, as in the case of black liquids for volumetric solar concentrators [1] or for subsequent chemical processing of the nanostructures, as in the case of covalent functionalization [2]. Since CNHs, as other graphene-based materials, are not easily dispersible in water due to the hydrophobic nature of the surface [3], surfactants are commonly used to achieve proper colloidal stability. Although the use of surfactants for the preparation of these colloids is simple and well established, they have some drawbacks like formation of foam, chemical interaction in covalent functionalization, degradation in extreme conditions, easy desorption from the surface to cite some, with consequent destabilization of the colloids.

In order to get stable suspensions in water of CNHs without using surfactants, a surface oxidation using concentrated HNO<sub>3</sub> at different temperatures and treatment times was performed. Colloidal suspensions of the treated nanopowders at the concentration of 0.05 g/L have been prepared by sonication and subsequent high-pressure homogenization. The microstructural characterization of the treated material has been obtained by FE-SEM. The thermal stability and an estimation of oxidation degree of nanopowders was investigated by means of simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) coupled with residual gas analysis (RGA). Dynamic Light Scattering (DLS) was used for the evaluation of aggregate size distribution within the colloids and  $\zeta$ -potential and the optical absorption characterization has been performed in the UV-visible range.

It has been found that an optimal surface oxidation degree of CNHs can be obtained, leading to improved colloidal stability due to the higher  $\zeta$ -potential modulus with respect to the use of surfactants. The optical properties of the prepared colloids, that are influenced by the oxidation, are also discussed.



**Figure 1**  $\zeta$ -potential of colloids prepared with CNHs at increasing oxidation degrees (left). FE-SEM micrograph of oxidised nanopowder (right).

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# Study of the properties of thin films based magnetic nanoparticles

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# Antibacterial polymeric biofilm with colloidal silver nanoparticles

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This study aims to develop a polymeric functional biofilm [1] with antimicrobial properties, with the final goal of being used for antimicrobial protection of food products. The biofilm was obtained by incorporating colloidal silver nanoparticles in a polymeric matrix of biocompatible sodium alginate polymer. The silver nanoparticles were obtained by reducing the silver nitrate with lysosime [2], an antibacterial protein extracted from egg white. The silver nanoparticles were characterised by UV-Vis spectroscopy, Fourier Transform Infrared Spectroscopy and Transmission Electron Microscopy. The synthesised nanoparticles showed antimicrobial properties. Their antimicrobial properties were assessed by the disk diffusion method using four bacterial strains: *Staphylococcus aureus*, *Escherichia Coli*, *Salmonella tryphimurium*, and *Enterococcus faecalis*. The silver nanoparticles were further incorporated in a polymeric film of sodium alginate, with the final purpose of using the film in a food packaging.

**Acknowledgements** This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-2211.

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# When is round round PA light scattering study

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Nanoparticles as building blocks for large scale structures with controlled shapes and sizes depend among other factors on the sphericity or anisotropy in shape. In our study, we try to fathom the limits of detection for non-sphericity of gold nanoparticles.

After production, a certain non-sphericity is expected. We irradiate the particle until they melt and after stopping the irradiation recrystallize. These particles show in polarized and depolarized light scattering no sphericity. The results are compared with SEM.

To study the origin of the depolarized scattering in spherical particle we built around gold nanorods spherical Si-Latex particle and study the influence on the depolarized light scattering.

# Novel nanocomposites based on epoxy and nano sized phthalocyanine for corrosion protection application

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In this study, epoxy/phthalocyanine nanocomposite (H<sub>2</sub>Pc/Epoxy) is employed to protect carbon steel corrosion in 3.5% NaCl solution. The performance of the new nanocomposite coatings was evaluated by using electrochemical impedance spectroscopy (EIS), Open circuit potential (OCP), scanning electron microscopy (SEM) measurements. The mechanical property of new nanocomposite coating was investigated using nanoindentation technique. The incorporation of H<sub>2</sub>Pc pigments into epoxy resin coating significantly enhances the corrosion resistance as well as the hardness of epoxy coatings. H<sub>2</sub>Pc pigment is able to cure the defect in epoxy resin and prevent the diffusion of corrosive electrolyte to carbon steel

# In-line measurement of colloids by 180° DLS in processes and high-throughput robotics

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Dynamic Light Scattering (DLS) is a prevalent tool for determining particle size distributions in fine particulate material suspensions, emulsions and colloids in general. Usually optical arrangements are used that demand dilution of samples. 180° backscattering, however, allows for considerably higher concentrations and is the right choice for concentrated samples which incur in processes [1].

The 180° backscattering is especially suitable for direct in-line use in reactors, because the handling of the measurement probe head with a diameter of 8mm is just as easy as a pH head. A newly developed probe cap effectively shields the Brownian motion from the process fluidics (figure 1). At higher concentrations, where particle-particle interactions are present, on-line systems with automated dilution have been successfully implemented [2].

The external control of the DLS measurement software also allows for using robots in High-Throughput Screening (HTS) and fully automated formulation stations. Those work stations, equipped with liquid handling and parallel reactors, perform programmed formulation steps like mixing, stirring, heating and shaking. Apart from the aforementioned particle size distribution, rheological attributes and spectroscopic measurements are also included. Thus DLS has finally arrived as an automatized tool for process and HTS.

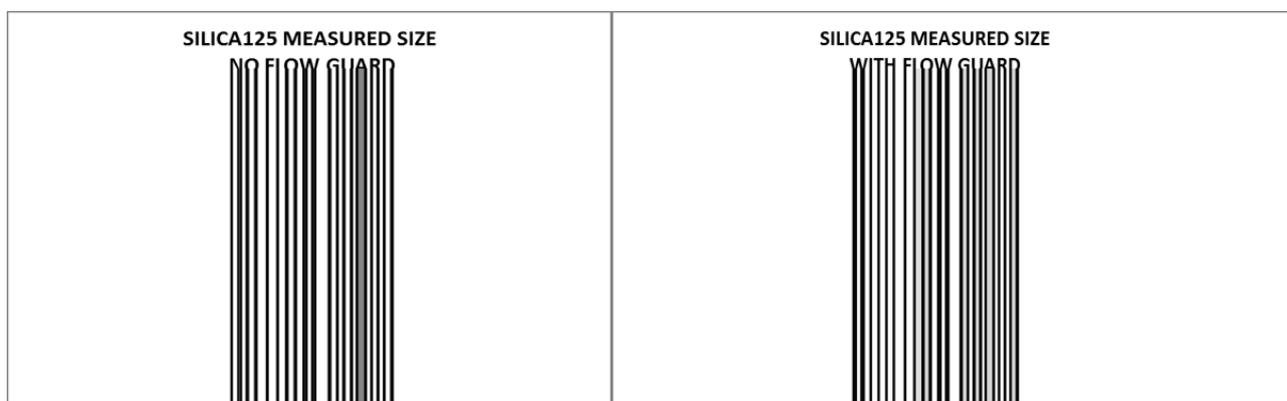


Figure 1. The Brownian motion, underlying principle of DLS measurements, is efficiently shielded from reactor stirring by a flow guard, making 180° backscatter measurements possible in-situ.

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Bruno Alonso<sup>1\*</sup>, Laura Cardoso<sup>1</sup>, Alexander Sachse<sup>1</sup>, Krassimir L. Kostov<sup>2</sup>, E

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We have developed a versatile colloid-based approach allowing for the synthesis of hybrid organic-inorganic nano-composites with a high level of control of the texture. This approach combines the self-assembly properties of polysaccharide  $\alpha$ -chitin nanorods (~ 23 nm) of monocry-

inorganic precursors like siloxane nanorods and siloxane oligomers, in concentrations beyond ca. 2%. The ordered phase fields (shearing, electric, magnetic fields, solvent evaporation across the solvent) in hybrid colloids are being assessed (SAXS, DLS) and mechanical properties are being studied.

Besides, microparticles are also being synthesized, more recently fibers by electrospinning. We are studying composites (morphology, texture, properties) in the 5-20 nm range) [1,4] with applications, titanium alkoxides have been used for the dispersion of Ti sites by playing with porous alumina microparticles with  $Al_3O_3$ ) as colloidal precursors simply as compared to the chitin nanorods by cellulose nanofibrils chemistry and the interactions between the components in a colloidal approach to form hybrid nano-

A simple colloidal assembly approach allows the formation of polysaccharide-oxide nanocomposites.

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# Patchy nanoparticle preparation and self-assembly

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Our recent results on the preparation of anisotropic colloidal particles with chemical patches and their self-assembly properties with spherical particles are presented.

Patchy gold nanorods are obtained by site selective replacement of the original CTAB ligands by cysteamine at the rod tips, rendering this region of the particle positively charged. Neutral PEG molecules are attached in a consecutive step to the side of the nanorods. The assembly of these patchy rods with spherical particles is investigated in-situ at the single-particle level. A flow cell combined with an optical microscope is employed where the localised plasmon mode associated optical scattering spectrum of well-separated, individual objects can be reliably investigated. The gold nanorods are first immobilized on a substrate and the assembly itself is carried out by filling the cell with a solution containing the spherical particles. Correlated scanning electron microscopy measurements performed after the assembly process provide direct ex-situ structural information.

It has been shown earlier that depending on the rod-to-sphere size ratio, different structures can be observed after the assembly: for small spherical particles, tip-selective assembly is the dominant structure, while for particles exceeding the rod diameter side-selective attachment of single nanosphere is obtained. [1] In the present study, it is demonstrated at the individual particle level, that the formation of the sphere-rod heterodimer can be readily detected in-situ in the aqueous phase and that the heterodimer scattering spectrum can be used to conclude on the structure of the assembly. By performing finite element calculations, it is shown, that the interplay between patchy surface charge-distribution associated electric double layer interaction and the PEG related steric repulsion determines the arrangement of the particles in the heterodimer. The approach can be also utilized to assess the influence of the drying associated immersion type capillary forces on the final structure.



**Figure 1** Schematic representation of the particles used for the assembly (a) and of the experimental setup (b). During the in-situ measurements characteristic changes in the scattering spectrum of individual objects are detected (c).

**Acknowledgements** This work received funding from the Hungarian Scientific Research Fund NKFIH-K-112114 and K-119532 and the Hungarian Academy of Sciences (INFRA 2016).

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# The role of conformational entropy in Conjugated Polymers dispersions of Carbon Nanotubes

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Macromolecular hybrids that combine conjugated polymers and carbon nanotubes (CNT) are expected to offer improved functionality for a variety of photovoltaic applications. It is well known that the electronic, optical and thermodynamic properties of conjugated polymers are dominated by the delocalization length  $\dots\dots\dots$ -electrons along the chain backbone, known as the *conjugation length*. In derivatives of polythiophenes, poly(3-alkyl) thiophene, (P3ATs) the conjugation length is determined by the interplay between steric interactions among the side chains that interrupt the co-planarity, the structure of the backbone, and the solvent. In my talk I will present our experimental investigation of systems that combine CNT and P3AT and describe the role of chain-flexibility in P3AT- CNT interactions, the effect of dispersed CNT on self-assembly of the host polymer matrix, the mechanism leading to CNT-induced chain stacking and enhanced crystallization of the P3AT chains. Finally, I will describe a surprising observation indicating that small concentrations of inorganic salts in a concentration range of 0.08 to 10mM enable the dispersion of CNT in THF solutions of P3HT. More specifically addition of salt to a polymer solution that contains a non-dispersed powder of CNT results in the formation of a stable dispersion. The "salting effect" is generic; induced by different salts and is affective with different derivatives of polythiophenes. I will discuss the dispersion mechanism and the relation to conformational entropy of the polymers.

# Plasmon-Enhanced Light Trapping in Ultrathin Films of Organic Chromophores

Alexandra I. Zvyagina,<sup>1</sup> Alexander A. Ezhov,<sup>3</sup> Ivan N. Meshkov,<sup>1</sup> Vladimir K. Ivanov,<sup>2</sup> Kirill P. Birin,<sup>1</sup> Burhard König,<sup>4</sup> Yulia G. Gorbunova,<sup>1</sup> Aslan Yu. Tsivadze,<sup>1</sup> Vladimir V. Arslanov,<sup>1</sup> Maria A. Kalinina<sup>1</sup>

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Plasmon resonance enhancement of absorption in thin organic nanostructures increases the efficiency of conversion of visible light for numerous applications such as solar cells, photocatalysis, and organic electronics. Because the extinctions of metal nanoparticles and organic molecules are different, it is extremely difficult to tune the optical properties of hybrid materials though direct observations of the enhancement effect. We suggest a new method that makes this direct tuning possible by using flexible gold plasmonic antennas with tunable plasmon coupling. When deposited onto the monolayers of various dyes (mono- and double-decker tetra-15-crown-5-phthalocyanines and 5-carboxytetramethylrhodamine), these plasmonic sensitizers boosts the absorption by more than 500 %. This plasmonic effect strongly depends on the aggregation state of the dye in the interfacial film. We did not observe any enhancement of light absorption at interfaces presenting thin layers of J-aggregates of perylene or tetrapyrrolyl porphyrin. The results suggest that non-additive absorption because of plasmon resonance effect can occur only in condensed organic thin films, which do not exhibit optically collective behavior. Our findings provide a significantly new insight into the interactions between light and complex interfaces that might be useful for rational design of nanostructured optical materials.

**Acknowledgements** The work is supported by Russian Foundation for .  $\text{A}\text{a}\text{E}\text{w}\text{g}\text{g}\text{A}\text{E}\text{U}\text{S}\text{T}\text{A}\text{E}\text{w}\text{O}\text{p}$ -29-05284) and Russian Science Foundation (grant  $\text{O}\text{p}$ -13-10512).

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# Colloidal stability of hydrophobic nanoparticles in presence of starch

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Starch is a natural polymer consisting of two components: the low molecular weight, linear amylose polymer and the high molecular weight, highly branched amylopectin polymer. Starch is used in many applications in its oxidized form in combination with hydrophobic nanoparticles.

In the present study we have investigated the mechanism of formation of oxidized starch/cationic particles complexes. Whereas the colloidal stability of the nanoparticles was highly affected by the anionic starch the particle/starch aggregates formed upon mixing exhibited a maximum in turbidity and size around charge neutralization, as monitored by Zeta potential (Figure 1a). Aggregation was partly reversible as an excess of starch restabilized the system due to the selective adsorption of the amylopectin fraction of the starch that gave rise to a steric contribution. Furthermore we demonstrated that the relaxation kinetics of the formed aggregates was molecular weight dependent. However, the size of the equilibrated aggregates was similar irrespective the molecular weight of the starch, confirming the conclusion of a patchwise flocculation mechanism.

As expected, the cationic nanoparticles alone formed larger flocs when the ionic strength was increased and the effect was more pronounced with Na<sub>2</sub>SO<sub>4</sub> than with NaCl, demonstrating a strong anion effect. When the ionic strength was raised for the formed particle/starch aggregates we observed an interesting phenomenon (Figure 1b); with time, an initial drop in turbidity was followed by an increase. This was explained by the combination of two phenomena related to the starch adsorption that are screening reduced adsorption and screening enhanced adsorption. However, this was only seen at intermediate ionic strengths. At higher ionic strengths the system collapsed and particle aggregates were formed. The salt effect was also found to be depending on the amount starch adsorbed on the particle surface.

The results from this study clearly show the importance of controlling the colloidal behaviour in order to achieve efficient processes, as for instance in paper surface hydrophobization where these starch/hydrophobic nanoparticles systems are more and more commonly used.

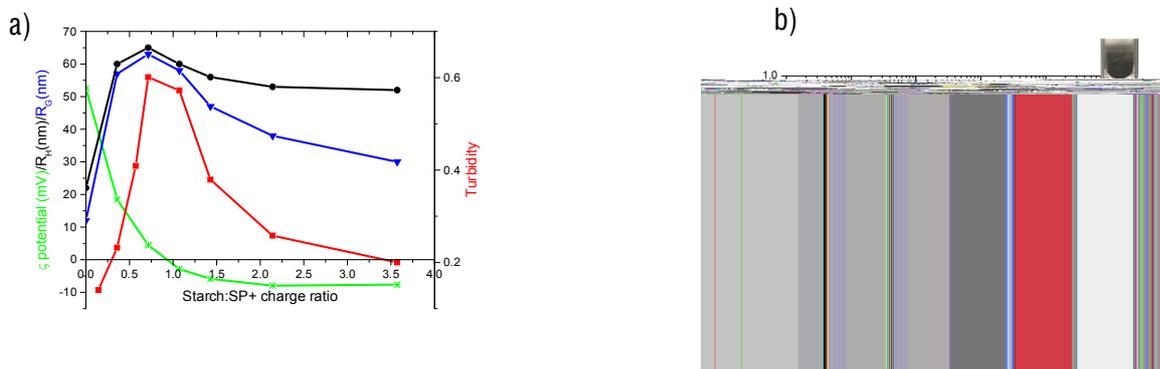


Figure 1a) Plot of hydrodynamic radius (circles) and zeta potential (stars) (left y-axis) and turbidity (squares) (right y-axis) vs. starch to particle charge ratio. b) Evolution of turbidity as a function of time when 26 mM NaCl was added to the particle/starch complexes.

# Acrylamide based core-shell microgels with linear thermo-response

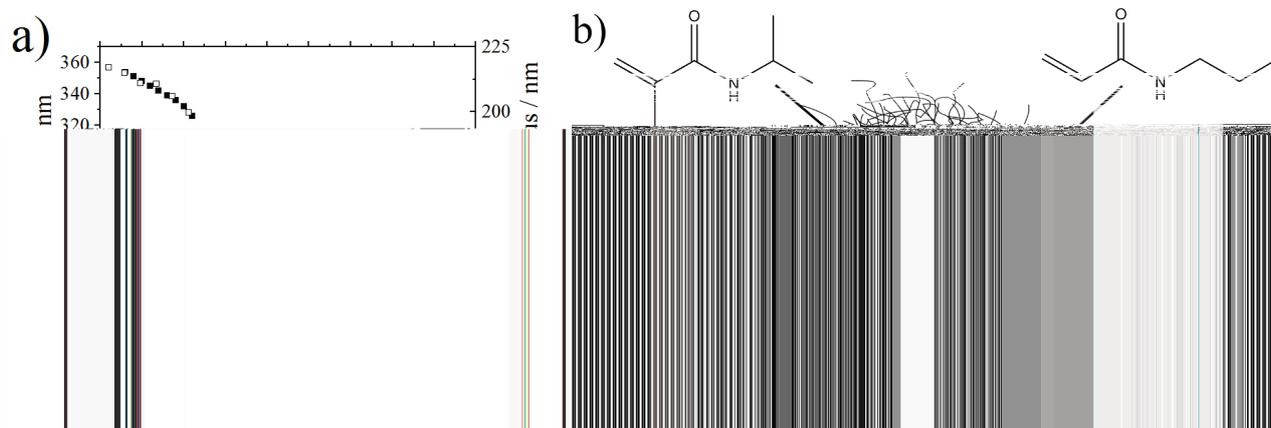


Figure 1:

## Acknowledgements

# Nanostructure of foamable polyol-rich CO<sub>2</sub>-microemulsions

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In recent years the properties of microemulsions of the type water-scCO<sub>2</sub>-nonionic surfactants, i.e. their phase behavior and nanostructure were systematically studied [1-2]. Besides fundamental questions, the *Principle Of Supercritical Microemulsion Expansion* (POSME) [3] which is a promising approach to produce low-cost, nanostructured polymer foams was the main driving force to study these new-type of microemulsions. State of the art polyurethane-foams exhibit a pore size of around 100 μm and a thermal conductivity of 0.030 W/mK. The envisaged nano-foams are expected to have a thermal conductivity of only 0.015 W/mK, which makes them exceedingly attractive for thermal insulation applications. Within this work foamable microemulsions of the type polyol-scCO<sub>2</sub>-surfactant are planned to be used as starting material for the POSME approach. By the addition of isocyanates, the mixture polymerizes followed by the expansion of the mixture, whereby the nanostructure of the microemulsion is expected to be preserved. In this work, we first formulated and studied the phase behavior of foamable polyol-microemulsions as a function of temperature and pressure. In order to prove the existence of scCO<sub>2</sub> swollen micelles SANS experiments were performed. Enhancing the scattering contrast using a partially deuterated polyol we indeed found micelles in the binary polyol-surfactant system. As can be seen, in Figure 1 the addition of CO<sub>2</sub> leads to the formation of weakly structured microemulsions. Due to the presence of nanoscaled CO<sub>2</sub>-domains these systems are very promising starting systems for the synthesis of first PU-nanofoams.

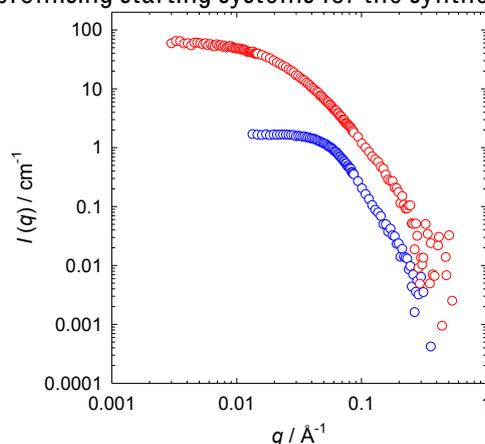


Figure 1 SANS curves obtained from the microemulsion polyol-CO<sub>2</sub>-surfactant and the corresponding binary system polyol-surfactant. The data were fitted using Teubner-Strey [4] and the form factor for polydisperse spheres [5].

**Acknowledgements** The studies were funded by the federal ministry for economic affairs and energy (03ET1409C). Furthermore we thank K. Schneider and D. Zauser for their help during the SANS measurements and the ILL for the opportunity to perform scattering experiments as well as for financial support.

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# Polymer micelles as fluorimetric nanosensors

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Micro- and especially nanostructures are reaching considerable attention in context of optical sensing applications. Particularly attractive are these nanostructures that can be obtained in simple procedures, for example taking advantage of spontaneous formation of micelles, especially formed from polymeric materials, bearing lipophilic hydrophobic chains. An example of such materials are alternating polymers bearing maleic anhydride groups.

Polymers as poly(maleic anhydride-alt-1-octadecene) spontaneously form micelles, that can be crosslinked (also in spontaneous reaction) to form nanoparticles, with size close to 250 nm. Upon hydrolysis of remaining anhydride groups, carboxyl groups are formed on the surface of crosslinked micelles, to result in stable nanostructures [2,3]. The lipophilic core is surrounded by charged surface groups, due to crosslinking the structure is stable in solution and does not undergo spontaneous reorganization. The lipophilic core of the formed nanostructures can be used to accommodate lipophilic probes both optically active and optically silent ones used in combination with fluorimetric transducers; as shown on example of hydrogen ions, zinc, nickel or potassium ions sensors. The presence of charged groups on the surface can be used to tailor dependences of optical signal (either emission or absorbance change) on analyte concentration to expose either high sensitivity over limited concentration range or wide linear dependence of signal on logarithm of analyte concentration [2,3,4]. Presence of surface carboxyl groups can also be explored to covalently attach reference dyes, yielding ultimately a ratiometric sensor [2].

**Acknowledgements** The financial support from National Science Centre (NCN, Poland), project 2014/15/B/ST4/04919, in the years 2015-2018, is gratefully acknowledged.

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# Conductive macroporous materials prepared by controlled assembly of polystyrene/polymer acid-doped polyaniline core/shell type nanoparticles

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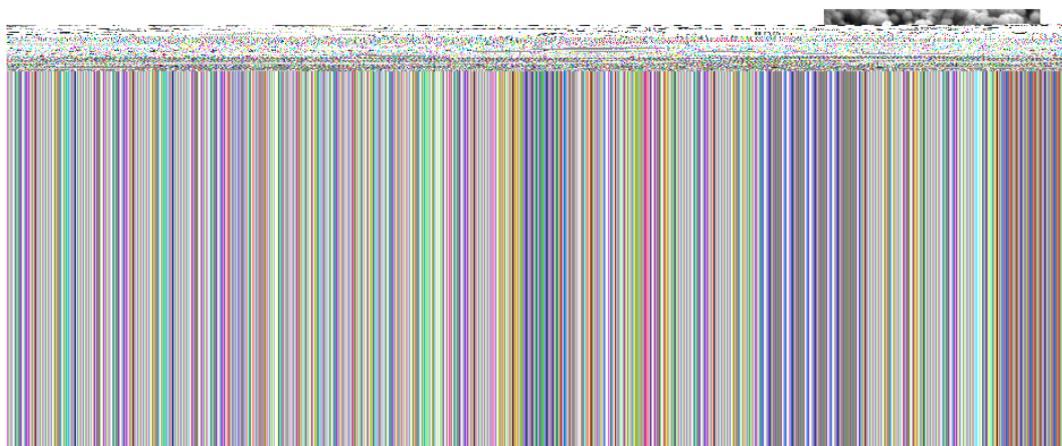


Figure 1: Schematic representation for the preparation of the conductive microclusters

**Acknowledgements** The financial support of Grant Agency of Czech Republic (Grant No. 16-22997S) is greatly acknowledged.

# Molecularly engineered polymer particles for stone protection

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## Acknowledgements.

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# Polyelectrolytes and iron oxide nanoparticles: from colloidal stability to aggregation and its role on hyperthermia

Jérôme Fresnais<sup>1\*</sup>, Clement Guibert<sup>1</sup>, Veronique Peyre<sup>1</sup>, Vincent Dupuis<sup>1</sup>

Polyelectrolytes (PE) are useful to stabilize colloidal dispersions. The interactions between charges on the PE insure multiple attachment toward the nanoparticle's surfaces. We successfully used poly(acrylic acid) (PAA) to cover iron oxide nanoparticles (IONPs) in a quantitative manner [1], so that PAA-coated nanoparticles are stable in complex medium such as brine or ionic liquid [2].

IONPs are recognized for their ability to heat up medium using alternating magnetic field (usually called magnetic hyperthermia). The role of their coating, as well as their magnetic interactions are of prime importance for their potential health applications. Indeed, aggregation of IONPs often happens in cells environments and always has a negative impact on their hyperthermia efficiency [3].

Here we want to show experimentally that aggregation effectively induces a decrease in hyperthermia efficiency. As an example, we used positively-charged polyelectrolytes to induce aggregation of negatively-charged nanoparticles. However, when IONPs are aggregated with non magnetic nanoparticles, we demonstrated that the hyperthermia efficiency could be recovered to its optimal value obtained on well dispersed IONPs (Fig. 1). Those results give hope to design nanostructured architectures composed with IONPs with optimal repartition in active matrices to be used as delivering systems for biotechnologies.

**Figure 1** SLP of aggregated Iron oxide and Cerium oxide nanoparticles versus  $\text{Fe}_2\text{O}_3/\text{CeO}_2$  ratio.

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# Probing the density variation of confined polymer thin films via simple model-independent nanoparticle adsorption.

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Despite an abundant literature, density variations in confined polymer thin films geometry still remain highly debated and controversial as the density is obtained through model-dependent methods (ellipsometry, reflectivity...). No definite conclusion on how density varies with the film thickness has thus been reached so far. The presence of interfaces and confinements known to deeply modify the conformation polymer chains may significantly affect the film density and thus the chains dynamics making this issue central in nanoscience. Indeed, it has been shown that the glass transition temperature [1], the mobility [2], the coefficient of thermal expansion, the physical ageing and dewetting... are directly related to the confinement of the polymer chains and thus to the film density. It is then of paramount importance to measure/assess in a very consistent and reliability manner the film density as a function of its thickness.

As subtle changes in the density are extremely difficult to evidence directly, we put forward in this paper a novel and model-independent method to detect density variations in polymer thin films via the simple adsorption of (ceria) nanoparticles onto their surface. In a first stage we show clearly that the NP adsorbed amount scales linearly with the refractive index  $n_p$  of different *bulk* polymers. In a second stage, we analyze the density variations in a confined geometry of two well-known and documented polymers, namely polystyrene (PS) and poly methyl methacrylate (PMMA), as a function of their thicknesses throughout our model-independent approach. We show here that the adsorption of ceria NPs does strongly vary with the thickness and the nature of the polymer films in full agreement with ellipsometric measurements [3-4]. Hence any increase/decrease in the NP surface coverage directly points out an increase/decrease in the film refractive index and thereby of its density. Although counterintuitive, our study clearly highlights that the mass density of PMMA thin films decreases with their thickness while it increases for PS.

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# PCL-based nanoparticles as potential candidate for drug delivery to the central nervous system

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Every day brings a progress in development of new drugs. Recently British scientists have published the results of a breakthrough research that showed two potential drugs to stop neurodegenerative brain diseases [1]. However, the efficient drug delivery to the central nervous system (CNS) is still the most problematic issue of temporary medicine. One of the major limitation is an inefficient delivery of neuroprotective substances through the blood-brain barrier (BBB). Therefore in this research, we were focused on the attempt of developing a new strategy of delivery of neuroprotective drugs by the nanocarriers that are able to overcome the BBB without imposing a side effect on its normal function.

We synthesized neuroprotectants-loaded nanocarriers/nanoparticles (NPs) using nanoemulsion prepared by the Phase Inversion Composition (PIC) technique. The NPs were composed of the biocompatible and biodegradable polymer, polycaprolactone (PCL), with encapsulated active agents, undecylenic acid (UDA) and/or fluorescent dye (Cumarin-6). Additionally, nanoparticles surface was functionalized using PCL co-polymer with poly(ethylene glycol) (PEG) to increase its bioavailability. The NPs were characterized by size, size distribution, zeta potential and imaged by Cryo-SEM. Biocompatibility and neuroprotective action of the synthesized NPs were evaluated in the SH-SY5Y human neuroblastoma cell line using biochemical tests (MTT, LDH assays). Cytotoxicity, cellular uptake, and transport through the in-vitro model of BBB were also studied.

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# Nanostructuring of alkynyl modified Si surfaces with tripodal oligo(*p*-phenylene)s

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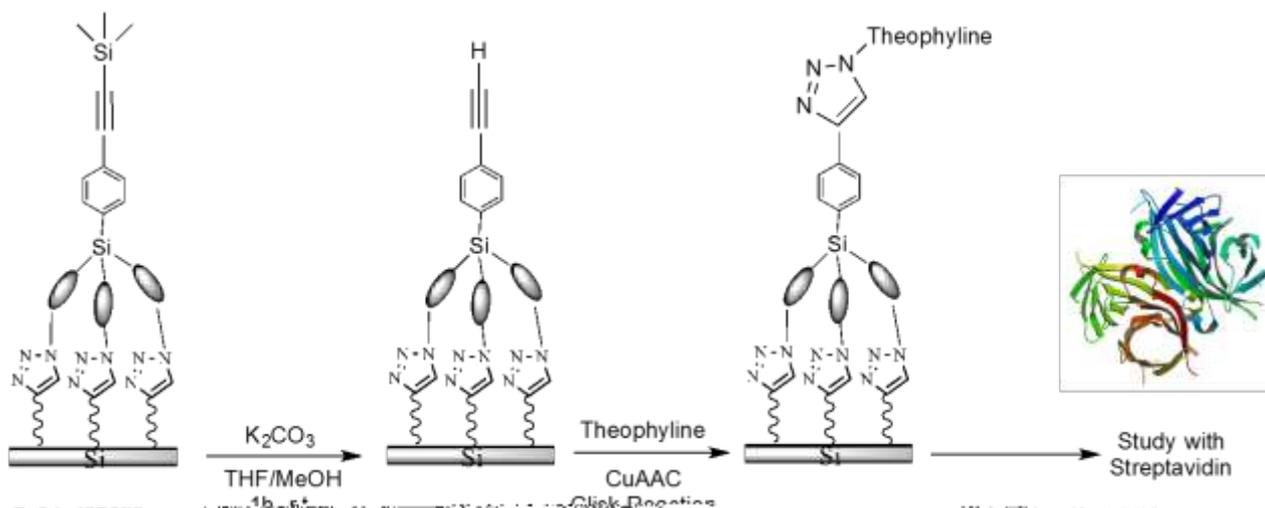
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Controlling the orientation and spacing of functional moieties in organic thin films is of great importance for both the study of fundamental biomolecular interactions at interfaces and for biosensor applications. Giant molecules as phenylacetylene[1], conically shaped dendron[2] and tripod shaped oligo(*p*-phenylene)[3] have been proposed for the functionalization of different surfaces.

We report here our results on the covalent grafting of tripod-shaped oligo(*p*-phenylene)s on alkynyl modified Si substrates. These tripod-shaped structures possess an azide terminal group in each leg, which can be covalently incorporated on alkyne-terminated Si wafers by copper catalyzed alkyne-azide cycloaddition (CuAAC/Click reaction). The tripod density on the Si surface was tuned by performing the click reaction at different concentrations of tripod molecule under different conditions.

The presence and distribution of the oligo (*p*-phenylene) on the surface can be demonstrated by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and high-resolution scanning electron microscopy (HRSEM). 3D relative position of the tripodal molecules and surface was confirmed by density functional theory (DFT): it depends on whether the tripod is grafted by one, two or three legs.

Nanostructured surfaces can be used as molecular templates for the incorporation of active molecules. A theophylline derivative with activity as adenosine receptor was selectively attached to the structured surface and his interaction with streptavidin studied.



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## **Kinetics study of the synthesis of gold nanoparticles in the presence of chitosan and citric acid**

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In this work, colloidal gold nanoparticles (GNPs) stabilized with a chitosan matrix were prepared using a green route. The synthesis was carried out by reducing Au (III) to Au (0) in an aqueous solution of chitosan and citric acid. We have demonstrated that by varying the temperature it is possible to tune the reaction rate of the gold reagent  $\text{HAuCl}_4$  and to modify the morphology of the resulting metal nanoparticles. The use of chitosan, a biocompatible and biodegradable polymer with a large number of amino and hydroxyl functional groups, enables the simultaneous synthesis and surface modification of GNPs in one pot. Because of the excellent film-forming capability of this polymer, GNPs–chitosan solutions were used to obtain hybrid nanocomposite films that combine highly conductive GNPs with a large number of organic functional groups.

The chitosan stabilized GNPs were characterized by UV-Vis spectroscopy, AFM and TEM microscopy. The particle size distribution of GNPs ranges from 5 to 15 nm with high particle stability after 120 days.

**Keywords:** Gold Nanoparticles, Green synthesis, Chitosan, Atomic Force Microscopy, Transmission electron microscopy, Fluorescence correlation spectroscopy.

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# Role of catalyst precursors and the effect of asphaltene concentration during slurry phase hydrocracking of vacuum residue

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Hydrocracking reaction of vacuum residue in the presence of various kinds of transition metal octoate precursors, such as Mo-octoate, Fe-octoate and Cu-octoate, was performed and compared in a high-pressure batch-type reactor [1]. Fe-octoate gave the highest coke formation (16.8 wt%), which was even higher than that obtained by thermal hydrocracking (15.8 wt%). Hydrocracking with Cu-octoate showed the highest gas formation (9 wt%), which was higher than that obtained by thermal hydrocracking (8.8 wt%). Mo-octoate showed the best catalytic activity in reducing coke and gas formation (2.1 and 5.4 wt%, respectively) [2]. The MoS<sub>2</sub> in the coke (toluene insoluble) formed during hydrocracking was monitored by XPS and TEM. The effect of reaction severity controlled by variation of the temperature (400-440 °C) and reaction time (0.5-5 h) in the presence and absence of Mo-octoate catalyst on vacuum residue hydrocracking was studied. Thermal hydrocracking results in high conversion, but a limitation of thermal hydrocracking is that coke and gas formation is high. The SIMDIS data of liquid products show the role of catalysts under similar reaction conditions in comparison to thermal hydrocracking. The presence of 250 ppm Mo from Mo-octoate catalyst precursor provides improved activity and selectivity (naphtha and middle distillate fractions). Under the reaction conditions of 440 °C, 1 h, 80 bar H<sub>2</sub> at 80 °C, catalytic hydrocracking produces a higher amount of naphtha and middle distillate (45.1 wt%) with much less coke and gas formation than thermal hydrocracking (3.78 and 6.83 wt% coke and gas formation with catalytic hydrocracking in comparison to 21.9 and 12.34 wt% with thermal hydrocracking). Regarding the effect of reaction time on catalytic selectivity, reaction time promoted naphtha yield 29.1 wt% after reaction for 5 h, while in the first 3 h of reaction, the middle distillate max yield was about 26 wt%, and then it decreased. The SARA and hydrogen consumption results of thermal and catalytic hydrocracking (430 °C, 1 h, 80 bar H<sub>2</sub> at 80 °C, 250 ppm of Mo in catalytic hydrocracking) show that the catalyst promoted a hydrogenation reaction when the saturate phase of the liquid product and the H<sub>2</sub> consumption per 1 g VR were increased from 10.3 to 16.6 wt% and from 0.18 to 0.67 wt%, respectively [3]. Regarding the effect of asphaltene concentration in the feed on coke formation, asphaltene seemed to be the main fraction converted to coke during hydrocracking reaction [4]. Coke formation increased from 0 to 20.2 wt% when the asphaltene concentration in the feedstocks was increased from 0 to 79 wt%.

**Acknowledgements** This work was supported by the National Research Council of Science and Technology (NST) grant by the Korea government (MSIP) (No. CRC-14-1-KRICT).

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# Molecular motion and structure of novel organometallic polymers

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In this work, we show the polymer dynamics and the internal structure of novel organometallic polymers (Fig 1) based on two metal-containing moieties  $\{\text{CpRuCNRuCp}\}^+$  and  $\{\text{Au}(\text{CN})_4\}$  bridged through a tridentate phosphine (PTA) [1]. X-ray and light scattering experiments reveal polymer self-association in aqueous solution to reach stable microparticles. They behave as polymer microgels, including properties as reversible thermally size transitions [2].

Neutron scattering experiments on dried polymer are performed to get the elastic intensity against temperature within the range  $[-243, 185 \text{ }^\circ\text{C}]$ . Decreasing intensity with temperature indicates increasing vibrational and rotational polymer dynamics. This observation is consistent with the dynamic structure factor broadening with temperature. In addition, it is observed hysteresis during the heating-cooling cycle, as well as elastic energy jumping, which suggests loss of structural water.

Small angle neutron scattering (SANS) profiles are markedly influenced by the polymer swelling state; Porod regime for swollen state and peaks for collapsed state indicates internal structural changes at two length scales.

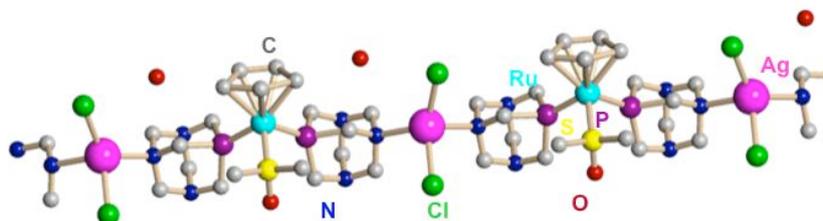


Figure 1 Chemical structure of the organometallic polymer.

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# Influence of amino acids on the crystallization of calcium silicates hydrates

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The hydration of Portland cement lead to Calcium silicate hydrates which are prominent for their high mechanical strength. Cement clinker production causes up to 7 % to the global CO<sub>2</sub> emissions. One promising strategy is the use of supplementary cementing material (SCMs) [1]. The application of SCM's possess several disadvantages when it comes to practical application. The, decreased in the evolvement of strength is an unfavourable disadvantage. A encouraging starting point for an extensive use of SCM's is the use of approaches of biomineralisation to effect crystal shape and size. Nature provides many examples for materials of high mechanical strength and chemical resistance like shells (Calcium carbonate) diatoms (SiO<sub>2</sub>) or bones (Calcium phosphates). Calcium silicate hydrates are not known in biomineralization processes. Focusing on the functional groups involved in biomineralisation processes, it can be stated that functionalities like -COOH-, -OH, as well as imidazolium-containing structures and amino acids are involved very often [2]. A model system starting from CaO with fumed silica in aqueous media was used to synthesize the Calcium silicate hydrate phase Tobermorite. L-Glutamine, L-Alanine, L-Serine, L-Histidine, 6-Aminohexanoic acid, Imidazole and Chitosan and Carboxy methyl chitosan were used to study their influence on the crystallization. X-ray powder diffraction measurements were performed. Tobermorite was used as structural model for all refinements, lattice parameters hereof were used as staring parameters for each refinement cycle [3]. Since detailed information about atomic positions is still lacking, a LeBail fit was performed. The presence of the amino acids lead in most cases to the enlargement of the unit cell. The a-axes of the unit cell is effected only in presence of Imidazole and 6-aminohexane acid. The b-axes is effected by the addition of Chitosan and Carboxy methyl-chitosan. The c-axes increases with  $\text{ACGFC}$ ,  $\text{G}$ ,  $\text{E}$ ,  $\text{U}$ ,  $\text{O}$  Amino acids Glutamine, Alanine and Histidin.

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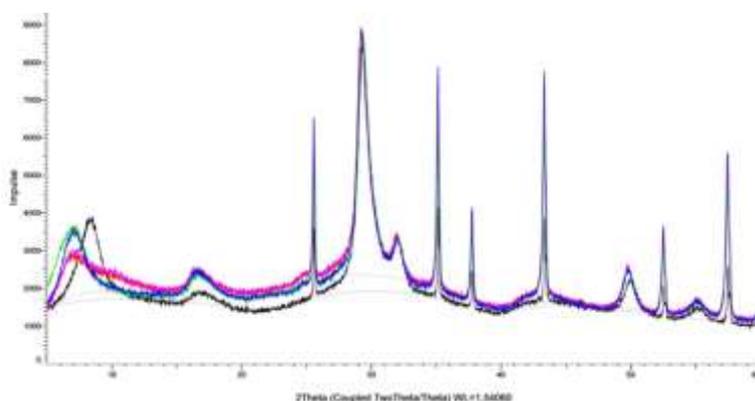


Figure 1 LeBail Fit of Tobermorite (without additive-black, L-Glutamine-green, L-Alanin-pink, Imidazol-blue)

# **Tight cohesion between glycolipid membranes results from balanced water–headgroup interactions**

Matej Kanduc<sup>1</sup>, Alexander Schlaich<sup>2</sup>, Alex de Vries<sup>3</sup>, Juliette Jouhet<sup>4</sup>, Eric Maréchal<sup>4</sup>, Bruno Demé<sup>5</sup>, Roland R. Netz<sup>2</sup>, Emanuel Schneck<sup>6\*</sup>

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Membrane systems that naturally occur as densely packed membrane stacks contain high amounts of glycolipids whose saccharide headgroups display multiple small electric dipoles in the form of hydroxyl groups. Experimentally the hydration repulsion between glycolipid membranes is of much shorter range than that between phospholipids whose headgroups carry single large electric dipole due to the zwitterionic charge distribution. Using solvent-explicit Molecular Dynamics simulations and accounting for the water chemical potential, we quantitatively reproduce the experimentally observed, different pressure versus-distance curves of membrane stacks composed of phospholipids and of the glycolipid digalactosyldiacylglycerol (DGDG). We show that the short-ranged water uptake into the glycolipid membranes is solely driven by the hydrogen-bond balance involved in non-ideal water/sugar mixing. Water structuring effects and lipid configurational perturbations, responsible for the more long-ranged repulsion between phospholipid membranes, are inoperative for the glycolipids [1].

Acknowledgements Financial support by Deutsche Forschungsgemeinschaft (DFG) via Emmy-Noether grant SCHN 1396/1 is gratefully acknowledged.

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# Effect of headgroup structure on counterion binding in surfactant adsorbed films studied through total reflection XAFS

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**【Introduction】** The counterion binding in the electrical double layer of surfactant adsorbed films is considered as a key for the understanding of specific ion effects that control micelle formation, surface adsorption and dispersion of colloidal particles etc. Our previous study showed that total reflection X-ray absorption fine structure (TR-XAFS) technique enabled us to evaluate counterion binding as the fraction of the Br<sup>-</sup> ions bound to the headgroups of surfactant ions with partial dehydration (bound-Br) and the fully hydrated Br<sup>-</sup> ions distributed in the diffuse double layer (free-Br) [1]. In this study, the strength of counterion binding on headgroups was deduced from competitive binding of Br<sup>-</sup> and other counterions coexisting in the adsorbed films by using TR-XAFS. With adopting trimethylammonium (TA) headgroups and 3-methylimidazolium (MIM) headgroups, the headgroup effect on counterion binding was discussed.

**【Experimental】** Competitive counterion binding was examined for the binary mixed adsorbed films on the aqueous solutions of (1) dodecyltrimethylammonium bromide (DTABr)-DTACl, (2) DTABr-DTABF<sub>4</sub>, (3) DTABr-DTA<sub>2</sub>SO<sub>4</sub> and (4) 1-hexyl-3-methylimidazolium bromide (HMIMBr)-HMIMBF<sub>4</sub> mixtures. Total reflection XAFS was performed at Beam Line 7C in KEK at 25°C and constant surface tension 45 mN m<sup>-1</sup> as a function of the counterion compositions in the adsorbed films obtained from our previous thermodynamic studies. X-ray absorption spectra of Br<sup>-</sup> counterions in the surface region were analyzed according to the procedure reported previously [1].

**【Results & Discussions】** 1. Counterion binding on trimethylammonium headgroups. In the mixed adsorbed films of DTABr-DTA<sub>2</sub>SO<sub>4</sub>, for example, the fraction of bound-Br was higher than that for pure DTABr. This means preferential binding of Br<sup>-</sup> to SO<sub>4</sub><sup>2-</sup> are realized in this mixed system. In a similar manner, the order of the counterion binding strength was deduced as shown in Figure 1(a). These results agree with the water affinity [2]. This indicates that for TA headgroups, the binding strength is primarily determined by the matching between the degrees of hydration of headgroups and counterions.

2. Counterion binding on 3-methylimidazolium headgroups. For HMIMBr-HMIMBF<sub>4</sub>, the ratio of bound-Br was almost zero, meaning the binding of BF<sub>4</sub><sup>-</sup> ions to MIM<sup>+</sup> headgroups is quite strong and almost all Br<sup>-</sup> ions are expelled from the vicinity of MIM<sup>+</sup> headgroups. The fraction of bound-Br in 1-decyl-3-methylimidazolium bromide (DeMIMBr) pure adsorbed film obtained in our previous study was lower than that for DTABr. Thus, the order of the counterion binding strength is deduced as shown in Figure 1(b). The MIM<sup>+</sup> headgroup form two-hydrogen-bonded ion pair with BF<sub>4</sub><sup>-</sup> ion and one-hydrogen-bonded ion pairs with Br<sup>-</sup> [3], whereas TA<sup>+</sup> headgroups form one-hydrogen-bonded ion pair with BF<sub>4</sub><sup>-</sup> ion and one-hydrogen-bonded ion pairs with Br<sup>-</sup>. Taking them into account, the significance of site specific effect due to H-bonding was suggested, that is the competition between H-bindings of MIM<sup>+</sup>-counterion pair and MIM<sup>+</sup>-water pair may control the counterion binding strength.

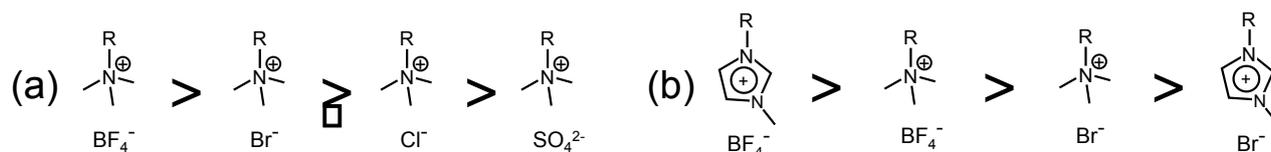


Figure 1 Proposed counterion binding strength from total reflection XAFS. (a) Series for trimethylammonium headgroup. (b) Series including imidazolium headgroup

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# Modification of Surface Interactions by Liposome-Bearing PEO layers

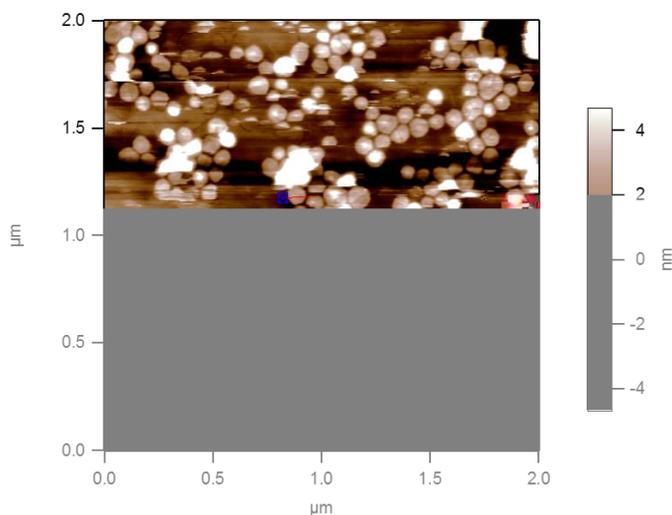
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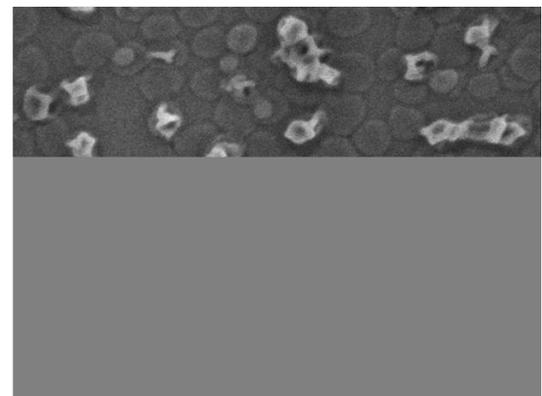
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The concept of friction, lubrication are crucial for maintaining physiological functions in living systems whenever surface in contact slid past each other [1]. Abnormal high friction in joints may be correlated to joint pathologies such as Osteoarthritis (OA). Highly efficient lubricating boundary layers at biological surfaces such as cartilage have been proposed to comprise phospholipids complexed with biomacromolecules exposed at the surfaces [2-4]. To examine such friction modification at a synthetic polymer surface which is widely-used in biomedical applications, we carried out a systematic study on the normal and frictional forces between surfaces coated with polyethylene oxide (PEO;  $M = 300$  kDa) layers that were complexed with phosphatidylcholine (PC) liposomes, using a surface force balance technique. Structures of the resulting soft surface were determined by atomic force microscopy (AFM) and cryo-scanning electron microscopy (cryo-SEM). The lipid-polymer complexes could maintain their integrity up to high pressures (at room temperature) in terms of both normal and shear interactions between the surfaces, which were repeatable, reproducible, and revealed very low friction (coefficient of friction down to  $10^{-3}$ - $10^{-4}$ ), up to pressures of 100 atm. We attribute this remarkable lubrication capability ultimately to hydration lubrication acting at the hydrated phosphocholine headgroups of the PC lipids, exposed at the liposome surfaces.

AFM scans of Mica/PEO/DSPC dispersion



Cryo SEM images of Mica/300k PEO/DSPC dispersion



Acknowledgements The financial support of the European Research Council (Advanced Grant HydrationLube), the Israel Science Foundation and the McCutchen Foundation.

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# High field NMR and relaxometry studies of salt-specific effects in bovine serum albumin and lysozyme solutions

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In protein formulations, ions from buffer species and from added low-molecular weight salts interact with the sites on the surface of the proteins. These ion-protein interactions often lead to protein aggregation. Aggregation and possible phase separation represent instabilities of protein formulations. Such instability can be both desired (e.g. protein isolation, crystallization for structure determination) (e.g. shelf-life of biological drugs etc.) [1]. Different salts exhibit different effects on the stability of protein solutions, and the ranking is known as Hofmeister series. For many aqueous-buffer protein solutions, the interaction of anions of salts with a common cation follows the inverse Hofmeister series:  $\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{SCN}^-$  [1].

Present study utilizes NMR relaxometry and high field NMR experiments to test the effects of added salts (e.g. NaCl, NaI, etc.) in bovine serum albumin (BSA) and lysozyme solutions. Different buffers (acetic, phosphate, and HEPES) were used to set the solution's pH values and accordingly the net charge of the protein. In case of lysozyme the net charge was +11 (acetic) or +8 (phosphate), while the net charge of BSA was +10 (acetic buffer) or +20 (in HEPES buffer). Using low field NMR measurements, the longitudinal relaxation time,  $T_1$ , the transverse relaxation time,  $T_2$ , and the diffusion coefficient,  $D$ , of water in buffer-salt-protein solutions were recorded [2,3]. On the other hand, high field NMR spectroscopy was used to determine the chemical shift of the characteristic protein peak during the addition of various salts.

The chemical nature of the added salt had no quantitative influence on the diffusion coefficient, while there were salt-specific trends in  $T_1$  and  $T_2$ . All three quantities decrease with an increasing protein concentration. The chemical shift of the protein decrease linearly with an increasing concentration of the salt. The slope was bigger in case of NaI solutions in comparison to those containing NaCl.

**Acknowledgements:** This study was supported by the Young Researchers program of the Slovenian Research Agency and Program P1-0201 and by PICS grant (LINKPE). The authors want to thank Dr. N. Malikova for financial support and fruitful discussion.

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9<sup>g</sup>EIBD. Tg gijigEII D' TUG ũ TgEÄEED' I e<sup>g</sup>T g<sup>g</sup> EEDGÄ IBÜgIgi e<sup>g</sup>ÄEÄ T  
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WUA' . gEg' UBT <sup>ÄÄÄ</sup>ADÄYHT W IID' ÄWÄ gTE ÜÄ ÄAwÄI χI! ÄöÄ gHIID' ÄÄÄ ÄT  
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ÄsgBAET g' TDI / Üg' dTE Ä' Ga DgEχAE. DDI. áÜ' ügHÄT D DDIÜg' eχEÄDKEeDEÄä(' gCg'  
Ä5 üdD D t Ü IEÄ / Üg' dTE ä / g' TgED / Üg' dTE Ä' G / Üg' EÄ 9' TüggEÄ Iä[χ' GÜ' ügHÄT ä[χ' GÄ  
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a Dg'ä' ÄEÄDE g I. IE° I D iχDEÄ ÄEgIBÜgIgi e<sup>g</sup>ÄEÄ T IχEÄEg TEÄT D D D. IgtÜ' g' g' T. EDE  
E 9DÄ ÜÄ g e<sup>g</sup>g' IYgGÄ AI IÄT TÖχTgEIBD. Tg d ÄGGÄQÜg D' I ÄEg TUDχTUTD e<sup>g</sup> GgBgTgG ũ Tg  
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EgIχ' T T ÄPEÄED' d IÜD' " D e<sup>g</sup> D Iχijidg' TITg' TIO ÄT ÜTÜ g<sup>g</sup>EIBD. Tg E D' E<sup>g</sup> TEÄED' I D EÄYIg  
ÄTIEÄED' GgIBEg Tg " gÄEÄEg' E<sup>g</sup> D Tg IχÄ, Ä' GgEi ÄÄI ÄPEÄED' e<sup>g</sup>T g<sup>g</sup> BAEÄgIÄL DIÜGE  
' DGGÄTÜg IYg Gg' D' IIEÄEgIχ' Ä e<sup>g</sup>χDχI. TÄTÜg BD. ° gEIEÄTBÄ I ÄjÄE Dg BD ũ g' TDEg TÄÄ  
sχITED' TEÄEÄ Tü BDEED' g' T Dg. BEIg ° Dg D Ä, Ä' GgEi ÄÄI ÄPEÄED' ÄL ÄGGED' äTÜg GgBg' Gg' E<sup>g</sup>  
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BDIEg DÄEÄEÄE I. IE° I TÄTÄEg ũ BgE dχI DÄGGgGg<sup>g</sup>EIBD. TgÄ



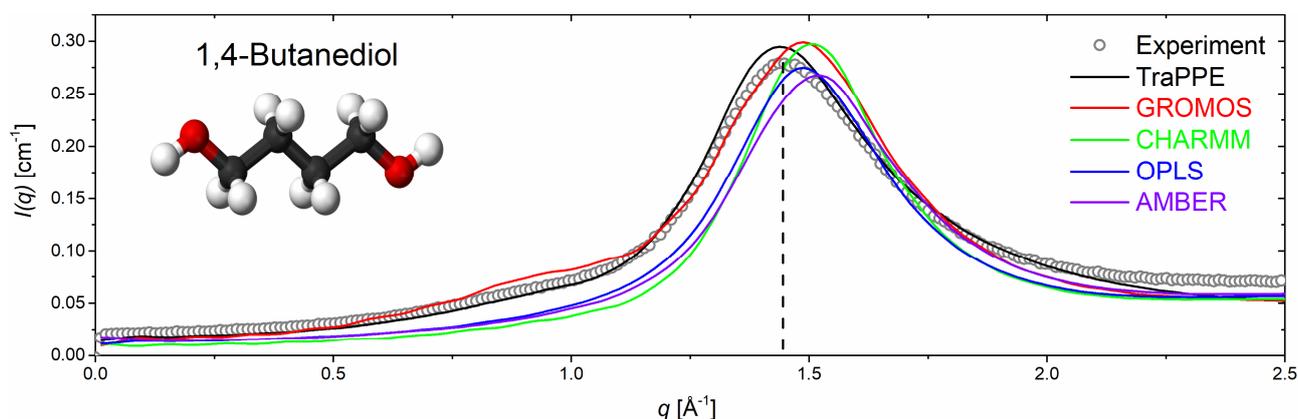
# Molecular Dynamics and Small- and Wide-Angle X-Ray Scattering Structural Study of Liquid 1,4-Butanediol

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Utilizing different force fields and the Gromacs 5.1 molecular dynamics software package [1] we have performed the molecular dynamics (MD) simulations of liquid 1,4-butanediol at 25 °C to study its structure on the nanoscale level. For this purpose, three all-atom (CHARMM27 [2], OPLS-AA [3], and AMBER03 [4]) and two united-atom force fields (GROMOS96-54a7 [5] and TraPPE-UA [6]) were used. Following the Complemented system approach method developed for the calculation of x-ray scattering from simulation data [7] small- and wide-angle x-ray scattering (SWAXS) intensities of model 1,4-butanediol were calculated from the MD results and were compared to the experimental SWAXS data. In this way, the quality of the structural performance of these models was tested. The simulation results showed that all the tested models reproduced the basic characteristics of the experimental SWAXS curves of 1,4-butanediol. However, the TraPPE-UA force field performed the best. This was somewhat surprising, as the same models showed more similar results in the case of modelling of n-butanol [8,9]. The simulation results were also analyzed for H-bonding characteristics and visualized via the radial and spatial distribution functions.



**Figure 1.** Calculated SWAXS scattering curves using various force field models compared to the experimental scattering for the 1,4-butanediol.

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# Finite Element Modelling of Thermal Transport in Colloidal Assemblies

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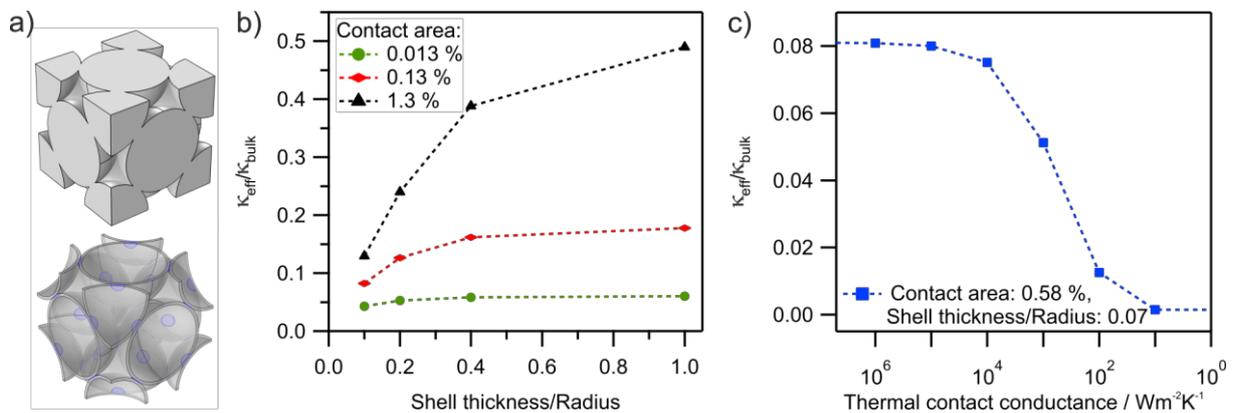
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The understanding of thermal transport properties of nanostructured materials is increasingly important. Colloidal assemblies consisting of solid spherical nanoparticles are an ideal model system to study thermal transport on these small length scales. They provide a simple and scalable access to materials, which can cover a wide variety of material compositions, interfaces, and length scales.

Finite element modeling represents a powerful tool to study the thermal transport in such colloidal superstructures. On the one hand, we can extract information on the heat flow itself, which cannot be measured experimentally. On the other hand, structure and composition can be varied in a much wider range and in an independent manner, which is experimentally not accessible. Both capabilities allow us to understand thermal transport in colloidal materials in a much more fundamental way.

Aspects to be focused on are the geometry of the particle (e.g. solid sphere vs. hollow sphere having different shell thicknesses), the size of contact area between adjacent particles, the thermal contact resistance between adjacent particles, and the symmetry of the assembly (crystalline vs. amorphous). Besides these fundamental studies, we use FEM as a complementary tool to further understand our experimental results. Here we show how gas in the closed pores of hollow silica colloidal crystals contributes to the thermal transport, and how the thermal conductivity of binary colloidal assemblies changes when two different materials are mixed.



**Figure 1** Thermal transport in colloidal crystals: a) Face-centered cubic unit cells consisting of solid spheres and hollow spheres. The contact area between the particles is marked blue. b) Influence of the shell thickness, the contact area, and c) of the thermal contact conductance between adjacent particles on the effective thermal conductivity.

# Computer simulation of double electric layer in AOT reverse micelles with and without salt

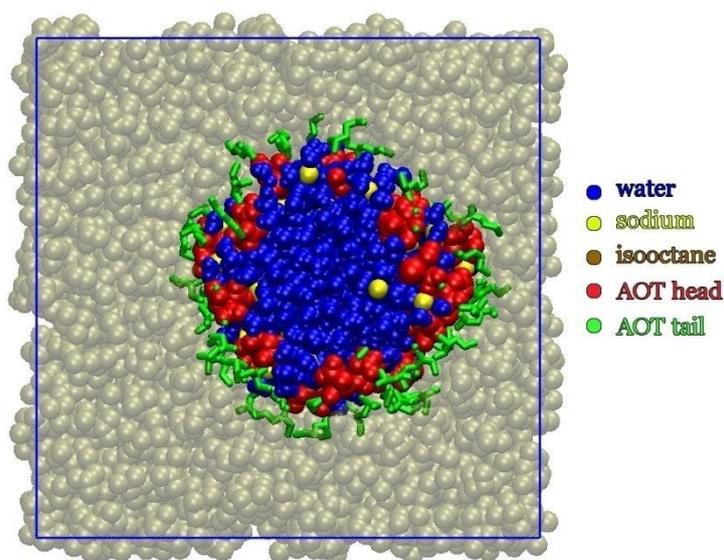
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Microemulsions are thermodynamically stable mixtures of oil and water stabilized by surfactants. When the amount of oil is significantly greater than water, hydrophilic head groups of a surfactant surround water droplets and hydrophobic carbon-based tails immerse in a non-polar solvent (oil), so the reverse micelles (RMs) form. RM can be used as a nanoreactor for the synthesis of nanoparticles and organic compounds, and as a shell for protein folding and thermal protection of enzymes. Since sodium Aerosol OT (AOTNa) is the ionic surfactant, a double electric layer is developed inside an aggregate. The local electric field in the RM is important due to its effect on the location and orientation of polar molecules inside the core.

Systems containing reverse micelles of sodium Aerosol OT (AOTNa) and water or aqueous NaCl solution in a liquid hydrocarbon medium (isooctane) are considered in this work. The molecular dynamics (MD) method is used to obtain data on the local structure of the reverse micelles of different sizes. The RMs were self-assembled spontaneously from an initially homogeneous mixture of the components during the MD simulation. The shape of the resulting aggregates is best approximated by an ellipsoid (the meridional eccentricity lays into the range 0.65-0.85). The structural data of the RMs makes it possible to calculate the profiles of the local electric potential  $\varphi$  (assuming the spherical symmetry of the aggregates). The plot of  $\varphi(r)$ , where  $r$  is the distance from the center of mass of a micelle, is a curve with a single maximum (peak). The position of this peak coincides with the region of localization of polar surfactant heads. Increasing the number of water molecules in the core leads to a shift in the peak position toward a greater distance from the center of the micelle. The half-width of the peak is increased. This also leads to weakening of the electric field ( $= -\text{grad } \varphi$ ). An increase in the charge density on the surface of the micelle (i.e. a decrease in the ratio of the amount of water to the surfactant,  $w_0$ ) leads to an increase in the peak in height (i.e., an increase of  $\varphi$  at the maximum).



**Figure 1.** AOTNa/water reverse micelle in isooctane.

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# 3D Monte Carlo simulations on a regime change in the internal structure of the aggregates of magnetic cubic particles

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A suspension composed of magnetic particles has a significant potential as an application in a variety of fields such as the fluid engineering, magnetic material engineering, colloid and interface science, and biomedical engineering. For instance, an application to the drug delivery system in the field of biomedical engineering is a challenging subject, and from a fluid engineering point of view, the behaviour of magnetic particles has to be controlled using a gradient magnetic field that is generated by arranging magnets in an effective manner. In the field of colloid and interface science, a magnetic particle suspension may be used for developing a technique for modifying the surface characteristics of a material. From this background, in the previous study [1], we considered a quasi-2D suspension in thermodynamic equilibrium in order to investigate the characteristics of magnetic cubic particles on a plane material surface. In the present study, we expand the previous study to a 3D system of magnetic cubic particles in order to discuss a regime change in the aggregate structure of these cubic particles, by means of Monte Carlo simulations for a thermodynamic equilibrium situation. From Monte Carlo results, we attempt to elucidate the dependence of a regime change in the aggregate structures on a variety of factors such as the magnetic field strength, the magnetic particle-particle interaction strength and the volumetric fraction. The main results obtained here are summarized as follows. If the magnetic interaction strength is sufficiently large for the cluster formation, closely-packed clusters are formed by repeat and expansion of a cluster unit composed of 8 particles, which may be the most preferred configuration and gives rise to a minimum energy. A regime change in the internal structure of aggregates appears in a narrow range with increasing magnetic interaction strength, which is clearly exhibited by the order parameter employed here. A closely-packed configuration can be clearly characterized by the orientational distribution function; 8 high peaks come to appear in the orientational space in the case of the closely-packed structure. As the magnetic field is increased, the closely-packed clusters are collapsed and transformed into wall-like clusters along the magnetic field direction. This is because the magnetic moment of each particle has a strong tendency to incline in the magnetic field direction in a strong field situation. The closely-packed structure is significantly stable and therefore exhibits a large resistance to the alignment of the magnetic moments with the field direction, which shows a more gentle increase with field strength than singly-moving particles. An increase in the volumetric fraction of particles induces a regime change from thick chain-like into wall-like clusters.

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# Phase Behavior of Mixtures of Colloids and Supramolecular Polymers

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Here we report a theory that enables to predict the phase stability of mixtures of colloids and supramolecular polymers. These polymers are considered as chains formed by reversible bonds between the monomers where the bond strength can be altered by external stimuli as light [1]. At thermodynamic equilibrium their size depends on the strength of the bond, the temperature and concentration, and is inherently polydisperse [2]. The polymer to colloid size ratio strongly affects the phase behavior for colloid-polymer mixtures as predicted by Free Volume Theory (FVT) [3, 4] and therefore the use of supramolecular polymers is worth examining for stimuli-responsive materials.

We have incorporated the polymer size distribution in FVT to calculate the phase behavior of mixtures of hard spheres and supramolecular polymers. We show that a change in temperature or bond strength can induce phase separation into a colloidal gas and liquid or solid phase. The phase diagrams are also quite similar to monodisperse polymers with the same average size, showing that polymer polydispersity has a minor effect. Further experimental studies could lead to sensors with stimuli-induced phase separation.

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# Weak Intramolecular Complexation within Star-like Copolymers: A Generic Model

Pascal Hebbeker<sup>\*,1</sup>, Alexander A. Steinschulte<sup>1</sup>, Felix A. Plamper<sup>1</sup>, Stefanie Schneider<sup>1</sup>

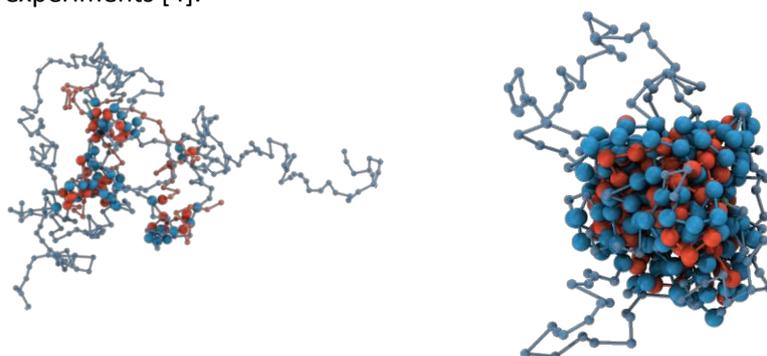
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Weak attractive interactions can lead to intramolecular complexation that can result in constructs of unprecedented structure and behavior [1]. Experimentally, it was found that such an intramolecular complexation occurs in systems of poly(propylene oxide) (PPO) and poly(dimethylaminoethyl methacrylate) (PDMAEMA).[2] It was found that differences in local mutual segment density in linear block-copolymers and miktoarm star polymers of the two components effect the complexation. A complexation of the PPO chain in the miktoarm stars was found for conditions under which the linear polymer is not complexed.

To rationalize these observations a generic bead spring model is employed. The polymers are modeled using a bead spring model with two types of hard sphere beads. The different spheres interact through an attractive Lennard-Jones Potential, mimicking the weak attractive interactions. This model allows for easy variation of architectural parameters (topology and composition) as the effect of these parameters on the complexation and the corresponding polymer structures. Using Monte Carlo simulations, the structures of miktoarm star-shaped polymers and diblock copolymers were investigated as a function of the attractive strength.[3] To deepen the insight into the mechanism, different topologies like comb copolymers were simulated in addition to the miktoarm star and the diblock copolymer topologies (Fig. 1). At intermediate interaction strengths, the complexation is more pronounced in miktoarm star polymers than in diblock copolymers.

By additionally comparing different compositions, it is shown that the influence of the composition increases with the interaction strength. The same degree of complexation of a diblock copolymer can be achieved by a miktoarm star of lower molecular weight in accordance with experimental observations. To enhance complexation one can bring the complexing polymers to a liquid-liquid interface, reducing the space available for the polymers. This spatial confinement in an increased complexation rate, as shown by both, simulations and experiments [4].



**Figure 1** Snapshots of the simulated heteroarm star polymers forming weak (left) and strong (right) complexes.

**Acknowledgements** The fundings of the German Research Foundation (DFG) and the Verband der Chemischen Industrie e.V. (VCI) are gratefully acknowledged.

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# All-atom simulations of SDS micellar solutions: aggregation and diffusion

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The real micellar solutions contain aggregates with different aggregation numbers [1]. These aggregates are very difficult to distinguish and, hence, to study separately by experimental methods such as, e.g., dynamic light scattering and nuclear magnetic resonance. At the same time, the methods of molecular modeling allow one to study transport, structural and kinetic properties of separate aggregates with arbitrary aggregation numbers. We report the results of molecular modeling of aggregation in sodium dodecyl sulphate (SDS) aqueous solutions [2,3,4,5]. Both salt-free solutions with different SDS concentrations and those containing NaCl and CaCl<sub>2</sub> additives have been studied. The all-atom molecular dynamics simulations have been performed within CHARMM36 force field using MDynaMix software package [6]. Formation of one or several aggregates have been observed in the molecular dynamics runs at several surfactant concentrations. Aggregation kinetics has been investigated, and the characteristic sizes of the aggregates have been estimated. The observed radial distribution functions (RDFs) of hydrogen and oxygen atoms of water molecules relative to the center of mass of an aggregate with aggregation number  $n=16$  in the salt-free solution have no local maxima near the aggregate surface; i.e., the surface is incompletely wetted with water. Corresponding RDFs of carbon atoms have one, two or three maxima depending on the surfactant concentration and on the index of a carbon atom in the hydrocarbon radical of the surface-active ion. We have also found the dependence of the diffusivity of a premicellar aggregate with a fixed aggregation number on the total surfactant concentration as well as the dependence of size and diffusivity of an aggregate/micelle on its aggregation number (16, 32, 48, 64) at fixed total surfactant concentration. By finding the mean force potential, the degrees of counterion binding for the aggregates having different aggregation numbers have been estimated. The potentials of mean force for the interaction of sodium and calcium counterions with an aggregate having the aggregation number  $n=32$  show that only calcium ions can be strongly bound to such an aggregate.

**Acknowledgements** The work is supported by Russian Science Foundation (grant 14-13-00112). Calculations has been performed using the resources of the Computing Center of Saint Petersburg State University Research park.

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# Phase behavior and dynamics of concentrated suspensions of soft semi-permeable colloids

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We present an experimental study of the structure and dynamics of suspensions of soft isotropic colloidal core-shell particles in the concentrated and glass regime. We use core-shell particles which consist of PMMA chains of specific molecular weight grafted on a hard silica core. The particles are suspended in a mixture of two solvents for refractive index matching that minimizes multiple scattering. In the concentrated regime, we used 3D Dynamic Light Scattering set-up (3DDL) to measure static and dynamic light scattering. The diffusion coefficient data,  $D(q)$ , were measured near and around the structure factor,  $S(q)$ , peak and interpreted through comparison with hard and permeable sphere models.

In the glass regime, where the dynamics are strongly non-ergodic Multispeckle Dynamic Light Scattering technique (MSDLS) was utilized to follow aging, which strongly depends on the effective volume fraction ( $c/c^*$ ). In the whole glassy regime, the evolution of the degree of correlation as a function of the waiting time shows a non-monotonic behavior which is also reflected in the slowest relaxation time. This behavior is consequence of structural rearrangements of the particles that, depending on  $c/c^*$ , may lead to crystallization of the system. Hence the phase behavior reveals a liquid, a liquid-crystal coexistence followed by a crystalline phase, while at large concentrations metastable glasses states are detected.

# EUSMI: European infrastructure for spectroscopy, scattering and imaging of soft matter

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EUSMI is an open-access research infrastructure for the soft matter research community, which is funded by the European Commission, under the biggest EU Research and Innovation programme Horizon 2020. EUSMI will provide the community of soft-matter researchers with an open-access infrastructure as a platform to support and extend their research, covering characterization, synthesis, and modelling. EUSMI consists of 23 partners across Europe, and is coordinated by Forschungszentrum Jülich.

The goal of EUSMI is to enhance the European competitiveness in soft-matter research and innovation through the integration and the extension of the scope of existing specialized infrastructures. A full suite of coherent key infrastructures and the corresponding expertise from 15 top-level institutions are combined within EUSMI, which will become accessible to a broad community of researchers operating at different levels of the value chain, including SMEs and applied research. Access is offered to infrastructures covering the full chain of functional soft-matter material research, ranging from advanced material characterization by a full suite of specialized experimental installations, including large-scale facilities, chemical synthesis of a full set of soft-matter materials, upscaling of laboratory synthesis, to modeling by high-performance supercomputing.

The existing infrastructure will be continuously improved by JRA to allow users to conduct research always employing the most advanced techniques and method. In addition, an ambitious networking programme will ensure efficient dissemination and communication, as well as continued education of established researchers and training of an emerging generation of scientist. This approach will drive academic research and innovation in soft nanotechnology by providing a multidisciplinary set of essential research capabilities and expertise to guide users, developing the next generation of techniques and instruments to synthesize, characterize, and numerically simulate novel soft matter materials and contributing to the creation of a broad knowledge basis.

EUSMI will officially start from 1 July 2017. The web portal for EUSMI will come up soon. All soft matter scientists are kindly invited to benefit from the open-access programme by submitting proposals under the EUSMI web portal.

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# Raman mapping: a tool for imaging nano- and microstructures after cellular uptake

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Raman mapping is a noninvasive, label-free technique with high chemical specificity and high potential to become a leading method in biological and biomedical applications [1,2,3]. As opposed to Raman spectroscopy, which provides discrete chemical information at distinct positions within the sample, Raman mapping provides chemical information coupled with spatial information. High spatial resolution imaging of biological samples, individual cells and tissues is possible, due to an excitation wavelength in the visible and near-infrared range.

In this study we were able to use Raman mapping for *in vitro* studies, first as a label-free method for monitoring the internalization of gold nanoparticles in adenocarcinomic human alveolar basal epithelial cells (A549). Raman spectra of cells were analyzed by principal component analysis (PCA) and the end result was an image of the sample, a false color Raman map containing highly precise structural and chemical information and showing cytoplasmic internalization of the nanostructures.

Next, we were able to successfully use Raman mapping for imaging of polyelectrolyte multilayer microstructures after cellular uptake in human retinal epithelial (D407) cells. Despite their relatively large size (1-5  $\mu\text{m}$ ), the microcapsules are engulfed by cells and found to be located in the cell cytoplasm. The Raman results are confirmed by transmission electron microscopy and fluorescence confocal microscopy.

Our study proves that Raman mapping enables the detection of internalized nano- and microparticles and the imaging of their intracellular distribution.

**Acknowledgements** This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-2211.

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# Confocal microscopy of the interactions of objects with a solidification interface

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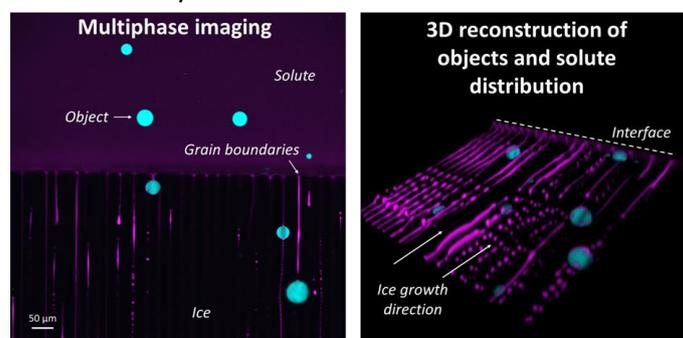
The interaction of objects (soft or hard colloids, bubbles, biological cells, etc.) with a solidification interface is a phenomenon encountered in many industrial and natural processes such as the solidification of metal and metal-composites, the cryopreservation of biological systems and food products, frost heaving, or the processing of porous materials by ice templating [1]. Many models were proposed to predict the interaction of a solidification interface with foreign particles (objects) [2]. While being able to correctly predict object behavior at the interface, these models, with a very few exceptions, give no information on the redistribution of solute and the role of its concentration in solidification process. This is partly due to the lack of experimental data caused by the complex physical nature of systems investigated: very fast or extremely slow kinetics, high temperatures, non-transparent materials, etc.

In this work we aim to develop a model system that allows us to overcome the mentioned limitations and get deeper insight into the interaction of objects with a solidification front and reveal the physico-chemical parameters that control it. We chose laser scanning confocal microscopy as an experimental technique and water/ice as model system. The objects investigated are oil droplets dispersed in water. This combination allows us multiphase in situ 3D imaging of solidification process (Figure 1, Left).

Freezing experiments we performed by displacement of the sample at a controlled speed over two Peltier elements (at different temperatures). Variations of the temperature of the Peltiers and sample displacement velocity provide access to different temperature gradients and cooling rates. Because ice excludes all foreign species, we recorded three phases (ice, water, and oil droplets) with only two photo detectors. Ice is black in this case, while other two phases are imaged with two fluorescent dyes.

With the setup, we have access to different information, from the solidification front dynamics to the dynamics of particles, but also the concentration gradient of solute close to the interface. Measurements of the fluorescence intensity profile indeed provide a semi-quantitative estimate of the solute concentration at each point of the sample. We can also track the flux during the engulfment by mixing two populations of the particles of very different sizes. Finally, we also have access to three-dimensional visualization of the phenomena, which provide unique insights into the evolution of such systems.

The proposed approach is quite universal. Due to the use of water as solidifying media it can be easily extended to many other solidification systems of interest.



**Figure 1** Laser scanning confocal microscopy images of oil droplets engulfment by solidifying water.

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# Thermal stability evaluation of cosmetic products by optical thermal analysis

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Thermal property characterization of food and cosmetic products are complicated due to their heterogeneous nature. They contain most often crystals, emulsion droplets or big particles. Consequently, conventional techniques, such as Differential Scanning Calorimetry (DSC) are often limited by the small non-representative quantity of sample, which can also induce denaturation of the product.

Recently, Diffusing Wave Spectroscopy (DWS) has been coupled with an accurate temperature control, to analyze microstructure evolution, of a complex product during heating or cooling. Multi Speckle Diffusing Wave Spectroscopy (MS-DWS) [1, 2, 3], in which the backscattered light of a coherent LASER is analyzed with a temporal resolution, allows a correlation of the particle motion in the sample and the intensity fluctuation of the backscattered light. The combination of this technique with an accurate temperature control provides information about the microstructure evolution during thermal processing. Indeed, during phase transition, the microstructure evolves faster, which can be observed as characteristic peaks. Various number of cosmetic products are based on fatty compounds, such as esthers, waxes, oils, etc. The formulation of these products must be carefully chosen to avoid, exudation, oil segregation or other phenomena of destabilization. Especially, cosmetic products are stressed thermally by important variations of temperature (indoor, outdoor, summer, winter,...), which can provoke quality problems (surface crystallization and/or exudation).

Characterization of crystalline forms and their variation after thermal stress (cycles) can be performed with RHEOLASER Crystal<sup>®</sup> and can improve significantly the formulation process.

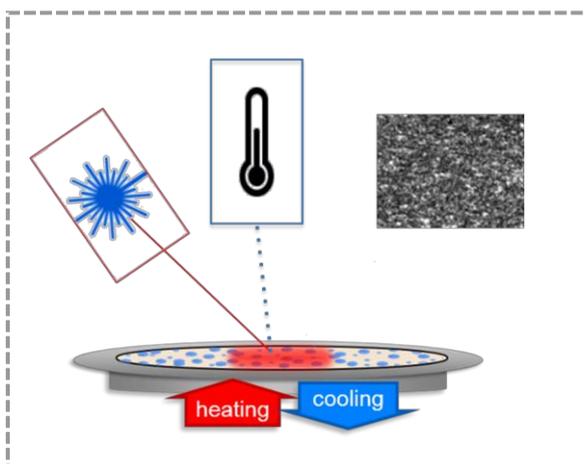


Figure 1 Instrument principle

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# A Light Scattering Investigation on the Structure Factor of Concentrated Microgel Suspensions

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Microgels are polymeric micronetworks swollen by a solvent that display an intermediate behavior between that of hard spheres and polymer coils. Their structural and morphological properties can be varied depending on several parameters such as pH, temperature, concentration, suspending medium etc. [1]. The possibility to tune their features to optimize their properties for certain applications makes microgels a class of soft materials that has sparked tremendous interest in the colloids research community [2]. The softness of these systems is reflected in their structure. Thus, to improve their formulation and define their operative conditions, a detailed study of the development of their interactions as function of temperature and concentration is required [3]. Light scattering is one of the most powerful noninvasive technique used to follow this process. The concentrated regime however has not been fully accessible, because of multiple scattering effects. Here we employ the modulated 3D cross-correlation technology [4] to suppresses multiple scattering and hence gain access to the structure factor of highly concentrated microgels.

In the current work, we present modulated 3D static and dynamic light scattering (SLS and DLS) measurements on Poly-(NIsopropyl-Acrylamide)–N,N-Methylenbisacrylamide (PNiPAM-BiS) microgel suspensions as function of the temperature and concentration. Dilute suspensions are measured to obtain the temperature dependent form factor [5] using SLS, and temperature dependent hydrodynamic radius as a function of the scattering angle of the microgel particles. When increasing the concentration, structure build up, resulting in the appearance of a peak in both the structure factor and angle dependent hydrodynamic radius whose position depends on the particle nearest neighbor distance. By changing the temperature, the sample particle size varies which is reflected in a concurrent change of the form factor and structure factor. We demonstrate that to follow this evolution, and to disentangle changes in structure and size as a function of temperature, modulated 3D cross-correlation is a very powerful experimental tool that can provide access to information not accessible by traditional approaches.

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# Fast flow curve determination by microfluidic optical rheometer

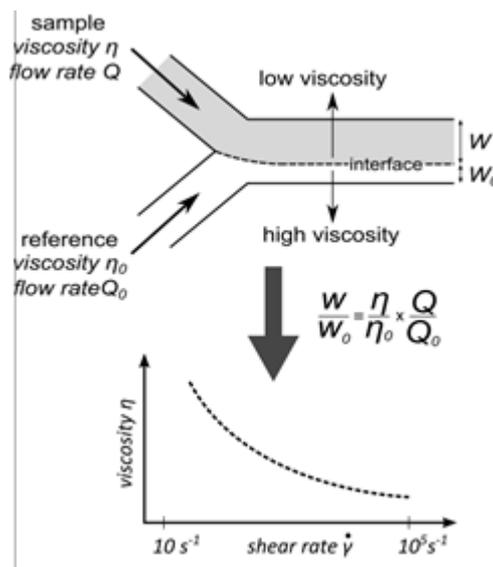
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Viscosity is an essential physical property when studying complex formulations. However rheological studies remain a challenging task for many laboratories as traditional techniques are time consuming and do not always allow to measure samples in desired conditions. We propose a new instrument: FLUIDICAM to measure viscosity as a function of shear rate and temperature in a single experiment set-up. Using a small sample volume, the technology allows flow viscosity measurements of liquid products from water-like inks to thick cosmetic formulations, under a wide range of shear rates (including high values up to  $10^5 \text{ s}^{-1}$ ).

During the measurement, a sample and a viscosity standard are pushed together through a microfluidic chip (Y-junction) at controlled flow rates. Images of the resulting laminar co-flow are acquired with digital camera and the position of the interface is measured. The position is related to the viscosity and the ratio of flow rates between the sample and the reference allowing to determine the viscosity.



We have successfully studied bio triblock copolymers (Ploxamers -  $(\text{PEO})_x(\text{PPO})_y(\text{PEO})_x$ ) well known for their reversible phase transitions (sol-gel) under specific thermal conditions, complex ink formulations and coatings, oil based lubricants and home and personal care formulation. Advanced technology of Fluidicam allows to characterize these formulations at real life conditions (printing, lubricating, injecting, etc.)

# Mechanical characterization and adhesion properties of microcapsules

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We present the characterization of melamine formaldehyde microcapsules on the single particle level by colloidal probe atomic force microscopy (CP-AFM)[1] This technique allows us the precise measurement of the mechanical response of a single capsule upon lateral linear elastic deformation in the regime of low deformation ( $\ll$  wall thickness). Furthermore, the adhesion properties of the capsules were studied by variation of the applied force. The resulting force-deformation curves were evaluated using contact mechanics model [2-3] for the elasticity and JKR model [4] for the adhesion energy calculations.

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# Imaging Mueller Matrix Ellipsometry for Isotropy/Anisotropy Imaging

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Mueller Matrix ellipsometry is an advanced technique necessary for the complete and accurate characterization of anisotropic and/or depolarizing samples. The Mueller matrix (M) according to Hans Müller, who introduced it in 1943, is a transformation matrix for the Stokes vector (S), which describes the polarization state of light.

$$S_{out} = MS_{in} \quad M = \begin{bmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{bmatrix}$$

In the isotropic case, the off diagonal blocks have the value zero. In microscopic mapping, this can be used to identify anisotropic areas of a thin film or crystalline nano plates on an isotropic substrate.

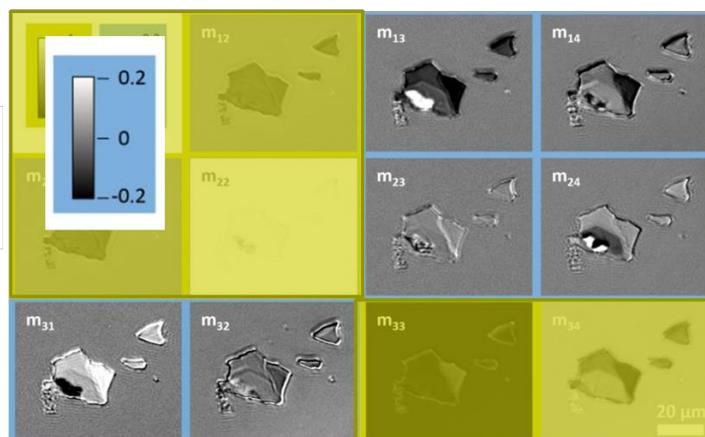
Here, we present imaging Mueller matrix ellipsometry (IMME) with high microscopic lateral resolution capable of measurements at a variable angle of incidence and variable wavelength. By operating Accurion's imaging ellipsometer EP4 (PCSA configuration) in a rotating-compensator mode, the ellipsometer yields Mueller matrix micrographs for the upper 3x4 matrix elements of the sample. We applied this imaging Mueller matrix ellipsometer for example to the characterization of microscopic flakes of anisotropic 2D-materials, such as black phosphorus (Fig. 1) and will report different examples for applications in the field of biophysics, inorganic oxide layers or organic electronics and will discuss what type of additional data can be obtained from this technique.

## The isotropic case

$$1 \quad M = \begin{bmatrix} 1 & m_{01} & 0 & 0 \\ m_{01} & 1 & 0 & 0 \\ 0 & 0 & m_{22} & m_{23} \\ 0 & 0 & -m_{23} & m_{22} \end{bmatrix}$$



Pixels = 0 (■) in all off diagonal block elements are representing isotropic areas of the sample - other greyscales represent anisotropic areas..



**Figure 1** Müller-matrix micrographs of micro-structured flakes of black phosphorus (anisotropic) on silicon substrate, recorded at  $\lambda=501 \text{ nm}$ .

# Study of $\beta$ -galactosidase-silica support interactions using IR and Raman data fusion

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The thermal and pH stability of the enzymes improves quite much by immobilizing the enzyme in a support. This, in turn, enhanced the possibilities for reusing those enzymes at the industry. The presence of the enzyme adsorbed on the support material can be identify by different techniques, although, it is still a challenge to study the interactions between the functional groups of the enzyme and the support. In this context, vibrational spectroscopy can play an important role, since reported studies showed that the interaction enzyme-support could be confirmed with the displacement and/or increment of the intensity of some spectral bands, or the appearance of new bands [1].

Infrared and Raman spectroscopy, based on molecular vibrational, are complementary techniques due to the selection rules providing a different chemical information. In general, infrared spectroscopy emphasize asymmetric vibrations of polar groups, whereas Raman spectroscopy tends to emphasize symmetric vibrations of nonpolar groups. Here, those were used to study the interaction between  $\beta$ -galactosidase (EC 3.2.1.23), used in the production of low-lactose products, and an in-house synthesized meso-macroporous silica support [2]. The Raman spectra proved the interaction of the  $\beta$ -galactosidase with the silica support by the displacement of the Amide I band, from 1672  $\text{cm}^{-1}$  in the free enzyme to 1666  $\text{cm}^{-1}$  in the adsorbed enzyme. The ATR-FTIR spectra confirmed the adsorption of the enzyme by the Amide I at 1651  $\text{cm}^{-1}$  ( $\nu\text{C=O}$ ), and Amide II at 1535  $\text{cm}^{-1}$  ( $\delta\text{N-H}$ ). The displacements of the  $\nu\text{Si-O-Si}$  and  $\nu\text{Si-OH}$  bands, characteristic of silica support, reinforced the conclusion of an interaction between the  $\beta$ -galactosidase and the silica support.

Afterwards, the IR and Raman data were fused, and then chemometric analysis (extended canonical variate analysis, ECVA) were applied to inspect the variability of each sample with different enzyme concentrations. The ECVA analysis renders results showing different groups in new space projection planes. In these planes, the samples of low enzyme concentration appeared in the same region of the Cartesian plot, while samples at high enzyme concentration appeared together in another region of the plot. That is, ECVA divides the spectra in several segments in order to help separating the samples into different groups according to their intrinsic or particular properties or interactions. As a result, the largest differences among the samples at different concentrations was found studying the Amide I and Amide II segment bands.

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# Rheological properties and microscopic dynamics of concentrated core-shell microgels with tunable interactions

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The microstructure, dynamics and mechanical properties of sterically and electrostatically stabilized aqueous suspensions of microgel particles are studied in concentrated liquids and glasses. Two different microgel systems are used comprising of the same trifluorethyl methacrylate (TFEMA) core, onto which a N-isopropylacrylamide (PNIPAM) shell crosslinked by 5%wt of N, N'-methylenebis(acrylamide) (MBAM) with different size, providing a thermosensitive character where interactions can be tuned from repulsive to attractive. When the temperature is below Lower Critical Solution Temperature ( $T < LCST$ ) the PNIPAM shell swells due to good solvent conditions, while for higher temperatures unfavorable interactions created by hydrogen bonding between amide groups and the aqueous solvent lead to shell collapse.

We use Static and Dynamic Light scattering in the dilute regime to determine the temperature dependent hydrodynamic radius  $R_h$  and the overall intermolecular interactions. Changing the temperature and/or salt concentration we tune inter-particle interactions in the concentrated regime switching between glass, liquid and gel states. As samples exhibit strong multiple scattering under such conditions, Diffusive wave spectroscopy (DWS) was used to probe the internal dynamics and to monitor the ergodic (liquid state) to non-ergodic (glass or gel state) transitions while rheology was used to study the linear and nonlinear properties of the glass and gel samples with emphasis on the yielding mechanisms. Moreover, confocal laser scanning microscopy at rest and under shear (using a rheo-confocal set-up) was used to probe microstructural changes (ordering and shear induced melting) and particle rearrangements. We finally employ Orthogonal Superposition Rheometry, which combines two deformation modes, steady shear and small amplitude oscillatory shear applied simultaneously and orthogonally to each other, to measure the internal relaxation and the full viscoelastic spectrum of flowing microgels varying their interactions through temperature.

# Microfluidic-based preparation of hyaluronic acid microgels for enzymatic-triggered release of hydrophobic drugs

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Ravaine V.<sup>1\*</sup>

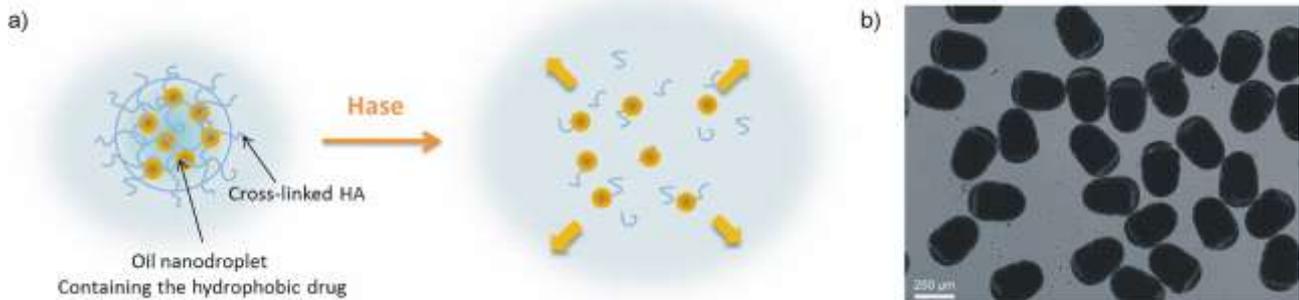
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The design and preparation of polymer microgels have attracted considerable attention due to their great potential in the biomedical field, particularly as drug delivery systems [1]. Hyaluronic acid (HA) is a naturally occurring glycosaminoglycan composed of N-acetyl-D-glucosamine and D-glucuronic acid. This polymer is biodegradable, biocompatible, nontoxic, and can be chemically modified [2]. The aim of this work is to prepare biodegradable HA microgels encapsulating hydrophobic drugs by a co-flow microfluidic strategy. The approach relies on three steps: (i) the drug is incorporated in an oil-in-water nanoemulsion, (ii) the nanoemulsion is further incorporated within a double oil-in-water-in-oil emulsion (O/W/O) using microfluidics, and (iii) the microdroplets are cross-linked by photopolymerization of HA precursors modified with methacrylate groups (HA-MA) present in the aqueous phase. The procedure is used for the encapsulation and controlled release of progesterone. Degradability and encapsulation/release studies in PBS buffer at 37 °C in presence of different concentrations of hyaluronidase (Hase) are performed. It is demonstrated that enzymatic degradation can be used to trigger the release of progesterone from microgels. This method allows a fine and robust control of the structural parameters and can be applied for the encapsulation and controlled release of different types of hydrophobic drugs [3].



**Figure 1:** a) Schematic representation of the oil-in-microgel system encapsulating a hydrophobic drug. The HA matrix degrades upon addition of Hase and releases the oil nanodroplets; b) Microscopy images of HA-MA microgels prepared by co-flow microfluidic.

**Acknowledgements** Carlos Busatto thanks to Saint-Exupéry program for the fellowship.

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# Microfluidic synthesis of drug-loaded PLGA NPs for plant therapy: a novel approach by using plant defense elicitors

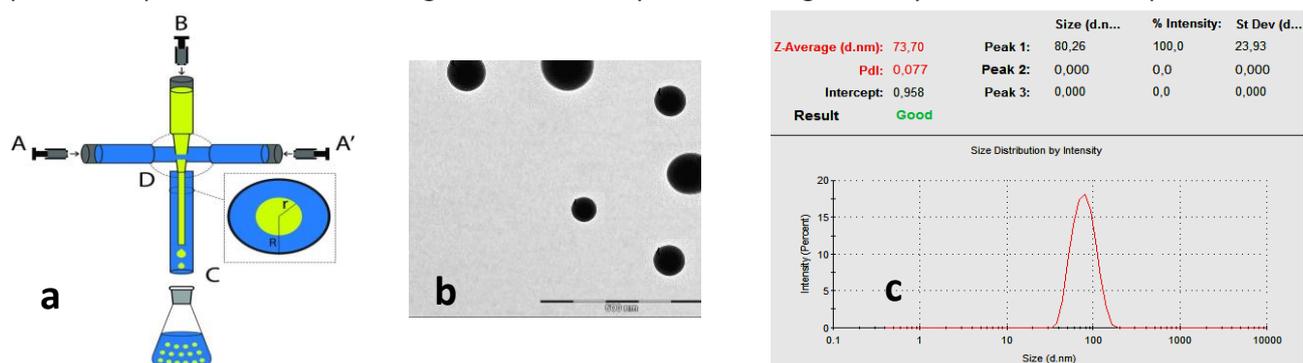
Marco Bramosanti<sup>1</sup>, Laura Chronopoulou<sup>1</sup>, Livia Donati<sup>2</sup>, Roberta Rosciani<sup>2</sup>, Alessio Valletta<sup>2</sup>, Gabriella Pasqua<sup>2</sup>, Cleofe Palocci<sup>1</sup>

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Recently, researchers have begun to explore the potential of nano-systems as pesticide carriers in the field of plant biology. Nowadays the farming market demand needs approximately 2.5 million tons of pesticides but almost of 90% do not reach the desired target but are dispersed in air, water and soil, increasing environmental pollution. The ability to deliver selected bioactive molecules to plant cells could play an important role to match these problems in order to develop new products and strategies for agro-food applications. We are currently pursuing a novel strategy, focusing not on the pathogen but on the natural defense mechanisms of the plant. As is well known, a common defense mechanism for many plants is the synthesis of phytoalexins, that is mediated by specific chemical signals called elicitors. Methyl Jasmonate (MJ) is a relatively volatile phytohormone that acts as an elicitor in many plant species [1]. We have synthesized solid monodispersed PLGA NPs with diameters ranging from 30 to 200 nm containing MJ by using a microfluidic reactor (MFR) with a flow-focusing geometry. In our micro-device the dispersed organic phase containing PLGA and MJ (i.e., acetonitrile) is continuously focused by the continuous phase (i.e. distilled H<sub>2</sub>O) using two syringe pumps (Figure 1). We optimized MJ loading and NP size by acting on different operating conditions, such as polymer molecular weight and concentration, polymer/MJ mass ratio, flow rate ratio,  $\tau_{mix}$ , mixing channel diameters and length [2,3]. NP characterization was performed by Dynamic light scattering (DLS) measurements (size, polydispersity index and Z-potential), and by scanning and transmission electron microscopy. The determination of MJ content inside PLGA NPs was carried out by gas chromatography. Treatments on *Vitis vinifera* cell lines with synthesized MJ-loaded NPs showed an encouraging induction of the synthesis of phytoalexins. Periodic treatments with MJ-loaded NPs could protect crops from insects and fungi attacks, in a way that could significantly reduce the use of pesticides.



**Figure 1** (a) MFR reactor system used for the synthesis of PLGA NPs. One mixing channel (C) connected by a cross junction (D), with a central stream (B) and 2 side streams (A and A'). (r) can be varied by altering the volumetric flow rates of the 3 inlets or the internal dimensions of the mixing channel. (b) TEM micrograph showed solid spherical morphology, scale bar = 500 nm. (c) DLS measurements highlighted very low polydispersity index value.

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# Flow Dynamics of Healthy and Deformed Red Blood Cells in a Microchannel

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Red blood cells (RBCs) are the major cellular component of blood (~ 45% by volume). The RBCs in matured state are typically biconcave discs with a characteristic diameter of 8 microns. Various diseases result in abnormal RBC shapes such as Microcytic RBC (resulting from Thalassemia, anemia), Macrocytic RBC (resulting from liver diseases, vitamin B12 deficiency), echinocyte (resulting from uremia), Spherocyte (resulting from hereditary spherocytosis), Stomatocyte (resulting from hereditary stomatocytosis) etc<sup>1</sup>. Such variations in RBC shape are cumulatively termed as Poikilocytosis. In the present work we have studied the flow dynamics of both biconcave and deformed RBCs inside a microchannel. Fresh blood is collected from a peripheral vein of a healthy volunteer. The collected sample is first centrifuged at 4000 rpm for 15 minutes to separate the RBCs from the blood plasma. It is then diluted with phosphate buffer in a ratio of 1:100. Poikilocytic agent (tritonX-100) has been used to incite deformation amongst the erythrocytes in the previously diluted sample. A PDMS microchannel (Fig. 1a) of dimension  $60\ \mu\text{m} \times 25\ \mu\text{m} \times 5000\ \mu\text{m}$  is fabricated by soft lithography from a master mould that has been made by photolithography using negative photoresist (SU8-2050). The surface of the microchannel is rendered hydrophilic by oxygen plasma treatment, thereby initiating capillary flow<sup>2</sup>.  $4\ \mu\text{l}$  of diluted blood sample is poured into the reservoir and the flow dynamics is monitored at a location  $1.5\ \text{mm}$  from the reservoir for the first 5 minutes using high speed camera (373 fps). The RBCs are tracked using ImageJ software and their local velocities are measured through repeated measurements. It has been observed (Fig. 1b) that the flow velocity of the discoidal shaped RBCs distinctly differs from the deformed RBCs (echinocytes). The difference is probably due to the enhanced frictional drag force, causing the deformed erythrocytes move slower than the normal (biconcave) erythrocytes. This observation may pave the way in sorting healthy blood cells from the diseased ones inside a microchannel.

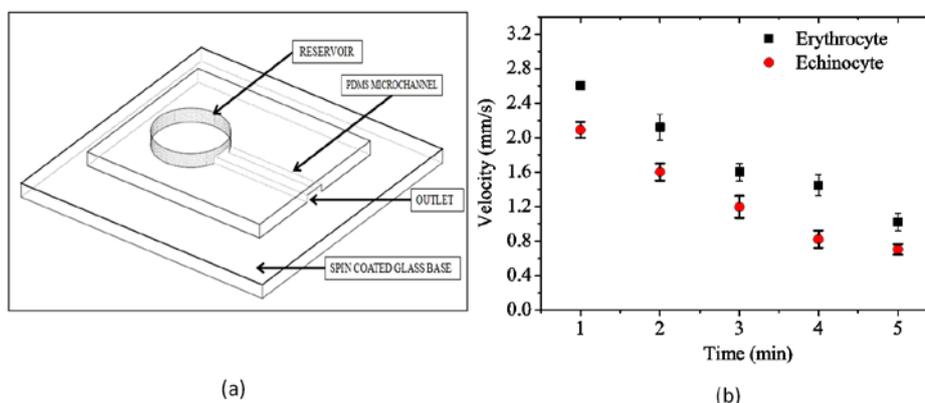


Figure 1 a) Experimental set-up b) Average velocity of erythrocytes and deformed RBCs (echinocytes)

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# Binary Colloidal Mixtures: Influence of the Order on the Thermal Conductivity

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Polymers are suitable heat-insulating materials since they have a low thermal conductivity typically around  $0.1\text{--}0.3\text{ Wm}^{-1}\text{K}^{-1}$ . Polymeric colloidal crystals consisting of spherical nanoparticles show even lower thermal conductivities due to the decreased density and small contact areas between adjacent particles. It is well known that monodisperse nanoparticles self-assemble in a highly ordered face-centered cubic packing [1]. A rather high density of 74 % of the bulk material's density limits the reduction of the thermal conductivity of such assemblies. One way to decrease the thermal conductivity further is the lowering of the density of the colloidal assembly by introducing disorder.

Here we show that the crystalline structure is transferred from order to chaos by mixing two differently sized polystyrene particles (particle size ratio:  $D_{\text{small}}/D_{\text{large}} = 0.8$ ). For a detailed mixing study, the large particle volume ratio is varied between 0 – 100 %. Thereby the colloidal crystallinity is destroyed. The density of the obtained colloidal glass is reduced by maximal 10 % compared to the colloidal crystal. However, the effective thermal conductivity drops even more: from crystalline to amorphous by around 22 %. Thus, this decrease is not only caused by the reduced density. Molecular dynamics simulations were used to determine the structure of the colloidal glass and the number of next neighbors per particle. We find a change from 12 in the crystalline state to an average value of around 10 in the amorphous state. Using finite element modeling (FEM), we could show that the lower number of next neighbors leads to increased heat transport pathways. This effectively hinders the heat transport and results in an additional decrease of the thermal conductivity.

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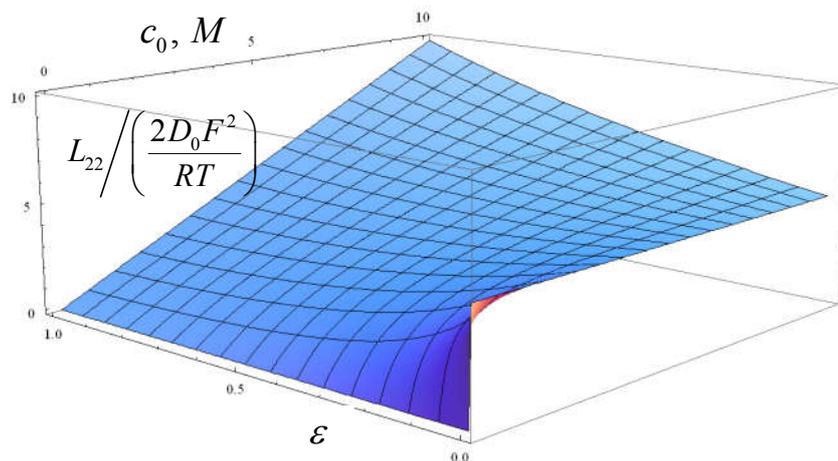
# Calculation of Electric Conductivity of Ion-Exchange Membrane by the Cell Method

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The cell method is one among significant effective methods to investigate dense dispersion systems such as, for example, porous ion-exchange membranes. A formation of the cell model for the dense swarm particles may be based on replacement of real system of randomly spatially located particles by a periodic structure of identical spheres to be arranged in spherical cells. Attempts to systemize the variety of electrokinetic, electrodiffusive and diffusiokinetic processes were undertaken recently elsewhere using thermodynamics of irreversible processes. An advantage of such approach leads to measure directly all thermodynamic variables, fluxes and forces, involved in governing equations, in experiments. The hydrodynamic permeability  $L_{11}$  in case of uncharged membrane consisting of cylindrical and spherical partly porous particles was calculated in our works [1, 2]. Similar problem we examine here for calculation of specific conductivity of an ion-exchange membrane basing on Onzager's approach. We have posed the boundary value problem for the unique porous charged spherical particle which is embedded into a fluid envelope. The motion of liquid (electrolyte solution) inside the envelope is subjected to Stokes' equations with additional electro-massive force and motion of electrolyte inside the particles is described by extended Brinkman's equation also with adding electro-massive force. For electric potential determination we apply the Poisson equation, while for ion fluxes we use the Nernst-Planck equations with appropriate boundary conditions. Figure 1 shows 3D-dependence of electric conductivity of the cation-exchange membrane as function of electrolyte concentration  $c_0$  and porosity  $\varepsilon$  under high ion-exchange capacity  $\rho=10$  M.



**Figure 1** Dependence of dimensionless electric conductivity  $L_{22}$  on electrolyte concentration  $c_0$  and porosity  $\varepsilon$ .

**Acknowledgements** This study was supported by the Russian Foundation for Basic Research (Grant No 17-08-01287).

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# Application of the Onsager reciprocal relation to the electro-acoustic coupling.

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Electro-acoustic coupling, in solutions and suspensions, is a class of phenomena in which an input of one kind (acoustic or electric) results in an output of the other kind. It includes acoustophoresis (creation of an electric field by an acoustic wave), CVI (creation of an electric current by an acoustic wave) and ESA (creation of an acoustic wave by an electric field)[1][2]. These phenomena are mostly used for the zeta potential determination of colloids in suspensions, and two commercial devices and at least one prototype are based on them. A common approach is a Debye-like approach[3], i.e. a mechanical, i.e. based on the resolution of the equations of mechanics, for acoustophoresis. In this presentation, a thermodynamical approach, based on the derivation of Onsager reciprocal relationship, will be shown [4]. Although the mechanical approach allows computations of solutions, it is not suitable for establishing link between phenomena. With the thermodynamical approach, the link between acoustophoresis and electrophoretic mobility will be confirmed, and also the link between the three electro-acoustic methods. We will mostly focus on qualitative modeling and qualitative interpretation, rather than on mathematics and computations. We will do only a brief reminder of the mechanical approach, to solve a tricky point: the question of the pressure applied on an ion with a negative volume[5].

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# Droplet generation with quasi 2D flow

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The development of digital microfluidics has attracted considerable interest towards generation of highly monodisperse microdroplets. T-junction[1] and axisymmetric step emulsification[2] devices have become an essential element of most of microfluidic chips. Despite its importance, theoretical analysis of droplet formation in such devices is still incomplete due to the complexity of the physics involved. We focused on droplet generation for two examples of quasi-2D flows. The effect of various experimental parameters, such as channel geometry, flow rates, surface tension and fluid viscosities, was thoroughly investigated. Our results show that the experimental system exhibits various distinct regimes (squeezing, dripping and jetting regimes) and point out the effect of confinement on the transitions. Quasi-2D flow equations allow us to perform numerical simulations which show good agreements with experiments.

**Acknowledgements** The Microflusa project receives funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 664823

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# Soft self-assembled nanostructured nanoparticles for gene and drug delivery

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Formulations based in lipid systems (e.g. liposomes) hold the promise of becoming safe and efficient delivery systems for drugs and genes in therapeutic applications [1]. Yet, the efficiency of such systems is still relatively low and further progress in the technology is needed to achieve the required performance for therapeutic applications.

In this presentation I will talk about our recent advances in the development of novel methodologies capable of making soft self-assembled nanoparticles of controlled size and nanostructure, and which are capable of incorporating polar and apolar drugs simultaneously.

Particular emphasis is placed on the development of novel microfluidic-based methods to aid in the assembly process. These devices allow not only a versatile and automated way of producing nanocarrier particles of controlled size and distribution, but also to take advantage of the out-of-equilibrium nature of flow to further manipulate the materials and produce novel complex structures of therapeutic interest.

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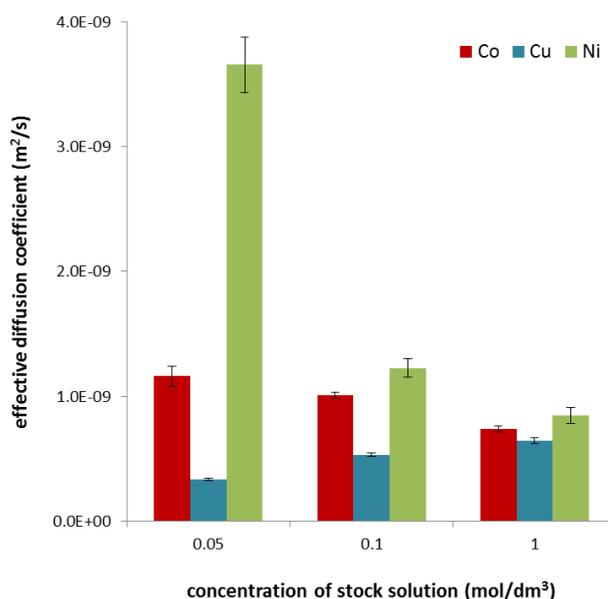
# Transport of metal ions in hydrogels containing humic acids as active complexation agent

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The complexation and transport/immobilization ability of humic acids are the most important environmental qualities of these substances. Therefore, the study on these properties are important both for understanding role of their role in natural systems and human-driven applications [1,2]. This contribution is focused on metal ions diffusion (Co, Cu and Ni) studied by the method of diffusion couple [1] and their immobilization in humic hydrogels. It was found that the diffusion characteristics of metal ions are strongly affected by their reactivity and their initial concentration. Concentration dependence of Cu diffusivity had different trend comparing Co and Ni, which was caused by high affinity of Cu to humic acids. When the metal ion is first complexed by humic acids, it is bound in an exchangeable mode, which can be transferred to a nonexchangeable one [3]. Our results indicated that the dynamic equilibrium established in the diffusion process includes mainly Cu ions in the exchangeable mode as a result of their high affinity and high amount of bound metals. Their transformation in strong Cu-humic complexes is very slow [4]. On the other hand, Co and Ni had much lower affinity to humic acids, thus their diffusivity is less affected by their reaction with humic acids.



**Acknowledgements** The Materials Research Centre at the Faculty of Chemistry, Brno University of Technology is supported by Project No. LO1211 from the Czech Ministry of Education, National Sustainability Program I.

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# Dissolution of Iron Chromium Oxide by Decontaminating Agent for a Foam Decontamination

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Prior to confirming the decontamination performance of a foam decontaminating agent, a study was conducted to optimize the composition of a chemical decontaminating agent available for use in a foam decontaminating agent. To confirm the decontamination performance of three kinds of chemical decontaminators varying in the concentration of Ce (IV) and HNO<sub>3</sub>, which are the main components of an oxidizing chemical decontamination agent, decontamination specimens were prepared to form FeCr<sub>2</sub>O<sub>4</sub> oxide on SUS 304 metal in autoclave. The weight loss and SEM / EDX of the specimens were measured before and after decontamination, and the concentration of Fe and Cr ions in the solution after decontamination was analyzed using AA spectroscopy.

At lower concentrations of a 0.1 M Ce (IV), the amounts of Fe and Cr dissolved increased by 25% and 67%, respectively, as the HNO<sub>3</sub> concentration was doubled, whereas the amounts of Fe and Cr dissolved were increased at higher concentrations of Ce (IV) by 2.6-fold and 1.3-fold, respectively.

It seems to be possible to use it as a chemical decontamination agent necessary for optimizing the foam decontamination composition, which is effective in reducing the liquid waste.

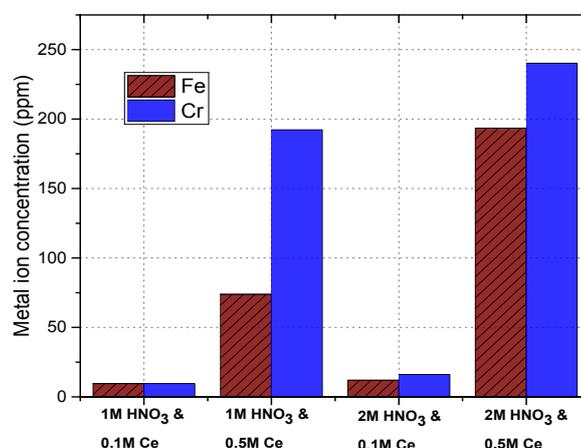


Figure 1. AA results of FeCr<sub>2</sub>O<sub>4</sub> in the decontamination solutions at 8 h after decontamination.

## Acknowledgements

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# Engineering the structure of biopolymer microgels for the controlled release of proteins microgels

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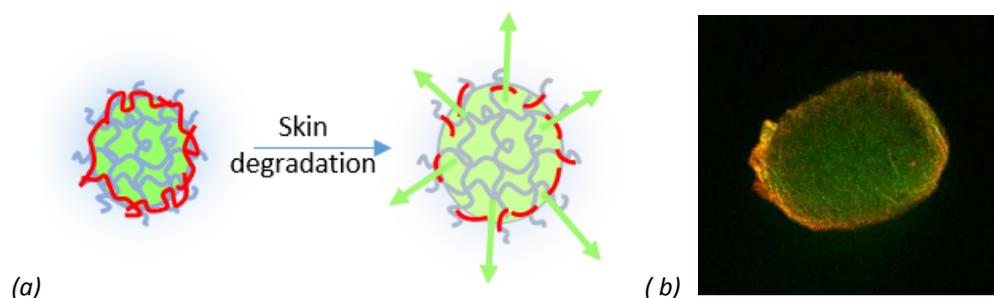
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Hydrogels made of polysaccharides are widely used for medical applications such as reparative medicine or drug delivery, at different size ranges from macrogels down to nanogels. Among them, hyaluronic acid (HA) has unique properties in terms of biocompatibility and biodegradability. This work aims at understanding how the structural parameters of the gels and the drug/matrix interactions impact the encapsulation and release. In this purpose, hydrogel particles of about 100 $\mu$ m were prepared by microfluidics and individually studied using micromanipulator-assisted optical and confocal microscopy in the presence of protein models. Their size and the distribution of the encapsulated species were studied in real time.

In this work, microgels made of methacrylated HA [1] were prepared using co-flow microfluidics to ensure control of the porosity, good reproducibility and to enable the encapsulation of hydrophobic or hydrophilic species [2]. Two models of protein were studied as encapsulated species: one is non-interactive, while the second binds strongly with the matrix through electrostatic interactions. The distribution of the protein is correlated to the crosslinking density of the gel and the molecular weight of the protein. High molecular interacting species cannot enter the pores and remain blocked at the periphery of the gels. It creates an impermeable skin which hinders enzymatic degradation of the gel.

In addition, the release properties have been studied. Whereas a non-interactive protein is released in a non-specific way by diffusion across the matrix, we propose a new strategy to overcome this issue, where the protein is locked inside the gels thanks to the blocking skin-macromolecule. (Fig. 1). We can provoke the release upon various external triggers that will dissolve the skin layer: by dissociation of the skin-macromolecule or by enzymatic degradation of the skin layer. This work opens new opportunity for the controlled delivery of proteins from responsive hydrogels.



**Figure 1** concept (a) and example of confocal microscopy image (b) of the skin-protected microgels (red) with loaded protein (green) and its release upon skin dissolution

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# Kinetic stability of oil-in-water nanoemulsions prepared by ultrasound technology using biodegradable amphoteric surfactants

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Colloidal nanocarriers, in their various forms, provide almost endless opportunities in the area of biotechnology, pharmaceutical technology, nanomedicine and drug delivery [1]. Recently an important role may be played by nanoemulsions - bluish/translucent isotropic dispersions, which involve water and/or oil nano-domains with common sizes 20-500 nm and high kinetic stability, i.e. given sufficient time, a nanoemulsion phase separates [1-3]. Surfactant/emulsifier molecules play an important role in stabilizing the nanodroplets through repulsive electrostatic interactions and steric hindrance. Thus, the selection of the right stabilizing agent is key for the creation of the small sized droplets as it decreases the interfacial tension i.e., the surface energy per unit area, between the oil and water phases of the dispersion [2,3]. Over the past decade, nanoemulsions have been prepared through various approaches, broadly classified into two primary categories: high-energy and low-energy methods with application of ionic and nonionic surfactants [2]. Nevertheless, the physico-chemical properties of nanoemulsions, their kinetic stability and biocompatibility may depend on various control parameters such as composition, size, structural features and concentration of surfactants/emulsifying agents as well as oil phase and their properties of the liquid/liquid interface [3].

Thus, in our research we investigate the potential of two commercially available amphoteric surfactants of high biodegradability, *i.e.* cocamidopropyl betaine (Rokamina K30B) and coco betaine (Rokamina K30), in fabrication of kinetically stable oil-in-water (o/w) nanoemulsions obtained by ultrasound approach. Initially we examine the phase behavior (ternary phase diagrams) of surfactant-oil-water (SOW) systems containing different ratios of the selected surfactant (S), oil (O) and water phase (W) by titration-ultrasound method. The oleic phases are selected from esters of naturally occurring- as well as omega-6 and omega-9 fatty acids. Then, the systems with a known composition are characterized by visual and microscopic observations, the particle size and size distribution as well as nanoemulsion zeta potential measurements. Finally the all characterized dispersions are subjected to kinetic stability studies by turbidimetric technique. Due to evaluation of both Backscattering (BS) and Transmission (T) profiles as well as Turbiscan Stability Index (TSI), the selection of the long-term nanosystem is provided. The analysis of the obtained results clearly demonstrates selective influences of examined surfactant, oil composition, and surfactant-to-oil ratio on the droplet size, charge and stability of the systems produced. The biological stability studies provided in physiological fluids exposed the nanoemulsions ability to overcome various specific barriers to efficient drug and gene delivery. Our results highlight the potential advantages of the o/w nanoemulsions containing amphoteric betaine-origin surfactants and may serve as a promising platform to design and prepare of new nanoemulsion-based delivery systems for future biological applications such as drug or gene delivery, anticancer therapies and diagnostics.

**Acknowledgements** The financial support of statutory activity subsidy from Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Science and Technology.

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# Selective Bactericidal Activity of Divalent Metal Salts of Lauric Acid

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Bacteria play a crucial role in skin health. For example, *Staphylococcus aureus* (*S. aureus*) and *Propionibacterium acnes* (*P. acnes*) cause skin roughness and acne, whereas *Staphylococcus epidermidis* (*S. epidermidis*) enhances innate barrier immunity[1, 2]. Therefore, controlling the bacterial flora is important in dermatology and cosmetic chemistry. Previously, we revealed the effect of alkyl chain length and unsaturated degree on bactericidal activities[3, 4]. In this study, the bactericidal activities of different metal salts of lauric acid was evaluated[5] (Fig. 1). The bactericidal behavior of the salts changed according to the type of metal ion. Specifically, Mg-, Ca-, and Mn-containing salts effectively sterilized only *S. aureus* and *P. acnes* (Fig. 2). Their Co, Ni, and Cu salts sterilized all bacteria, including *S. epidermidis*, whereas the Zn salt proved ineffective. The Cu salt displayed the strongest bactericidal activity. Spin-trapping, detected using electron spin resonance showed that this salt catalyzed the generation of hydroxyl radicals, which can destroy bacterial cell membranes (Fig. 3). These findings demonstrate that metal-ion selection is an important factor in the design of bactericidal agents for healthcare products.

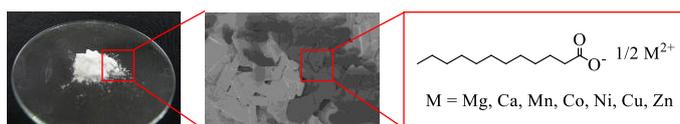


Fig. 1 Molecular structure of divalent metal salts of lauric acid.

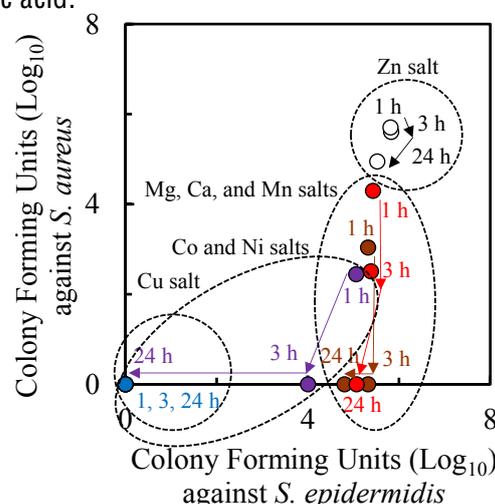


Fig. 2 Bactericidal activities of divalent metal salts of lauric acid.

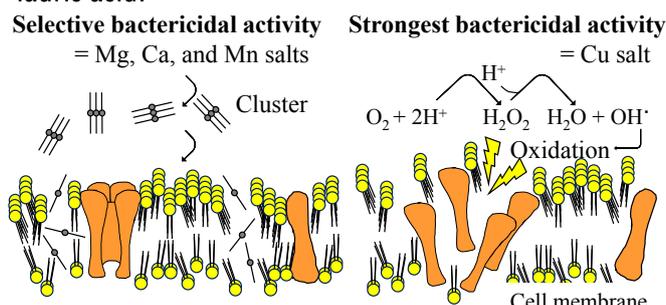


Fig. 3 Bactericidal mechanism of divalent metal salts of lauric acid.

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# New chitosan-based microgels for internal wound healing therapies

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Microgels are crosslinked polymeric particles that can swell appreciably in a good solvent.[1] Recently the unique functional and structural properties of microgels have attracted much attention due to their potential applications in the biomedical area: tunable softness which can mimic different human tissues, a high porosity which allows for bioactive agent encapsulation and release, and a functionalisable outer shell that can provide additional properties such as recognition or cell adhesion. [1-3] Polysaccharide-based microgels are especially attractive in the design of scaffolds for tissue engineering for internal or chronic injuries[4] due to their biocompatibility, biodegradability, low manufacture costs and renewability, but also owing to their biological activity ranging from cell adhesion to immunologic activities.

Herein, we report the synthesis and physico-chemical characterization of novel functionalised chitosan microgels for tissue engineering applications. Chitosan was readily derivatised by exploiting the high nucleophilicity of its nitrogen to provide a range of functionalised polymers that could be crosslinked *via* click chemistry. Microgels with a diameter of around 200 nm were prepared by using water-in-oil nanoemulsions as templates, with gelation facilitated by *in situ* photo-initiated cross-linking. The microgel particles were then isolated and characterised by dynamic light scattering (DLS), Zeta potential measurements and electron microscopy. The outer shell of the microgels was successfully functionalised by click chemistry to allow further generation of complex wound healing materials. Initial cytotoxicity studies carried out in human cells confirmed the non-toxicity of the materials, thus highlighting their potential in future tissue engineering applications.

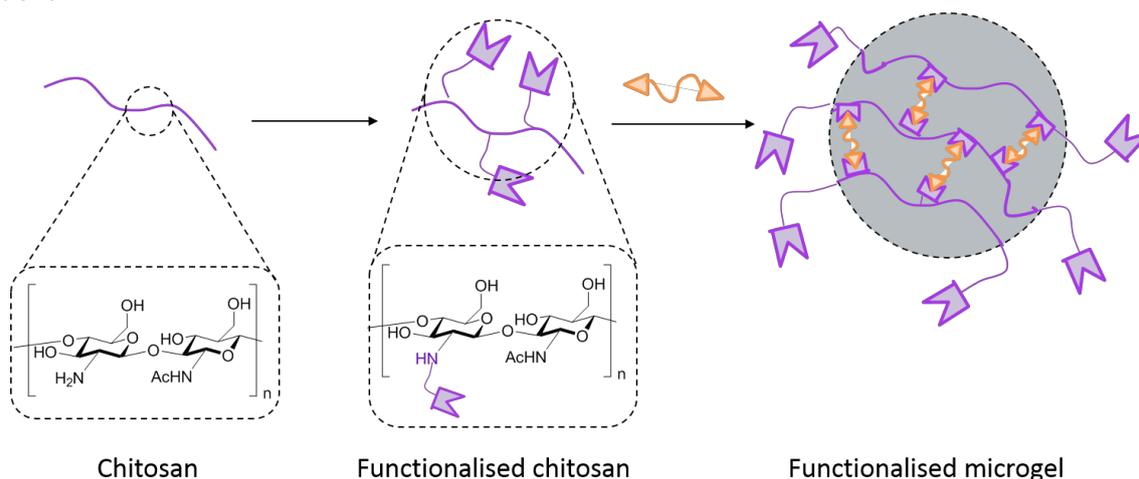


Figure 1. Synthesis of chitosan-functionalised microgels.

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# Differences in the binding of the fibrillogenic peptide hormone somatostatin-14 on plasmonic nanoparticles addressed by physicochemical conditions

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Nanoparticles (NPs) play an important role in the fields of biology and medicine, drug delivery as much as diagnosis. They present a large surface/volume ratio allowing big concentration of medication to achieve disease tissues or changes in the rate of certain biological processes. In addition noble metal NPs exhibit enhancement of spectroscopic signals due to localized surface plasmon resonances (LSPR), being especially important SERS (Surface Enhanced Raman Spectroscopy) and SEF (Surface enhanced fluorescence).

Human amyloid disorders are directly related with Alzheimer disease [1] and more directly with the presence of brain plaques of  $\beta$ -amyloid peptides such as somatostatin-14 (SST-14) [2]. Several studies have related submillimolar concentrations with unstructured loop of SST-14 or high order self assemblies if concentration reaches 20 to 60  $\mu$ M range. Better knowledge on structural features of SST-14 on an aqueous environment will help to understand its molecular aggregation as well as the binding mechanism to peptide receptors. Gold and silver NPs exhibit, besides their enhancement spectroscopy properties related above, inhibition of the aggregation of short size A $\beta$  peptides, acceleration of fibrillation of cysteine-free peptides or retardation of insulin fibrillogenesis process. On a previous paper [3] we shown the ability of novel metal nanoparticles to bind SST-14 thus allowing detection of low traces of peptide and characterizing the vibrational markers arising from the group located in the vicinity or at the surface NPs.

In this work we present a novel SERS study on the binding sites of SST-14 to NPs surface at different pH's trying to imitate physiological conditions, we also analyze influence of a second molecule (drug emodin) in the peptide-NP nanocarrier system or the presence of an aggregation agent. We check differences in the vibrational bands that could determine important features in structural architectures or in subsequent recognition of peptide receptors.

**Acknowledgements** The authors would like to gratefully thank the Spanish Ministerio de Economía y Competitividad (grant FIS2014-52212-R).

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# Nanocapsules as a Drug Delivery system for Endothelial Progenitor Cells' secretomes

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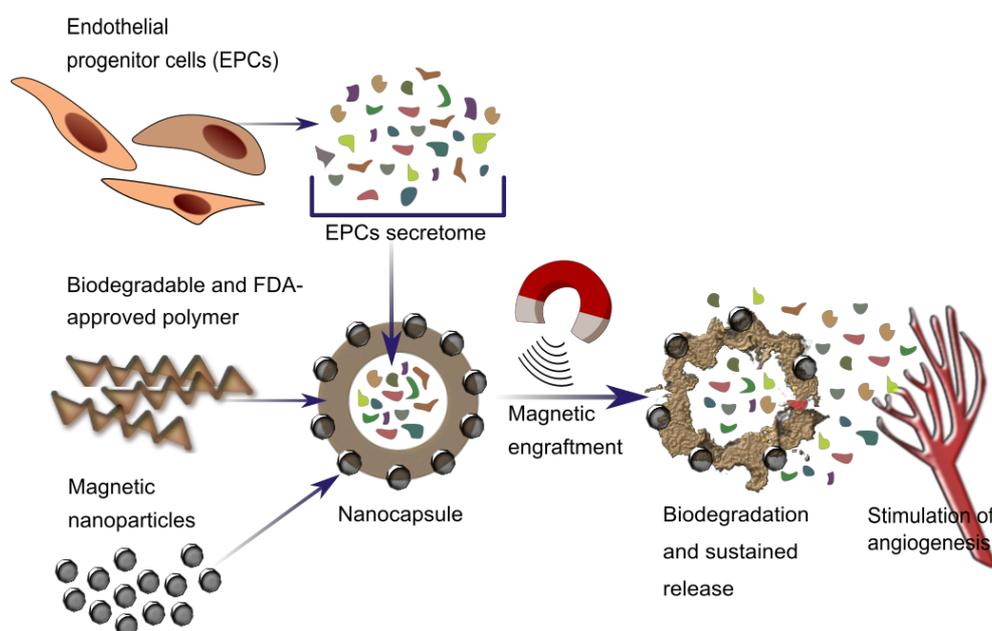
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After stroke, Endothelial Progenitor Cells (EPCs) migrate from the bone marrow towards ischemic tissues where they secrete a plethora of supportive growth and angiogenic factors. Accordingly, EPCs secretomes represent potential therapeutic agents to induce vascular plasticity and neurorepair after stroke. However, to date, its effective administration remains complex. We will present an innovative nanotechnological approach to encapsulate human EPCs secretomes into magnetic nanocapsules to assist its targeted delivery.

Firstly, we will expose how EPCs-secretomes are harvested and characterized. Then, we will describe EPCs-secretomes encapsulation into poly (lactic-co-glycolic acid) (PLGA) nanocapsules by a double emulsion-solvent evaporation method. We will demonstrate that this technique is highly reproducible and yields size-homogeneous spherical nanocapsules. Also, we will show the inclusion of Superparamagnetic Iron Oxide Nanoparticles (SPIONs) into the polymeric matrix of this nanocarriers. In that way, the nanocapsules acquire magnetic properties which are useful for retention and engraftment.

Finally, we will introduce our ongoing work in the study of the secretome encapsulation efficiency and its release kinetics. Moreover, we will present the assays performed to evaluate the angiogenic potential of the encapsulated EPCs secretomes.



**Figure 1** Schematic illustration of the constituents of our proposed nanocapsules and the expected action mechanism.

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# Pellets with Amphotericin B micellar dispersion for oral administration

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Amphotericin B (AmB) is a low soluble drug useful for the treatment of systemic fungal infections and visceral leishmaniasis (VL) [1]. Currently, all marketed AmB formulations require parenteral administration to achieve systemic effect although an oral formulation would be very interesting [2]. The aim of this work was to prepare amphotericin B loaded pellets.

**Methods:** Three different types of pellets of 500 µm mean size were used: microcrystalline cellulose (MCC), tartaric acid (TAP) and non-pareil sugar beads. Sodium deoxycholate (NaDoC) AmB micellar dispersions were loaded to the pellets to increase the AmB solubility [3]. The effect of two different binders: PVP K90 and HPMC AS was also investigated. The aqueous solution containing NaDoC/AmB/Binder (50:40:10, w:w:w) was sprayed using a fluidized bed coater equipped with a Wurster insert (Mini-Glatt, Glatt®, Binzen, Germany). Once the solution was sprayed, the coated beads were dried inside the fluidized bed. Once the first layer was dried, a second layer containing 1% Eudragit L-100 dissolved in ethanol was sprayed. Different conventional physicochemical techniques (SEM, DSC, XRD, DVS and dissolution rate) were used to characterize the products.

**Results and Discussion:** The coating process was successful when using the MCC. However, non-pareil sugar and TAP beads due to their high aqueous solubility were dissolved during the spraying of the AmB micellar solution and it was not being able to recover any solid product after the process. The yield was higher for those beads coated with HPMCAS as binder than with PVP K90. SEM micrographs showed that the coating technology was efficient to obtain spherical and uniform coated pellets. It was noticed that beads with HPMCAS as binder have less soft surface than the PVP K90 ones which are also less porous. Finally, four different AmB pellet formulations were developed: A1 (AmB-NaDoC-PVPK90), A2 (2<sup>nd</sup> layer on A1-Eudragit L-100), B1 (AmB-NaDoC-HPMCAS) and B2 (2<sup>nd</sup> layer on B1-Eudragit L-100). At DSC and XRD, beads of HPMC AS were less stable than PVPK90 ones. HPMCAS coated beads have a lower T<sub>g</sub> (135°C) so they were less stable than PVPK90 ones (T<sub>g</sub> 165°C). The results of DVS technique were that beads are more stable to changes of temperature and relative humidity after the coating. The change of mass was increasing progressively until 12% of the total weight. They are able to lose the mass in the same order that they took it, which represents a stable formulation. The formulations provided a sustained release profile, which was close to the predicted values and highly pH dependent. The drug release from the enteric coated pellets with Eudragit L 100 after 60 min in the basic media, was almost double than the AmB coated pellets without Eudragit. The drug release profile versus time and pH showed that, due to the pH-dependent aqueous solubility of the drug, the release profiles were relatively higher at pH 6.8 than for any other pH value ranging between 1.2 and 4.5.

In conclusion, it can be stated that the coating of pellets by AmB micellar systems can be considered as a suitable technique to increase the dissolution of AmB for oral administration.

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# Production of controlled and reliable novel emulsions for skin care applications with membrane processes

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This study is part of the H2020 project PeptiCaps whose goal is to design new formulations of emulsions for skin care applications. In this multidisciplinary environment, several key aspects are addressed such as macroemulsifier chemistry, emulsion production, encapsulation and release of active ingredients and skin assays.

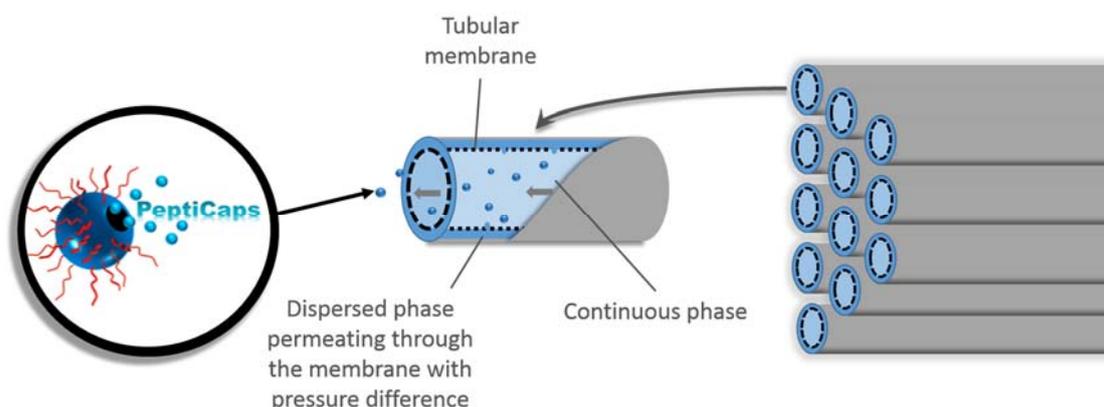
The role of our group within the consortium is to produce both water-in-oil and oil-in-water emulsions using a technique called tubular membrane contactor at pilot scale. This process has many advantages compared to industrial microfluidic processes. These include lower energy consumption and better scalability which are more appropriate for sensitive actives.

Membranes can be used for emulsification either in direct membrane emulsification or premix membrane emulsification [1]. The first technique consists in injecting under mild pressure the dispersed phase through a microporous membrane to the continuous one, whereas premix emulsification relies on injecting a coarse emulsion through the membrane. Both techniques offer their own advantages, premix emulsification produce emulsions of smaller size range and with greater flowrate but direct emulsification does not require a premix step.

In this study, we investigate the ability of membrane process to produce stable oil-in-water or water-in-oil emulsions with the macroemulsifier developed within the project [2].

The influence of both formulations (concentration of emulsifiers, amount of dispersed phase...) and process parameters (flowrate, pressure, membrane length...) on the emulsions obtained (size distribution, stability...) is investigated and systematically compared with model compositions.

Overall, it is shown that the process can be operated for the production of specific emulsions with controlled size distribution. The technique could be an alternative to other emulsification techniques at pilot scale for industrial emulsification.



**Figure 1** PeptiCaps emulsion production with membrane process.

**Acknowledgements** PeptiCaps is funded by EU framework program for research and innovation Horizon 2020 under grant agreement 686141

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# Study of properties of natural adsorbents using for the triclosan treatment

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Nowadays, one of the most promising technologies is the processing of natural raw materials, the utilization of wastes and attraction of ecologically friendly secondary products in economic recycling. At present, different sorbents are used for the treatment of industrial waste waters [1-2], including special artificial adsorbents with hierarchical ministrant structures [3]. Aluminosilicates like diatomite, kaolinite, bentonite and etc. [4-5] are interesting to be studied as sorbents for the waste water treatment due to their folded structure which is reflected in high dispersity, hydrophilicity and good ion exchange properties. Moreover, they are low cost sorbent materials with easy accessible sources.

In this work the physicochemical and adsorption characteristics of natural sorbents of kaolinite, bentonite and diatomite were studied, their sorption parameters were calculated, the morphological structure was studied by the SEM method, nitrogen sorption measurements were performed using the automated surface area of Quadrasorb SI and a pore size analyzer from Quantachrom. It was obtained that the natural sorbents contain SiO<sub>2</sub> is 45.66%; 57.68%; 43.17% respectively. SEM measurements showed gap pores, with a specific surface area from 6.1 to 32 m<sup>2</sup>/g.

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# Composites of glucan microparticles with curcumin targeted to treatment of inflammatory bowel diseases

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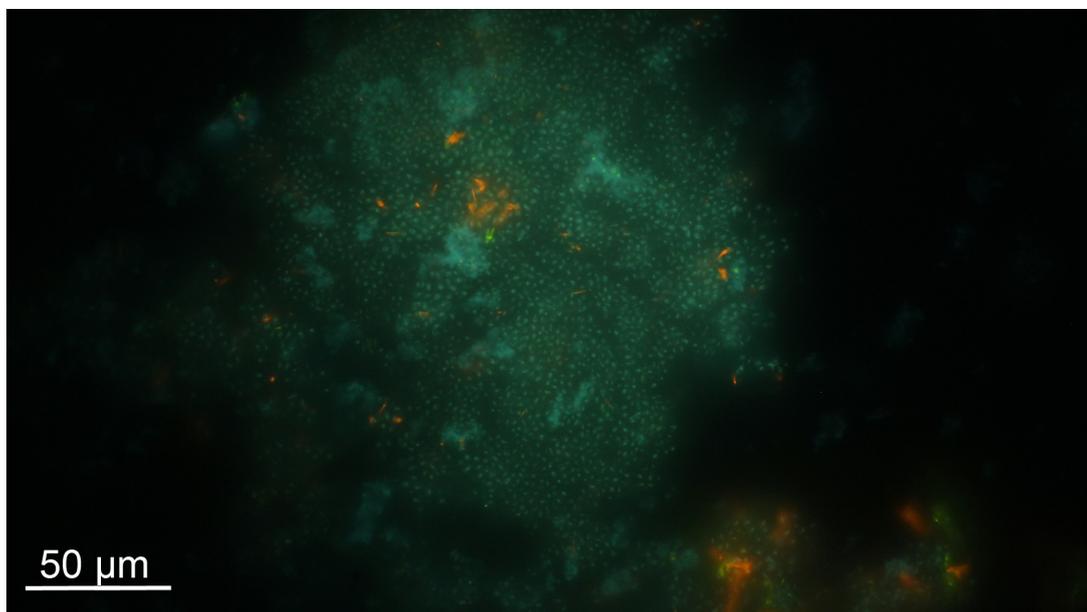
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Glucan particles (GP) are porous hollow microspheres (2-4  $\mu\text{m}$ ) prepared from purified *Saccharomyces cerevisiae* (baker's yeast). Most of the organelles are removed by alkaline and acidic extraction steps. Resulting particles contain some traces of chitin, proteins and lipids but are composed mostly of water insoluble  $\beta$ -glucan polymers that can cause enhanced macrophage activation and modulate immune system response [1].

Curcumin (CC) is a biologically active polyphenolic compound with promising anti-inflammatory potential. On the other hand, curcumin, practically insoluble in water, shows low bioavailability and chemical instability in a biological setting [2]. Incorporation of curcumin into GP-CC composites can improve its bioavailability and enhance its anti-inflammatory effect.

GP-CC composites were prepared using several methods. Briefly, curcumin was dissolved in an organic solvent, mixed with pre-prepared GPs and solvent was then evaporated using different protocols. Resulting composites were then examined via SEM, confocal microscopy, vibrational spectroscopies, XRD and other methods. Achieved content of curcumin in composites was quantified. Anti-inflammatory properties of prepared GP-CC composites were tested *in vitro* and pilot *in vivo* test was also conducted.



**Figure 1** Fluorescence micrograph of one type of prepared GP-CC composites.

**Acknowledgements** The financial support of Ministry of Health of the Czech Republic, grant nr. 16-27522A is gratefully acknowledged

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# Innovative eco-compatible approaches for shale gas extraction

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The exploitation of shale gas, in Europe or elsewhere, can be hindered by a number of environmental concerns. The public is particularly concerned about possible leaks of chemicals used in the fracturing fluid formulations, as well as spills of produced fluids on the surface. While best-practice procedures are generally recommended to prevent such accidents, it could be advantageous to design formulations that minimize environmental risks.

In this study, aimed at formulating greener frac fluids for European shale gas plants, we developed aqueous dispersions of some polysaccharides (guar gum, sodium hyaluronate, sodium alginate and hydroxypropyl cellulose) or of some viscoelastic surfactants (mainly containing sodium oleate) and investigated the effects of different salts and/or surfactants on their thermal and rheological behaviors.

Furthermore we explored the potential efficacy of photo- or voltage-induced processes in order to control and modify the viscosity of frac fluids during the different stages of the shale gas extraction.

## **Acknowledgements**

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# Non-ionic water-in-oil microemulsions as vehicles for enzyme drug delivery: the model case of horseradish peroxidase (HRP)

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Enzymes are widely used as therapeutic agents due to their ability to bind and act on their targets with great affinity and specificity converting them to the desired products [1]. These characteristics lead to the development of enzyme drugs for a wide range of disorders. As nanodispersions are increasingly becoming very important drug delivery systems, the incorporation of enzyme drugs in their microenvironment offers the potential for localized and sustained delivery but also improved absorption and bioavailability [2]. The structure of water-in-oil (w/o) microemulsions, composed of water nanodroplets dispersed in a non-polar medium, provides several benefits for use as media for enzymatic encapsulation and biotransformations. They have the ability to overcome solubility limitations, enhance the enzymatic activity and stability, while providing an interface for surface-active enzymes. Additionally, the need of non-ionic microemulsions, as drug delivery systems arises from their numerous beneficial properties. They are, generally, less toxic and less irritating to cellular surfaces and also act as transcellular permeation enhancers. Although non-ionic surfactants due to being not charged are generally characterized as “mild” for the enzymes, studies regarding this particular type of microemulsion lag behind the amount of work done in other categories [3].

In the present study, nonionic water-in-oil (w/o) microemulsions composed of Extra Virgin Olive Oil (EVOO) and/or Isopropyl Myristate (IPM) as the continuous oil phase were constructed. Both systems consisted of Polysorbate 80 (Tween 80) and distilled monoglycerides (DMG) as surfactants and a mixture of water and propylene glycol (PG) as the dispersed phase.

Structural characterization of the proposed systems, regarding particle size distribution was obtained using Dynamic Light Scattering (DLS) and the interfacial properties of the investigated systems were evaluated by Electron Paramagnetic Resonance (EPR). These systems, which are appropriate for pharmaceutical applications, were successfully used as media to carry out enzymatic reactions. *Horseradish peroxidase* (HRP) retained its catalytic activity towards oxidation catalysis of the synthetic substrate 2, 2'-azino-bis [3-ethylbenzo-thiazoline-6-sulfonic acid] (ABTS), in both systems studied. Furthermore, the influence of aqueous phase and surfactant content on the activity of peroxidase was investigated and a kinetics study was conducted.

The effectiveness of these systems in delivering the model enzyme drug is currently under investigation.

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# New ruthenium complexes as dyes for dye-sensitized solar cells

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The use of dye-sensitized solar cells is a well established strategy for solar energy conversion because of their inexpensive manufacturing and environmental friendly nature [1]. These devices use indistinctly natural or synthetic dyes to harvest energy from light. An electric current is then generated from excited electrons forwarded towards an electrode. Artificial dyes, usually based on transition metal coordination complexes such as ruthenium [2], are the most widely employed since they yield greater efficiencies than natural dyes [3]. At present, considerable development is focused on the design of novel dye structures to enhance the dye-sensitized solar cell performance.

In this work, two new ruthenium complexes (Fig 1) [4, 5] are investigated as potential sensitizers of solar cells. These complexes are soluble in organic solvents and water, which makes them useful for water-based photochemical processes. Complex I displays two absorption peaks at 330nm and 450nm, whereas complex II shows a broad band in the 400-600nm range. Dye-sensitized solar cells containing these two photoactive complexes are fabricated and tested (Fig 2). Efficiency values are slightly higher to previously reported data for natural dyes [6].

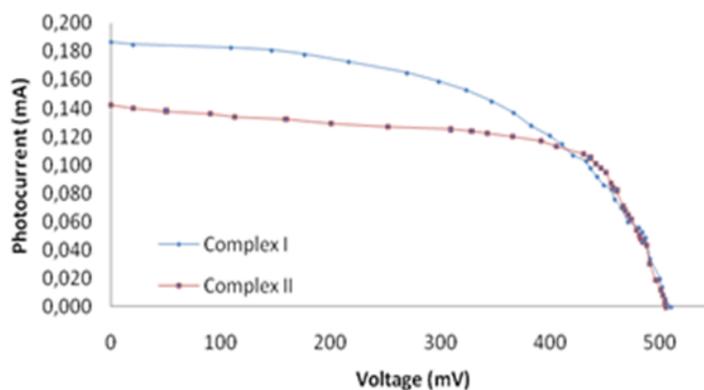
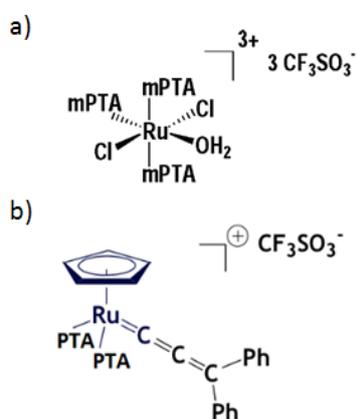


Figure 1 Structures of complexes I (a) and II (b)

Figure 2 Photocurrent-voltage curves of DSSC

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# Influence of silicon in calcium phosphate cements on the formation of nanopores

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A novel biomaterial system was developed to produce a composite of calcium phosphate-calcium silicate. We used calcium phosphate cements because they can be improved easily by the addition of substances to either solid or liquid phases during the setting reaction. This study reports the effects of silicon (Si) on brushite cement given that silicon is an essential trace element required for healthy bone and connective tissues [1,2]. The cement was prepared using a mixture of a solid phase, silicon-doped ceramic (Si-TCP) that is composed of  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) and silicocarnotite and monocalcium phosphate monohydrated (MCPM), with an aqueous solution. The structure of the silicon doped was determined by X-ray diffraction patterns and SEM images for fractural surface. X-ray diffraction patterns of CPC and Si-CPC at 10%, 20%, 40%, 60% and 80% showing the main peaks of brushite, silicocarnotite, hydroxyapatite,  $\beta$ -TCP, monetite, and calcium silicate. The silicon doped cements (Si-CPC) prepared with low Si content were composed of crystalline phases of brushite and silicarnotite. However the cements prepared with high Si content were composed of amorphous phases with silicarnotite, hydroxiapatite and calcium silicate. The cement porosity was about 40% with a shift of the average pore diameter to nanometric range with increasing Si content. Interestingly this new cement system provides a matrix with a high surface area of up to 29 m<sup>2</sup>.g<sup>-1</sup>.

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# Brushite hybrid prepared with aqueous extract of *Hibiscus sabdariffa*

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We prepared a hybrid material with good bone regeneration, made up of Brushite cements whose liquid phase is formed by dissolution of an aqueous extract of *Hibiscus sabdariffa*. *H. sabdariffa* is a medicinal plant, whose aqueous and ethanol extracts act as antimicrobial agents for Gram-positive and Gram-negative bacteria. The aqueous extract of *Hibiscus* was prepared from the dried red calyces. The pulverized samples were subjected to maceration in shaking with hot water and lyophilized. Brushite cement was prepared from an equimolecular mixture of  $\beta$ -tricalcium phosphate and monocalcium phosphate monohydrate. For the setting reaction the aqueous extract at a powder to liquid ratio of 1 g / mL was used. *H. sabdariffa* extract showed the highest antibacterial activity against Gram-positive and Gram-negative bacteria, with Minimal Inhibitory Concentrations (MIC), ranged between 4-10 mg/mL and Minimal Bactericidal Concentrations (MBC), ranged between 5-25 mg/mL. The characterization of Hibiscus/cement was performed by X-ray diffraction pattern and DSC. The DSC analysis had a heating rate of 10 °C/min in all cases. The extract had an endothermic peak at 84.63 °C corresponding to water. The increase of the heat flow produces internal rearrangement, followed by two endothermic peaks at 193 °C and 238 °C. The mechanical properties of the cements with the *Hibiscus* extract improved notably, increasing the DTS by 75% compared to Brushite. The amount of polyphenols released from the *Hibiscus*/Brushite matrix was measured by UV spectroscopy at 520 nm, by the Folin-Ciocalteu method, being able to apply the equation of Peppas. Conclusions: This new material *Hibiscus*/Brushite collects the conditions of being potent bacteriostatic and bactericidal agent. It does not induce structural alterations in Brushite and improves its mechanical properties.

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# Application of thin-layer wicking method for surface free energy determination of commercial and biological hydroxyapatite

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Biological apatite is the major constituent of the hard tissues such as bones and teeth [1,2]. It is also known that the chemical formula and properties of synthetic hydroxyapatite are similar to those of main inorganic constituent of bones and teeth. Therefore, this mineral has been widely applied as a biomaterial for implantation i.e. for orthopedic and dental applications for repairing or substituting hard tissues, and also as the drug delivery systems. Hydroxyapatite (HA) can form a bond with bone tissue and facilitate osseointegration which refers to a direct structural and functional connection between ordered, living bone and the surface of a load-carrying implant.

The surface free energy changes are accompanying the all processes occurring at a solid surface. Therefore, the knowledge about these changes is very helpful for better understanding and prediction of their occurrence. In the case of a flat solid surface the contact angle measurement is principal method for the surface free energy determination. But many naturally occurring or artificial solids occur only as powders and they are widely used in pharmacy, cosmetic, painting, mineral enrichment, etc., where the solid particle wettability has a crucial meaning.

In this study the comparison between commercial and biological hydroxyapatite was made in the aspect of wetting properties, which was determined by thin layer wicking method with the help of Washburn equation [3].

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# Development of O/W nanoemulsions as carriers of vitamin D: A structural study

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Food fortification can be used to increase vitamin and mineral content of various processed foods thus preventing micronutrient dietary deficiencies. In the present study oil-in-water (O/W) edible nanoemulsions were developed and studied as carriers of vitamin D (cholecalciferol) to be used for the fortification of milk and juices [1].

The nanoemulsions were produced using polysorbate 20, soybean lecithin and their mixtures as surfactants. The dispersed oil phase consisted of soybean oil, cocoa butter and their mixtures. Coarse emulsion premixes were passed through high pressure homogenizer (800-1000 bar) to produce fine droplets. The influence of system composition and preparation conditions on the stability of the nanoemulsions was investigated using Dynamic Light Scattering (DLS).

Based on their stability and droplet size distribution, three (3) nanoemulsions were chosen as carriers of vitamin D: (A) 90% w/w water, 4% w/w Tween 20 and 6% w/w Soybean oil, (B) 90% w/w water, 4% w/w (Tween 20/Lecithin, 3:1) and 6% w/w Soybean oil, and (C) 90% w/w water, 4% w/w (Tween 20/ Lecithin, 3:1), 6% w/w Soybean oil /Cocoa Butter (1:1).

Different concentrations of vitamin D ranging from 0.1 to 0.5 µg/mL, were encapsulated in the oil cores of the proposed nanoemulsions and their physical stability was evaluated by the maintenance of size distribution for several weeks.

Finally, interfacial properties of the proposed nanoemulsions in the presence and absence of vitamin D were studied using Electron Paramagnetic Resonance (EPR) spectroscopy and an amphiphilic spin probe [2]. Spin probe's mobility was decreased upon increase of systems complexity and also the presence of vitamin D indicating the formation of more rigid interfacial layers.

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# Development of model lipid membranes based on non-hydroxy phytosphingosine for the studies of skin barrier properties.

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Stratum corneum (SC), which consists of multilayers of corneocytes and intercellular lipids, provides a physical barrier between inner human body and outer environments. The intercellular lipids are mainly composed of several kinds of ceramides (Cer), free fatty acids (FFA) and cholesterol (Chol), and arranged in a lamellar structure in SC. It has been considered that the lipid lamellar organization in SC plays a crucial role for the skin barrier. To clarify the effect of lipid characteristics on the skin barrier, artificial lipid membranes mimicking the lipid organization in SC would be an attractive model. In this study, we developed a simple preparation method for model lipid membranes containing a large amount of non-hydroxy phytosphingosine (NP), which is one of the major species of Cer [1] and considered to be difficult to homogeneously disperse in a model membrane due to its low miscibility [2].

Model lipid membranes consisting of mixtures of Cer (NP and NS (non-hydroxy sphingosine), Chol and FFA were prepared by modifying the spray method introduced by Jager et al. [3]. We analyzed their lamellar structures by synchrotron X-ray diffraction at SPring-8 (40B2). The X-ray energy and sample-to-detector distance were set to 14 keV and 530 nm, respectively. In order to make clear the phase behaviors of the model membranes, we collected their diffraction patterns between 25°C and 85°C with a heating rate of 1 K/min.

The X-ray diffraction measurements have revealed that a lamellar structure with a repeat distance of about 5 nm and the orthorhombic and hexagonal structures in the lateral lipid packing were formed in the model lipid membranes as observed in the mammalian SC. The phase transition temperature from orthorhombic to hexagonal lipid packing increased as the NP/NS ratio increased. Recent studies have reported a significant negative correlation between the content ratio of NP in SC and the TEWL value in the atopic dermatitis skin [1][4]. These results suggest that NP may promote the formation of a less water permeable lamellar structure by stabilizing the more tightly packed orthorhombic structure. In this study, we succeeded in preparing sufficiently homogeneous lipid membranes containing large amounts of NP, potentially serving as model membranes for the studies of skin barrier properties.

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# Isolation and quantification of peripheral Extracellular Vesicles

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Extracellular vesicles (EVs) are a heterogeneous population of cell-to-cell shuttles released into the extracellular environment. They are classified depending on their size and biogenesis into microvesicles (MVs) and exosomes (EXOs) [1]. The importance of EVs consists in their capacity to transfer information to other cells thereby influencing the recipient cell functions [2]. EVs contain cell specific biological information and their composition (proteins, miRNAs, mRNAs, lipids and nucleic acids) depends on cell type and its physiological data. EVs populate different biological fluids such as serum, plasma, cerebral spinal fluid, urine, saliva, modulating biological processes also at remarkable distance from their site of origin.

Despite the increasingly recognized relevance of EVs, their detection, physical characterization and classification are still actively debated and suffer from several issues that hamper their possible applications. In particular, most of the applied protocols for EV purification based on differential centrifugation (DC) suffer from low purity of EXOs for the presence of protein contaminants, while size and molar concentration determination remain critical factors for a complete profiling of exosomes [3].

In this study, we aimed to achieve an accurate separation of MVs and EXOs from serum samples belonging to two different studied populations (Multiple Sclerosis patients and Healthy Control subjects).

A first DC step was employed to separate MVs from EXOs, then two different strategies were followed for EXOs purification. The first strategy was based on a classical sucrose cushion centrifugation while the second one was a novel approach based on a proteinase K treatment. Results obtained from the two different used routes in terms of residual protein contaminants were compared, showing that the proteinase K treatment allows a better purification of EXOs from proteins.

After this, to investigate the purity grade of EV preparations and accurately assess their size distribution and amount, a combined approach consisting of Dynamic Light Scattering and a Colorimetric Nanoplasmonic Assay was used.

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# Nanoformulations based on essential oil as a modern form of fungicide

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Pathogenic fungi cause infections in humans, plants and animals. Among the species of fungi that can cause mycoses of plants, the most serious threat are the representatives of *Fusarium* and *Alternaria* [1-3]. Whereas for humans and animals, mycosis of the skin and its appendages are caused by dermatophytes (*Trichophyton*, *Microsporum*, *Epidermophyton*), yeast-like fungus (*Candida*, *Pitorosporum*, *Cryptococcus*) and mold fungus (*Aspergillus*, *Scopulariopsis*) [4]. For this reason the pharmaceutical, cosmetic and agrochemical industry is still looking for active ingredients, of the natural origin, showing antimicrobial activity. In addition to the active compounds, also the form of carries plays the important role in the effectiveness of the product [5-10].

The aim of this work was an elaboration of new carrier forms of fungicide formulations characterized by high biological activity.

The nanoemulsions containing four various essential oil (*INCI: Cinnamomum Zeylanicum Oil, Melaleuca alternifolia Leaf Oil, Lystospermum Scoparium Oil, Thymus vulgaris oil*) were obtained using both, the low-energy (PIC) and the high-energy emulsification methods (ultrasonication). The systems were stabilized by Polysorbate80. The physicochemical properties e.g. stability, viscosity and droplet size of the dispersed phase were determined. Additionally the activity of prepared systems, against strains of pathogenic fungi of plants (*F. culmorum*, *Ph. Cactorum*), dermatophytes (*T. mentagrophytes M. gypseum*) and molds (*S. brevicaulis*, *A. niger*) was examined. Macroemulsions and pure essential oils were used as comparative samples. Fungicidal activity was tested by the method of linear growth of mycelium on an agar medium.

On the basis on the obtained results, it was found that nanoemulsions based on essential oils could be applied as the effective form of fungicide products. The elaborated formulations was characterized by higher fungicidal activity, compare to pure oils and macroemulsions. Moreover, the best activity against the studied fungi showed the nanoemulsion based on *Lystospermum Scoparium Oil* (manuka essential oil).

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# The application of ion selective electrode to monitor calcium adsorption from solution onto metal oxides particles

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Ion selective electrodes (ISE) were successfully applied to determine free calcium concentration in blood plasma [1] or river water [2]. Calcium ions play very important role in soil aquatic chemistry [3]. All these systems (plasma, natural waters) are complex colloidal solutions. Nevertheless, this cheap and simple potentiometric technique enabled to determine the level of calcium in investigated samples.

Metal oxide particles dispersed in electrolyte solution are charged due to ion adsorption. Especially adsorption of  $H^+/OH^-$  ions and multivalent ions like  $Ca^{2+}$  influence on surface charge and colloid stability. Two popular techniques using to investigate cations adsorption are ICP-MS and radioisotope method [4]. These methods are reliable and precise but applied equipment is very expensive or analytical procedure is cumbersome and long.

In our presentation we will show how  $Ca^{2+}$  ISE can be used to monitor free calcium concentration in  $TiO_2$  and  $Al_2O_3$  suspensions. We will check how pH, indifferent electrolyte concentration, oxide loading, temperature, influence on the results of ISE measurement. Our results will be compared with data obtained by using other analytical techniques like ICP-MS or spectrophotometry. Finally, we will analyze the experimental results using surface complexation modelling (SCM) of calcium adsorption on oxides.

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# Glucose Biosensors Based on Electrochemically Deposited Polymer Layers

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Glucose oxidase (GOx) based electrodes are used in design of glucose biosensors [1-4] or biofuel cells [5,6]. GOx-based electrodes are suitable for the generation of electrical current, which is proportional to glucose concentration in the sample [1-4]. If GOx is used in biosensor design an efficient redox mediator, which is capable to transfer electrons efficiently from the active site of GOx to the electrode is required. For example one natural electron acceptor of GOx is oxygen, but some other redox mediators can be used for the same purpose. Some electrochemically deposited polymers are showing good mediating properties therefore they can be applied as redox mediators in enzymatic biosensors [1-5]. In addition the application of electrochemically deposited polymers currently is rapidly expanding in such areas as actuators, gas separation membranes, and charge storage devices. Electrochemically deposited polymers can be encountered in a range of charge storage devices such as electrolytic capacitors and high capacity rechargeable batteries. The key property of the polymers used in such systems is the ability of the polymer to accumulate and to store electrical charge.

During this research 1,10-Phenanthroline-5,6-dione (PD) and 9,10-phenanthrenequinone (PQ) was electrochemically polymerized on a graphite electrode and on carbon nanotube and/or graphene oxide modified electrodes using potential cycling, electropolymerization conditions were optimized. Modified electrodes were studied by means of cyclic voltamperometry (CV), electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM) and scanning electron microscopy. Formed polymer layers demonstrates electric conductivity, unique oxidation/reduction properties and great electrochemical activity and applicability in GOx-based biosensor design. Gathered EIS data were evaluated applying most suitable equivalent circuits. The study revealed redox mediating properties of some here evaluated electrochemically deposited polymer layers, which were deposited on graphite electrodes.

**Acknowledgement:** This research was funded by a grant (No. SEN-21/2015) from the Research Council of Lithuania.

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# Layer-by-layer system based on Cellulose Nanofibrils for capture and release of cancer cells in microfluidic device

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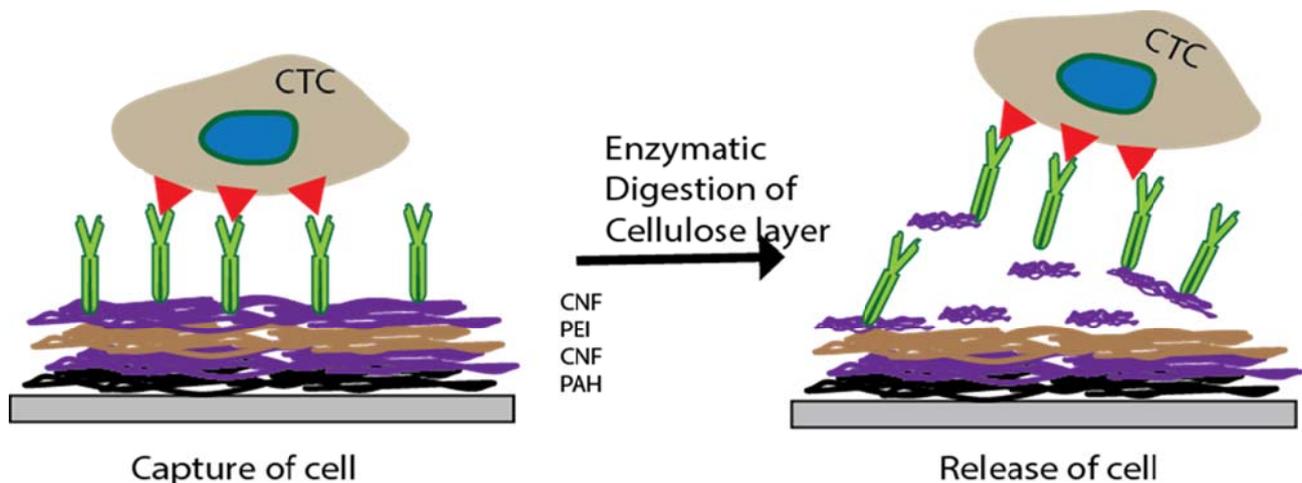
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Selective isolation of cells, without inducing any phenotypic changes and maintaining cell viability will preserve the information necessary for down stream analysis. Here we present an ultra-thin coating on the surface of disposable microfluidic device based on cellulose nanofibrils (CNF), that is modified to capture cells and for later release.

Layer-by-layer technique facilitates the production of the thin coating of cellulose onto polymeric surfaces, using PAH/CNF/(PEI/CNF)<sub>n</sub> layer structure and the outermost CNF layer is modified by grafting antibody via EDC coupling to form an affinity based cell capture surface. We demonstrate an efficiently capture and release of cells. The release is done by selectively degrading the cellulose layers using enzyme and cells can be collected without losing cell viability.



**Figure 1** Schematic of the developed coating in the microfluidic device; used for capture and release of circulating tumour cells (CTC).

# Effect of protein corona on the immunological specificity of functionalized lipid nanocapsules.

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The surface of nanoparticles in the circulatory system is in contact with a biological system containing a complex mixture of ions, proteins, lipids and sugars which can alter the surface characteristics, forming a “biocorona” [1]. Thus, the protein corona formed by proteins adsorbed onto the original nanoparticle surface can reduce the targeting ability of such functionalized nanosystems and additionally promote their opsonization and recognition by the mononuclear phagocyte system which drive to a rapid clearance of the intravenously injected nanoparticles [2].

In this work, we have tried to simulate the formation of the protein corona on the surface of functionalized lipid nanocapsules with the aim of analyzing: a) the corona composition; b) the effect on the colloidal characteristics of the nanoemulsion; and c) the influence on the surface. For that, we have used lipid immuno-nanocapsules, which have been recently developed as nanocarriers for lipophilic drugs delivery. The surface of this nanocapsules has been previously modified with antibody molecules by means of a covalent conjugation obtaining a vectorized nanosystem with immuno-specific recognition [3].

The experiments of protein adsorption on lipid immuno-nanocapsules have been studied by incubating these systems in different serum protein solutions (including fetal bovine serum and human serum) at 37°C. The presence and characteristics of the protein corona have been studied by gel electrophoresis measurements and electrokinetic behavior. The colloidal characterization include size analysis and colloidal stability experiments in different media. Finally, the immunological response of the immuno-nanocapsules with and without protein corona was also quantified against the specific ligand of the surface antibody molecules. Our results suggest a loss of specificity when immuno-nanocapsules are in contact with a complex biological medium as a consequence of the formation of a protein corona that can alter the surface properties of the nanosystem.

**Acknowledgements** The authors wish to express their appreciation for the financial support granted by the research projects: MAT2013-43922-R and MAT2015-63644-C2-1 –European FEDER support included– (MICINN, Spain).

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# Slipdisc: A versatile platform for point of care diagnostics

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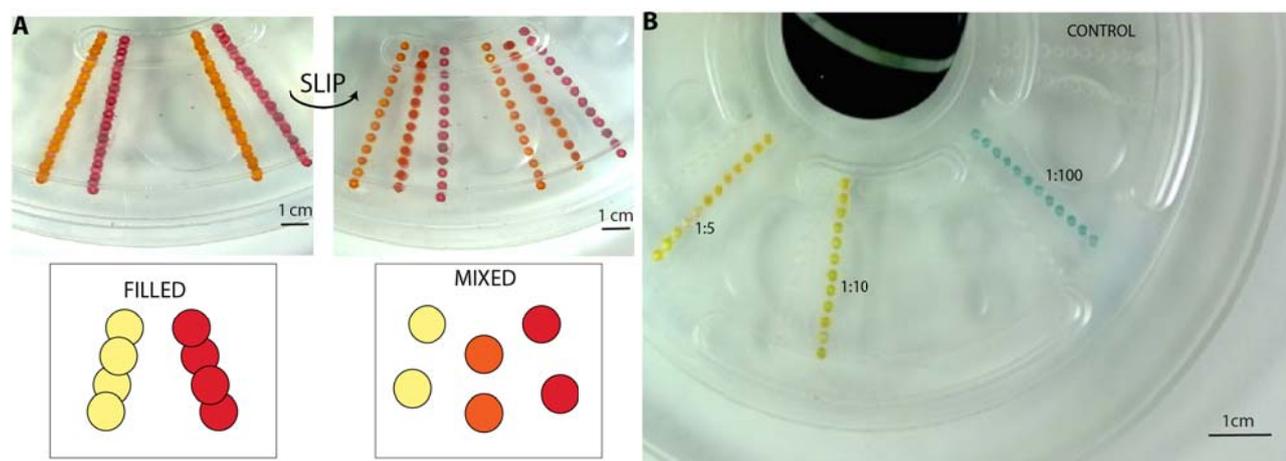
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We report a microfluidic sample preparation platform called “Slipdisc” based on slipchip technology. Slipdisc is a rotational slipchip that uses a unique handwinded clockwork mechanism for precise movement of specially fabricated polycarbonate discs.

In operation, the microchannels and microchambers carved on the closely aligned microfluidics discs convert from continuous filled paths to defined compartments by the slip movement, the surfaces of the discs outside of the microfluidic channels have a superhydrophobic coating. The clockwork mechanism introduced here is characterised with a food dye experiment and a conventional HRP TMB reaction, using digital camera and colorimetric analyse.

In a last step lactate dehydrogenase (LDH) enzyme levels were detected with the Slipdisc platform. LDH is a crucial biomarker for neonatal diagnostics. The colorimetry based detection of LDH was performed with an unmodified camera and an image analysis procedure based on normalising images and observing changes in Red channel intensity. The analysis showed close to unity coefficient of determination ( $R^2 = 0.96$ ) in detecting the LDH concentration when compared with a standard time consuming Chemical Analyser. This demonstrates the excellent performance of the Slipdisc platform. The versatile point of care sample preparation platform should ideally be suited for multitude applications at resource-limited settings.



**Figure 1** Two different characterisation of the Slipdisc: A) Schematic representation of the filling and mixing process food dyes that are filled first in a series of alternating wells forming a continuous path on the bottom and top discs. A slip step compartmentalizes the wells and the reagents on the top wells are mixed with reagents in the bottom wells. B) characterisation with a two-step enzymatic bioassay using the same principle to A. Three different concentrations of the HRP enzyme to PBS solution (1:5, 1:10, and 1:100) reacting with the TMB substrate with a single click step and producing three different colours. A control solution with no HRP enzyme produces no colour.

# Polymeric nanocarriers loaded with organoselenium compounds: fabrication and antimicrobial evaluation

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Organoselenium compounds, among them benzenoselenazol-3(2H)-ones and diphenyl diselenides have been studied as antioxidant, anti-inflammatory, antitumor, antiviral and antimicrobial agents, showing promising biological activity [1-5]. However, even though these compounds have a great potential as new pharmaceuticals, their practical use is still limited due to their low solubility in water. Herein we present a way to overcome this disadvantage through the development of polymeric nanocarriers.

Polymeric micelles, as versatile drug delivery systems, have demonstrated particular strength in solubilizing hydrophobic drugs while eliminating the use of toxic organic solvents and surfactants. In this work we present two types of polymeric nanocarriers composed of poly(ether) and poly(ester) block copolymers for entrapment of various biologically active benzenoselenazol-3(2H)-ones and their open chain analogues – diphenyl diselenides. The polymeric micelles were prepared by thin-film hydration or co-solvent evaporation methods and characterized by dynamic light scattering, electron and atomic force microscopy to provide information on their size, shape and morphology. The physically stable systems, with high solubilization efficiency were evaluated as potential antimicrobials towards various gram-positive bacterial strains and yeasts.

**Acknowledgements** The financial support of the National Science Centre (NCN) under grant no. UMO-2013/09/D/ST5/03814 is much appreciated.

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# A new generation of cutting oil: triple nanoemulsion potentiates the effect of machine cutting performance and its stability.

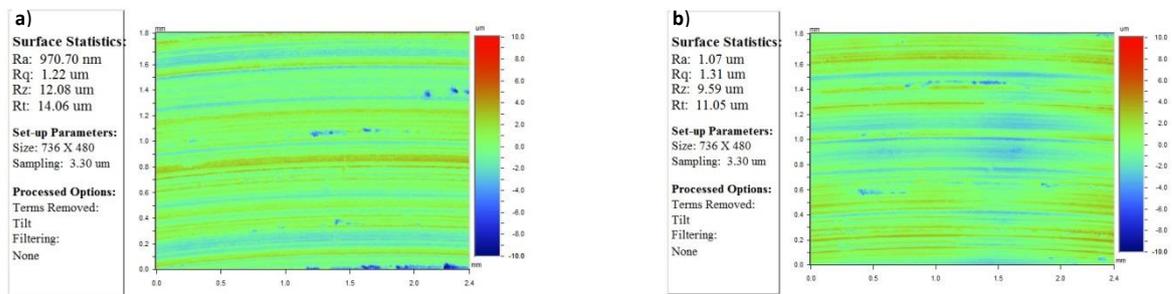
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Cutting fluids role is to reduce manufacturing costs by lubricating and cooling the tool that is by reducing the tool wear, increase tool life and achieving the desired size, form and surface finish of the work piece[1, 2]. This paper aims to formulate a new generation of metal working fluid nanoemulsion (triple nanoemulsion type) based on vegetable oils and study the effect of its composition on metalworking performance. It also focuses on the action of cutting fluids, and the factors affecting stability of emulsions formed from the cutting oils. The most important objectives of this paper is discussed as follows: **1)** preparation of different oil-in-water emulsion with selected combination of emulsifiers, corrosion inhibitor and as biocide, **2)** identifying the optimum Different hydrophilic-Lipophilic Balance (HLB) value that gives the more stable emulsion and **3)** evaluation of the cutting fluid performance different tolls as tool chip tribometer and drill dynamomseter. The surface morphology of the cutting mild carbon steel using 3D optical profilometer for selected mild carbon steel sample after and before cutting process. The results obtained decided that the new formulated cutting oil (E1) shows a good metalworking fluid in compare with commercial sample.

**Figure 1:** 3D optical profilometer for **a)** E1 and **b)** Comercial cutting oils at rotating speed 30 rpm.



**Acknowledgements** The financial support of.....

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# Controllable particles from proteins insoluble in water

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Many vegetable proteins, such as zein and other cereal proteins are poorly soluble in water and are therefore underused as food ingredients. This poor solubility can be turned into an advantage by using a solvent-antisolvent sequence [1] to produce sub-micron particles by nucleation and growth. Aqueous suspensions of such particles behave as a solution in many respects. The method provides therefore an important step towards more intensive use of sustainable protein sources.

The work presented here focuses at the stability and functionality of the protein particles as Pickering particles, both in oil-water and water-water emulsions [2]. During formation of the particles, the effect of pH and the effect the presence of specific food-grade polymers on the size and aggregation was studied [3]. The suppression of aggregation is essential for a wide applicability of protein particles. It turned out that both non-charged (dextran, pullulan) and charged polymers (chitosan, pectin) adsorb on zein and gluten particles, and are able to enhance or weaken the tendency to aggregate. The adsorption complicates the description of the polymer/particle systems in terms of only depletion.

**Acknowledgements** The financial support of the EU (ITN 2012 SOMATAI grant 316866) is gratefully acknowledged.

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# Associative natural systems with antibacterial and antioxidant properties based on polysaccharides and aminoguaiacol

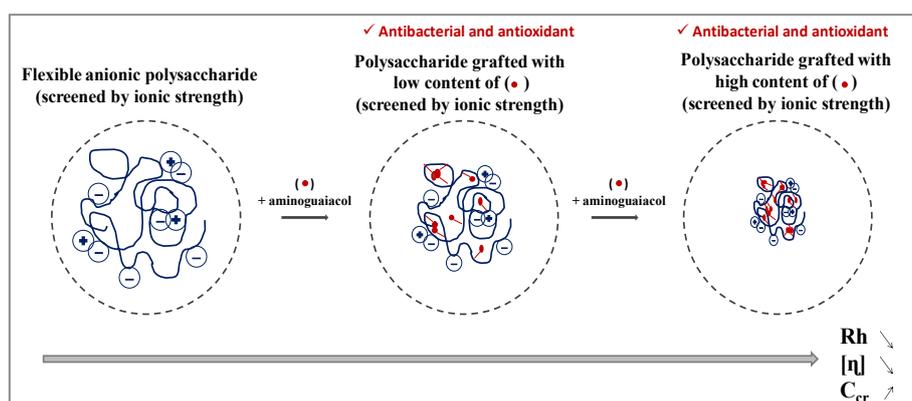
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Preservatives are essential additives in the composition of cosmetic and food aqueous formulations. They protect these formulations and prolong their shelf-life by preventing microbiological contaminations and also by protecting against oxidation. For a long time, human used synthesized molecules as conservators. However, today, some of them are suspected to be toxic and dangerous for health. Consequently, there is a considerable interest to find alternatives. The use of natural antimicrobial products such as plant-derived compounds could be a good alternative. Indeed, many studies have found that these molecules are active and possess various properties as antimicrobial [1] and antioxidant [2] and/or antifungal [3]. Furthermore, it is often necessary to control the rheology of the aqueous formulations by the use of viscosifying agents such as polymers, in particular polysaccharides.

The aim of our project is to create new natural preservatives for aqueous formulations based on polysaccharides and molecules issued from plants. Polysaccharides could act as viscosifying or emulsifying agents and natural compound could bring antibacterial and/or antioxidant properties to the whole system. To elaborate these type of system, aminoguaiacol (a molecule derived from the natural compound guaiacol) has been chemically grafted onto a polysaccharide (carboxymethylpullulan, CMP or alginate, Alg) [4], [5]. The grafted polysaccharides were characterized by FTIR and <sup>1</sup>H-NMR spectroscopy to confirm and quantify the grafting. Then, to evaluate the viscosifying properties of the synthesized systems, their physicochemical properties were studied in a dilute regime and a semi-dilute regime by light scattering, fluorescence and rheology. The antibacterial activities of the synthesized products against *Staphylococcus aureus* were assessed using a counting method. The antioxidant activities of the derivatives were also highlighted using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method.



**Figure 1** Associative properties of a polysaccharide grafted with various contents of aminoguaiacol in salt media.

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# Silica nanoparticles assembly at the liquid-liquid interface to improve the selectivity of the electrochemical extraction of active molecules.

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Electrochemistry at the liquid-liquid interface (LLI) permits the transfer of electrically charged species from the aqueous to the organic phase. At the same time, the selectivity of the electrochemically modulated extraction is one of the limits of this methodology [1].

Liquid-liquid interfaces are known to act as a scaffold for the ordering of nanometer-sized objects. Research is ongoing into the use of nanoparticles assembly at the LLI as a platform for tunable optical devices, sensors and catalysis. For instance, Fang *et al.*[2] have self-assembled gold nanoparticles at the water and dichloroethane interface and demonstrated mirror-like properties of these monolayers.

Our research focusses on the assembly of silica nanoparticles at the LLI, as a way to improve the selectivity of solutes electrochemical extraction and the sensitivity of their detection.

Two type of silica nanoparticles have been considered : Dense silica nanoparticles and mesoporous silica nanoparticles synthetized according to Bein *et al.*[3] The assembly of these particles on the interface has been followed by AC voltametry. These results show that increasing concentration of nanoparticles in a 10mM aqueous LiCl solution caused a shift in the potential of zero charge and higher initial capacitance values when the particles are at the interface, proving that the nanoparticles assemble at the LLI.

Two dye molecules were considered as model molecules for this study: the cationic Methylene blue and the anionic Eosin B. The thermodynamics of the interaction of these molecules with the colloidal dense and mesoporous particles has been described by the means of spectrophotometry and ultrafiltration and the kinetics of adsorption of methylene blue was investigated by the means of the stopped flow technique. As adsorption on non-porous silica is just on the surface of the particles, the process occurs very quickly. However with the mesoporous nanoparticles, diffusion of Methylene blue through the pores results in a much slower adsorption rate than with the dense nanoparticles.

The effect of the particles assembly at the LLI on the transfer on these ionic dyes were monitored electrochemically. Unlike Methylene blue, the Eosin transfer is not modified by the presence of nanoparticles at the interface. When both dyes are present in the system, the voltammogram reflects a perturbation of the interface, presumably by the formation of a hydrophobic ion pair, inducing non-controlled peak currents. The addition of nanoparticles at the interface, by dissociation of the ion pair, allow the control of the electro-modulated transfer of the dye. Finally, nanoparticles allow the decrease of the Methylene blue limit of detection by electrochemistry at the liquid-liquid interface.

Ongoing research is now focusing on molecular imprints in the nanoparticles assembling at the interface.

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# Formulation of a natural antimicrobial agent: food grade essential oil nanoemulsions with long-term stability containing a natural surfactant

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Nowadays, food products comprising of natural ingredients are in a great demand. Addition of food preservatives to increase the shelf life of the products or keep the properties constant is unavoidable. Moreover, the human life has been facing a critical situation in terms of food supply whereas tons of foods are lost or wasted due to the spoilage. Thus, Essential oils as natural alternative can play a strong role as an antimicrobial, antioxidant, anti-cancer, flavouring agent, and many others.

Oregano oil is one of the most powerful essential oils with considerable antimicrobial properties that can be applied in different foods. Oil-in-water nanoemulsions have been utilizing as a delivery system, however, nanoemulsions are highly instable due to Ostwald ripening and the presence of water-soluble compounds in essential oils makes them more prone to this instability phenomenon.

In this study, we attempted to formulate oregano oil-in-water nanoemulsions using Quillaja Saponin. Nanoemulsions were created successfully but instable to Ostwald ripening. Addition of a low amount of hydrophobic compound proceeded the formation of nanoemulsions with 75nm droplet diameter stable for at least 60days of storage at ambient temperature (25°C). Diffusion ordered spectroscopy using nuclear magnetic resonance (DOSY NMR) and Cryo-SEM technique were employed to characterize the formed nanoemulsions. Additionally, we evaluated the impact of storing temperature, salt, and pH on the stability of the nanoemulsions.

We also optimized the production conditions of the nanoemulsions using response surface method (RSM) and central composite design (CCD) to gain insight into the optimum production formula. This study provides valuable information about formulation of a real natural antimicrobial agent not only from a scientific point of view but also from a practical point of view for food industry.

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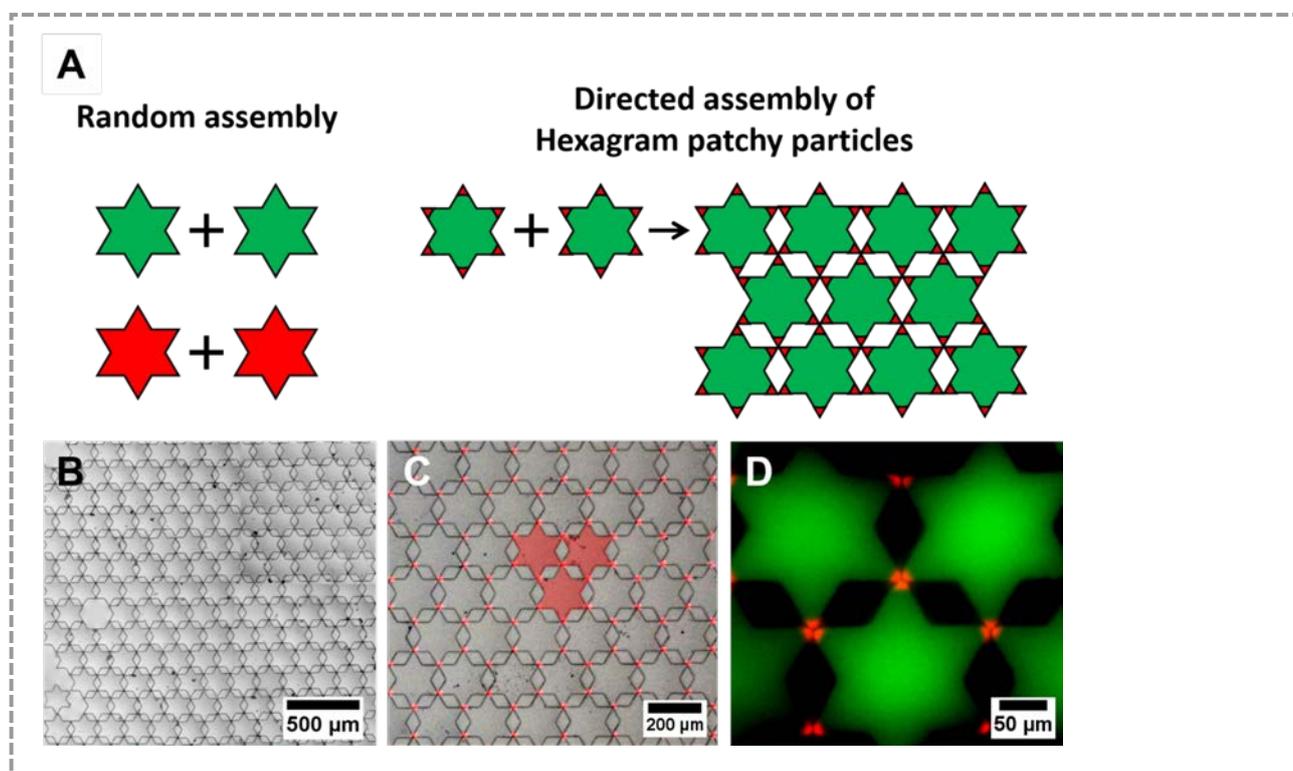
# Directed self-assembly of patchy hexagram particles at the air-water interface

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We present directed self-assembly of patchy hexagrams into macroscopic structures at an air-water interface. A micromolding technique is used to fabricate patchy hexagram particles that are composed of hydrophilic bodies and weak hydrophobic patchy vertices; the size of these hydrophobic patches can be controlled precisely using the micromolding technique. Interface deformation driven by geodesic curvature and the chemical heterogeneity of the particle surface induce capillary attractions and directs the assembly of patchy hexagram particles. Patchy hexagram particles assemble into millimeter-scale two dimensional regular structures by minimization of the interfacial free energy of the liquid-liquid interface. We discuss the importance of controlling the directionality as well as the magnitude of interactions to achieve macroscopic assemblies.



**Figure 1** Directed assembly of patchy hexagram particles

**Acknowledgements** This work was supported by Global Research Laboratory (NRF-2015K1A1A2033054) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT (Information and Communication Technologies) and Future Planning.

## Conductance measurements in Laponite-stabilized inner nanostructured emulsions in water.

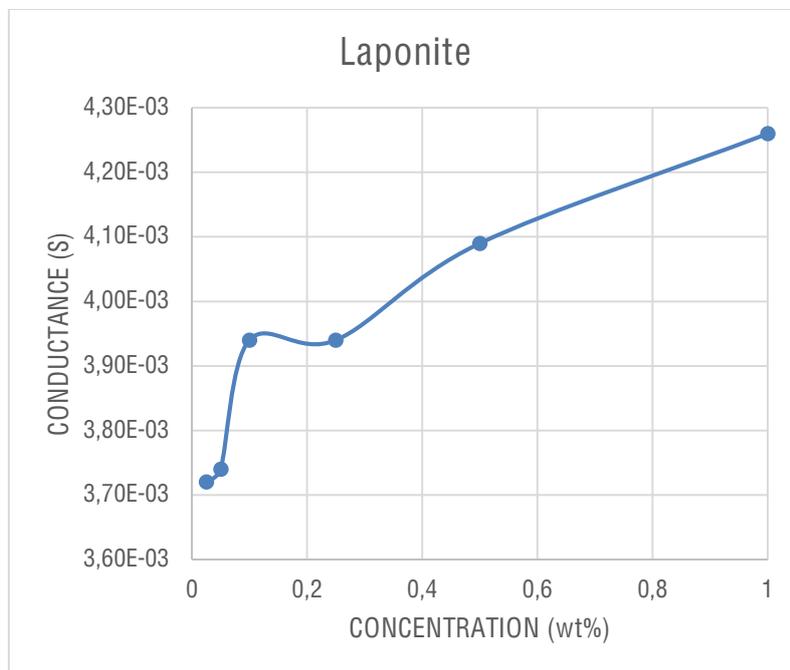
**C. Barth, S. Chenti, L. Denis, T. Dégoussée, W. Mouhali, F. Muller**

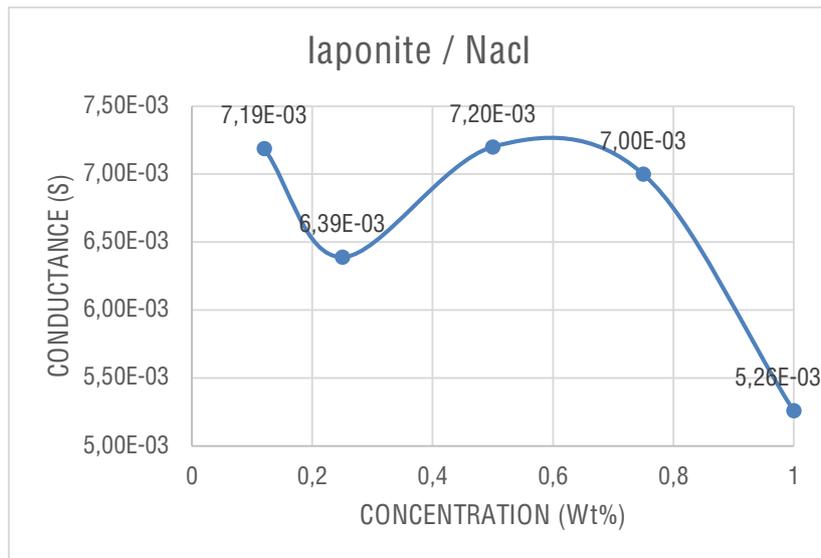
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We show the possibility of creating a dense cover around lipid-based liquid crystalline droplets using laponite nanoplatelets as stabilizer [1]. This is an interesting route for the design of new Colloid-ISAsome assemblies in which dense protective armours could be advantageous such as controlled delivery. The investigation of the structural by means of CRYO-TEM microscopy, DLS, and SANS with contrast variation conditions have been determined [2-4].

Herein, we use conductivity measurements as trigger to deduce the ratio between the free  $\text{Na}^+$  and the adsorbed laponite on the droplets. We used Phytantriol (PT, 3,7,11,15-tetramethylhexadecane-1,2,3-triol) as the lipid to create the nanostructured drops, laponite (radius of 14nm, thickness 1 nm). The conductivity measurements have been performed in AC conditions (ranging from 60 Hz to 600 KHz) in order to check out the electrical response of the soft materials. The results help in understanding the conditions in forming such complex and interesting smart assemblies.





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# Heteroaggregation of oppositely charged particles in the presence of multivalent ions

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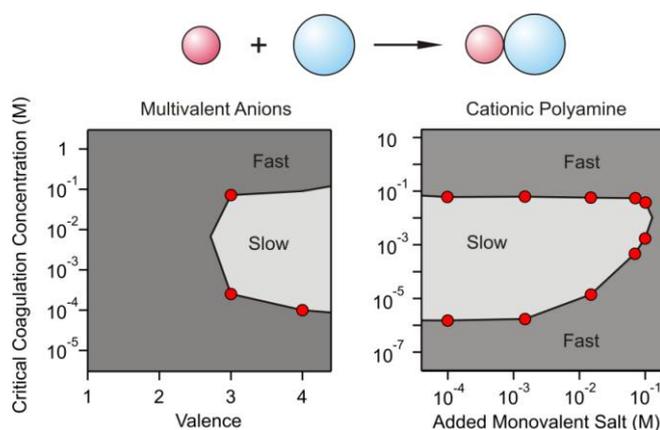
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Schulze and Hardy reported that colloidal suspensions can be effectively destabilized by multivalent ions [1, 2]. The classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory states that the aggregation of particles during the destabilization process of colloidal suspensions, which is induced by increasing the salt concentration, follows the mechanism of slow and fast aggregation regimes. The transition between these two regimes occurs at a certain concentration, referred to as the critical coagulation concentration (CCC). Particle aggregation can be categorized into homoaggregation and heteroaggregation due to the identity of particles involved. Homoaggregation, dealing with identical particles, has been well-studied. Researchers already have a reasonably good understanding of homoaggregation by proposing Schulze-Hardy rule and inverse Schulze-Hardy rule [3]. However, heteroaggregation, dealing with different particles, is understood to a much lesser extent.

In this work, heteroaggregation processes in the presence of multivalent ions were studied by time-resolved dynamic light scattering for the first time [4]. We investigated here binary suspensions of positively charged amidine and negatively charged sulfate latex particles. The two types of particles are oppositely charged in the presence of monovalent salt. However, in the presence of multivalent ions, the charge of one particle type becomes neutralized and then charge reversal occurs, while the other particle type remains highly charged. In this region, the heteroaggregation stability ratio goes through a maximum when plotted *versus* concentration. This region of slow heteroaggregation is wider than the one in homoaggregation. Furthermore, the calculated stability ratios for heteroaggregation based on DLVO theory sensitively depend on the boundary conditions used to calculate the double layer force.



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# Colloidal self-propelled rotators

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Self-propelled colloids, so called microswimmers, propel themselves through solution by consuming a chemical or physical fuel. Within this PhD-project, we develop novel wet-chemical syntheses to produce microswimmers that display non-linear motion such as, for example, rotating, circling and spiraling trajectories that can be studied in situ using optical microscopy. To achieve this goal, close-packed monolayers of colloidal particles are sputter coated under a large angle, resulting in an asymmetric platinum coating, as described by Archer et al. [1] This platinum coating catalyses the decomposition of hydrogen peroxide, which allows the microswimmers to propel themselves through solution. In order to achieve a more complex swimming motion, we further break the symmetry of the microswimmers by preparing them from colloidal cubes rather than spheres [2]. By aligning the crystal domains in the colloidal monolayer [3], we are able to control the shape of the resulting platinum coating of the microswimmers.

In addition to studying the trajectories of these microswimmers, we study their dynamic self-assembly into hierarchical structures to shed light on the general principles of dynamic self-assembly. Here, the self-assembled structures purely result from the self-propelled motion of the microswimmers.

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# Self-assembly in a colloidal system with tunable magnetic interactions

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In a suspension of microbeads in ferrofluid, the effective magnetic behavior of the microbeads can be altered. This is used to study the self-assembly of the beads with varying interactions. The beads are confined into two dimensions and observed by transmission light microscopy. The positions of two types of beads with different magnetic properties are extracted from the images by image analysis. In this way, phases can be mapped depending on the bead interactions and the composition of the two types. The experimental results can be reproduced by computer simulation, which can be used to predict the self-assembly with new parameters.

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# Superparamagnetic Microswimmers driven by a Rotating Magnetic Field

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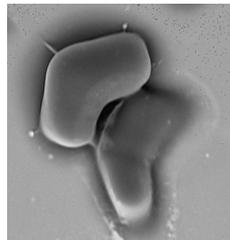
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Various micropropellers, such as bacteria flagella or artificial magnetic micro/nano helices, always exhibit chirality which allows them to move. Here, we introduce particles which are anisotropic but not chiral. Experiencing a rotating magnetic field, they exhibit chirality and propel like helices[1].

Unibody microswimmers are fabricated using continuous flow lithography [2]. It allows a large variety of shapes and components for this micro-object. Our Janus particles are functionalized in order to have one magnetic side. We put superparamagnetic nanoparticles inside the hydrogel matrix in order to ensure alignment of our particles with the magnetic field. In the absence of the field, particles lose their magnetic properties and do not experience remanence or hysteresis. Thus, high concentration of these particles can be reached without experiencing clusterization. The rotating magnetic field brings chirality to this chevron shape microswimmer and propels this object with speed comparable to an optimized helix.

Weak rotating magnetic fields can actually actuate remotely our micropropellers and steer them in different viscous fluids. Potential use of these superparamagnetic particles are biomedical applications, magnetic separation, data storage, enabled by the ability to control them with an external weak magnetic field.



**Figure 1** SEM image of chevron shaped micro propeler

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# Rheological properties of isolated telechelic star polymers.

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Telechelic star polymers (TSP's) are macromolecules formed by a number of diblock copolymers (arms) anchored to a common central core, being the internal monomers solvophilic and the end monomers solvophobic. Very recent studies [1-3] have demonstrated that TSPs constitute self-assembling building blocks with specific softness, functionalisation, shape, and flexibility: depending on different physical and chemical parameters, e.g. a number of arms  $f$ , solvophobic-to-solvophilic ratio  $\alpha$ , temperature  $T$  and solvent quality  $\lambda$ . In equilibrium, the geometrical conformation of TSP's features a well-defined number of attractive spots on their surface and therefore they may be considered as a realization of soft patchy particles. As a first step to understand the rheology of a suspension of this kind of polymers, we systematically study the behavior of one isolated TSP under linear shear flow by means of a combination of Multi-Particle Collision Dynamics for the solvent and standard Molecular Dynamics for the monomers. We evaluate the average star shape descriptors, patches distinctive features and the rotation frequency as a function of the shear rate ( $Wi$ ) for a wide range of the parameters mentioned above. We demonstrate that for low values of  $Wi$  ( $Wi < 3$ ) the geometrical properties and the patches behaviour of the TSP's do not change, while for  $Wi > 3$  the radius of the gyration ( $R_g$ ), the asphericity ( $S$ ) and the relative shape anisotropy ( $\delta$ ) increases for most cases, from spheric-like ( $S \sim 0$  and  $\delta \sim 0$ ) to ovoid-like geometry. Regarding patches behaviour, we find three different tendencies: depending on  $\alpha$  and  $\lambda$ , the number of patches can increase, decrease or remain the same as  $Wi$  increases. Finally, we present some results concerning the equilibrium structural properties of dilute suspensions of TSP's.

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# Unraveling the mechanisms for assembly and disassembly of dense complex of inorganic charged nanoparticles and polyelectrolytes of opposite charges in the regime of very high ionic strength

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In systems of inorganic charged nanoparticles (NPs) and polyelectrolytes (PEL), there is a critical threshold ionic strength at which the electrostatic interactions are so screened that complexation no longer operates [1]. Starting from a mixture of NPs and non-associated PEL in a highly salted solution, it is thus possible to induce complexation by desalting if the ionic strength is lowered below the critical threshold of transition. However, it has been demonstrated that the sizes and morphologies of the complexes are out-of-equilibrium systems whose structures depends on the kinetics of desalting [2]. The mechanisms operating during desalting have been investigated.

The experiments are carried out on a model system consisting of PDADMAC (PEL positively charged) and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles coated with negatively charged PAA [2]. Spectacular results were obtained by light scattering on the behavior of the system during several cycles of desalting/salting to cross the critical threshold ( $I_c \approx 0.6$  M NH<sub>4</sub>Cl) of complexation. When the system has undergone a "quench" of desalting initiating the formation of aggregates, these aggregates completely re-dissociate if a strong salt addition made a few minutes after quenching. By cons, if this addition is carried out several hours after hardening, there are persistent remaining aggregates. SAXS and SANS studies reveal that the overall size and morphology of these aggregates is dependent on the ionic strength of quench and time elapsed between the quench and the addition of salt. The quench of desalting can also freeze the system in particular structures and possibly can be utilized to tune the structures at nanometer scale as per the requirement [3]. The internal reorganization mechanism is found to be responsible for evolution of aggregates in these systems.

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