

POSTERS

1. Interactions in Colloids and at Interfaces:

*dispersive interactions, charged colloids, hydrophobic effect, colloidal
stability*

RHEOLOGICAL STUDY OF HYDROPHOBICALLY ASSOCIATING ALGINATE DERIVATIVES – NON IONIC SUGAR ESTER AQUEOUS SOLUTIONS

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Interactions between surfactants and water soluble polymers often play a key role on the rheological properties of industrial formulations. In this work, these interactions and their rheological influences were studied with mixtures of a hydrophobically-modified alginate derivative and a non-ionic sugar ester surfactant, trehalose caprate, obtained through enzymatic synthesis [1-2]. Due to its biocompatibility and biodegradability, such a formulation can be of great interest for cosmetic, food and pharmaceutical applications.

We studied the influence of the addition of trehalose caprate on the rheological properties of a 1.3wt% C₁₂-alginate aqueous solution. As the trehalose caprate concentration was increased, the zero-shear viscosity of polymer solution was observed to first strongly increase, whereas at higher surfactant concentrations, between 25 and 35 mg/L, the zero-shear viscosity decreased. The increase in zero-shear viscosity was attributed to the reinforcing action of the hydrophobic interaction network through mixed micelles formation between the surfactant and the hydrophobic alkyl chains of alginate. This decrease could result from the screening of the hydrophobic interactions through the formation of micelles around individual alkyl chains.

At higher trehalose caprate concentrations, above 35mg/L, the zero-shear viscosity starts re-increasing. This unexpected behavior may be explained by the capacity of the micelles to rearrange into rodlike structures at high surfactant concentrations [3]. These micelles, by creating bridges between the alginate chains, contribute to restore the hydrophobic network. This hypothesis is confirmed by dynamic rheological measurements and relaxation time evaluation.

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HETEROAGGREGATION AND STABILITY OF MIXTURES OF POSITIVE AND NEGATIVE SILICA COLLOIDS

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We investigate structure formation in mixtures of positively and negatively charged silica particles as a function of mixture composition. Primarily dispersed in water, the particles were transferred to ethanol. The positive charge is possible because of a thin alumina layer deposited on silica particles. The ethanol-based dispersions were diluted to 4% wt, mixed, and stirred to obtain a series of mixtures with a constant total volume. An unexpected stability was exhibited by the mixtures which contained up to 50% dispersion of negative particles. On the contrary, even an extremely small quantity of positive particle dispersion mixed with the negative particle dispersion, results in large aggregates, density fluctuations and sediment showing yield stress.

Atomic force microscopy was used to determine the particle diameter (12.1 nm for negative silica and 15.2 nm for positive silica) as well as the surface properties of the alumina layer. Electrophoretic mobility measurements confirmed the fact that the sign of particle charge did not change after the transfer to ethanol, but the mobility decreased. The mobility goes through zero at a certain composition of mixtures. Conductivity measurements showed a very low ionic concentration in comparison to the aqueous samples. Static and dynamic light scattering were used to investigate the presence of clusters mainly in the stable mixtures and in the supernatant of some sedimented mixtures. Optical microscopy and cryo transmission electron microscopy were used to observe the aggregate morphology. Long-term sedimentation experiments were performed on two series of mixtures to check the reproducibility of all observed phenomena.

Several hypotheses were considered to explain the phenomena which occurred in the stable samples: the screening of negative particles by the positive ones, redistribution of counter-ions around a primary cluster, and change in the sign of charge of the initially negative particles. The last hypothesis is the only one which does not come in contradiction to the experimental facts. We proved its validity by measuring the mobility of initially negative particles after the particles were dispersed in the supernatant of the centrifugated positive particles. Aluminium ions adsorb on the negative silica particles and change their surface charge.

*INTERFACIAL PROPERTIES TUNE THE ENZYMATIC ACTIVITY OF LIPASE
ENTRAPPED IN THE QUATERNARY WATER-IN-OIL MICROEMULSION
CTAB/WATER/PENTANOL/HEXANE*

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The enzymatic activity of Lipase VII from *Candida rugosa* was studied in the quaternary water-in-oil microemulsion CTAB/water/pentanol/hexane. The enzyme-catalyzed hydrolysis of p-nitrophenylbutyrate was found essentially independent from the water/surfactant ratio. On the other hand, the enzyme kinetics was strongly affected by the cosurfactant/surfactant ratio. The interfacial composition and the reverse micelles size, as well as, the substrate partition between organic bulk and surfactant aggregates, have been determined through pulsed gradient spin-echo NMR measurements. The correlation of the microemulsion structure with enzyme activity has therefore been possible. The lipase affinity for p-nitrophenylbutyrate is lower in microemulsion compared to water because the hydrophobic effect is weaker in the former system. The turnover number is unaffected from the reverse micelles size and from the interfacial bromide concentration while is strongly dependent on the interfacial composition. The data presented indicate a marked influence of the extent of interfacial surface on the catalytic efficiency of lipase.

THE COSURFACTANT ROLE IN A FOUR COMPONENT W/O MICROEMULSION

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The microstructure of the quaternary water-in-oil microemulsion CTAB/water/*n*-pentanol/*n*-hexane has been investigated by means of the pulsed gradient spin-echo NMR technique over a wide range of composition. The composition of the continuous organic phase and of the interfacial phase has been determined through the analysis of the *n*-pentanol self-diffusion coefficient. The size of the reverse aggregates has been evaluated from the CTAB self-diffusion coefficient. The correlation of the reverse micellar size with interfacial composition has therefore been possible. Results coming from both water dilution lines and interface dilution lines have been analyzed according to suitable models. A "master plot", i.e., a graphical representation that allows us to display the data collected at all the possible compositions of the four components system, is also proposed.

INTERACTIONS OF CATIONIC TENSIDES WITH MALEIC POLYELECTROLYTES: INFLUENCE OF THE HYDROPHOBICITY/HYDROPHILICITY OF THE COMONOMER ON BINDING

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The binding of dodecyl- (DPC) and cetylpyridinium chloride (CPC) to alternating copolymers of maleic acid (MA) with vinyl acetate (MAVA) and styrene (MASty), and to a block-like copolymer with methyl methacrylate (MA(MMA)₃), that is composed of a segment of three MMA units per one MA unit, was investigated by potentiometry and fluorescence probing. In these copolymers, the hydrophilic/hydrophobic is varied as follows: MAVA < MASty < MA(MMA)₃. All measurements were performed at 25°C in aqueous solutions containing 0 - 0.1 M NaCl. The binding isotherms were treated according to the model of cooperative binding of surfactants by polymers.[1] The results evidenced that the surfactant binding by MA(MMA)₃ shows the lowest cooperativity, still it starts at very low free surfactant concentrations, i.e. below 1×10^{-6} M. This observations was attributed to an important contribution of hydrophobic interactions between bound surfactant and hydrophobic segments on the MA(MMA)₃ chain to the binding. The binding by MASty copolymer starts at free surfactant concentrations comparable to the MA(MMA)₃ case, but the cooperativity is from 10 to nearly 200-times larger. The lower cooperativity for MA(MMA)₃ is explained by the fact that the ionized binding sites on the polymer are separated by relatively long neutral segments of the chain, allowing shorter lengths of the bound surfactant tails to interact with each other. MASty shows two-step binding isotherms with DPC, in agreement with literature data;[2] in the case of CPC, the second step of binding coincides with the formation of free CPC micelles in equilibrium with the polyelectrolyte-surfactant complex. The association behavior in the presence of the most hydrophilic MAVA copolymer is very different. The critical association concentration (cac) of CPC in the presence of MAVA is independent on salt concentration, so is the constant of cooperative binding. This type of dependence was experimentally observed for the first time. It was verified also by fluorescence technique for the system cetyltrimethylammonium chloride (CTAB)/MAVA and is in agreement with calculations based on a self-consistent field lattice model proposed by Wallin and Linse.[3]

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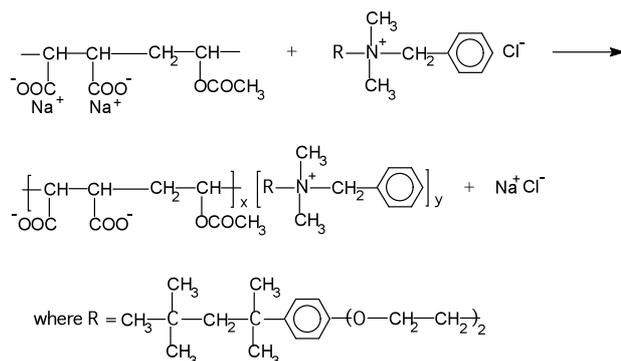
POLYELECTROLYTE TITRATION OF MALEIC POLYELECTROLYTES WITH CATIONIC TENSIDES

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Maleic acid polyelectrolytes (MP) are recommended in applications such as antiscaling agents for geothermal water, phosphate substitutes in detergent formulations, soil conditioners, additives in the tanning process of hides, [1, 2] etc. In these applications the polyelectrolyte (PE) is used in very low concentration or the effluents resulted are much less concentrated. Consequently, it was necessary to develop a sensitive method to detect very low concentrations (few ppm) of PE in aqueous media. In our contribution a new method of determination of very low amounts of a MP, namely maleic acid-alt-vinyl acetate copolymer in aqueous solution was developed. In this method the Na maleate-vinyl acetate copolymer (NaM-VA) was titrated with a cationic tenside (Hyamine 1622®) and the end point was assessed by turbidimetric measurements. The interaction between NaM-VA polyelectrolyte and Hyamine 1622® (Hy) is presented below.



The method is valid for MP concentration between 1.2-12.0 ppm, the sensitivity being 1 ppm. It was observed that the interaction between MP and Hy is influenced by the MP and Hy solution concentration. The presence of a low molecular salt (LMS) such as Na₂CO₃ disturbs the measurements if the ratio MP: Na₂CO₃ is higher than 1:0.25 g:g. A trend to deviations from a 1:1 stoichiometry (from the electrostatic point of view) was observed which increases when the tenside concentration or the LMS concentration increases. This kind of interaction can be considered as a borderline case to polyelectrolyte-polyelectrolyte complexes formation, including supramolecular structures.

Acknowledgement This work was supported by the MATNANTECH program, project no. C111/2002.

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FLUORESCENCE MICROSCOPY APPLIED TO THE DYNAMICS OF LATEX COLLOIDS

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The Brownian motion of carboxylated polystyrene latex, was investigated at low concentrations in aqueous solutions by dynamic fluorescence microscopy [1]. For three probe radii, i.e., 0.5, 0.265, and 0.1 μm , the estimated diffusion coefficients correspond well with the theoretical predictions if thermal and electrostatical contributions are included in the discussions. It was also possible to discriminate latex interactions with an added polymer. Added polyethylene glycol showed no or very weak interaction with the latex until the polymer overlap concentration was reached, when the formation of a polymer network slows down the latex diffusion. Polyvinylpyrrolidone, on the other hand, has a more pronounced interaction with the polystyrene latex and slowed down the diffusion even at polymer interactions in the ppm-range.

The behaviour of the latex probes with radii 0.5 and 0.1 μm were investigated in concentrated styrene-butadiene latex suspensions up to 40 % [2]. The long-time self-diffusion coefficient decreased as the volume fractions increased. For hard sphere suspensions the long-time self-diffusion has similar concentration dependence as the relative viscosity. The maximum packing fraction has to be predicted for the systems. Various theories concerning the dependence between the concentration and relative viscosity were evaluated.

Thus, dynamic fluorescence microscopy is a feasible technique for estimating the diffusion coefficients of small particles in the presence of additives. It can be used over a broad range of particle volume fractions, i.e., 0-40%, with high accuracy.

The next step in our project is exploring the interaction between starch and latex colloids. The starch can be used to tune the charge density and charge sign of the colloid surface. Beginning at low latex volume fractions and increasing the amount of colloid, microscopy measurements will yield information from a system resembling the composition of a real coating colours used for paper surface treatment.

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PHASE DIAGRAM FOR AN ATTRACTIVE SQUARE WELL POTENTIAL WITH A LINEAR TAIL WITHIN THE VAN DER WAALS-LIKE THEORY

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We study the phase equilibrium behavior of a typical colloidal dispersion by the van der Waals-like theory. In this theory, the colloid-colloid potential is split into two parts: a repulsive part modeled by the hard-core potential and an attractive part modeled by the square well potential plus a linear tail potential. The theory is numerically elegant for the colloidal free energy is analytic and, physically, the model can be used to study the role played by the strength and range of interactions on formation of coexisting phases. The effect of the strength of the interaction can be simulated by varying the width of the square well potential (γ parameter) while that range of interaction by changing the slope of the linear potential (λ parameter). In this work, we consider three separate cases. First, we fixed the threshold values γ_{th} , being $\gamma_{th}^{LL} = 0.221$ for liquid-liquid and $\gamma_{th}^{SS} = 0.0329$ for solid-solid, and increased λ to examine the appearance of the liquid-liquid and solid-solid coexistence curves which were both calculated with respect to their liquid-solid counterparts. Second, we fixed the threshold values λ_{th} , being $\lambda_{th}^{LL} = 0.325$ for liquid-liquid and $\lambda_{th}^{SS} = 0.0456$ for solid-solid, and increased γ to bring in the strength of the interaction. In these two cases, the calculations showed that a switching on of γ or λ has the consequence of inducing the stable liquid-liquid or the metastable solid-solid coexisting phases. Finally, we maintain a given γ plus λ . Here the calculated liquid-liquid and solid-solid phase diagrams can be analyzed in finer details to exhibit the combined influences of the strength and range interactions.

BILAYER RIGIDITY AND THE SIZE OF LIPID VESICLES

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We present experimental data and calculations showing a systematic effect of electrolyte on the behavior of lipid bilayers. Unilamellar, nearly monodisperse vesicles were prepared by repeated freeze-thawing cycles. Charged lipids (DOPG) in salt-free solutions were found to form vesicles of about 150 nm. When electrolyte is added, the size decreases rapidly to attain a minimum at about 10 mM. Upon further increasing the ionic strength, the size increases again; in this regime the nature of the added salt plays a role. Uncharged lipids (DOPC) behave likewise, except that at extreme (high or low) ionic strengths they form a dense lamellar phase rather than a vesicle dispersion.

Theoretical SCF (Self Consistent Field) calculations show that the Helfrich bending rigidity k_c correlates well with the vesicle size, in the sense that a larger rigidity leads to a larger size. This is supported by experiments and calculations involving lipid mixtures. It follows that the vesicles as we prepare them must be equilibrium systems. Indeed, the size responds to lipid concentration as well, which should be expected for equilibrium dispersions of this kind.

HYDROPHOBIC EFFECT AND POLYMORPHISM OF MICELLES

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Tendency of surfactant to form micelles in solutions is their fundamental property that affect their applications. This tendency is measured by critical micelle concentration CMC or concentration at which micelles first start. It is the CMC1, when micelles have the spherical shape. Principle of Gibbs-Kuri points on conditions of existence of different shapes of micelles as ball, cylinder and others at another CMC (CMC2, CMC3,...), which depends upon the structures of the hydrophilic and hydrophobic parts of the molecule and also upon temperature and additional electrolyte.

We have studied existing of different values of CMC of some surfactant by measuring of surface tension, viscosity and electroconductivity. From 25°C CMC increases with temperature. Value of CMC decreases with addition of the nonorganic salt. Thermodynamic values of activation energy of micellization are present in this work too. Results is discussed.

FLUORESCENCE CORRELATION SPECTROSCOPY, LIGHT SCATTERING AND ATOMIC FORCE MICROSCOPY STUDIES OF POLYSTYRENE-*BLOCK*-POLY(2-VINYLPYRIDINE)-*BLOCK*-POLY(ETHYLENE OXIDE) MICELLES

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Polymeric nanoparticles formed by triblock copolymer polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide), PS-PVP-PEO, in aqueous media were studied by fluorescence correlation spectroscopy [1], light scattering and atomic force microscopy. The studied polymeric nanoparticles exist in the form of (i) core/shell micelles in acid solution at pH lower than 4.8 and (ii) three-layer onion micelles [2,3] at higher pH. Since water is very strong precipitant for PS, both types of micelles have kinetically frozen spherical PS cores. The core of the former micelle is surrounded by a soluble shell formed by partially protonated PVPH⁺ and PEO, while the core of the latter micelle is surrounded by a compact insoluble layer from deprotonated PVP and a soluble PEO shell. The micellization behavior of PS-PVP-PEO micelles is accompanied by a secondary aggregation of micelles, which is provoked by stirring, shaking and also by filtration of the solutions. Therefore fluorescence correlation spectroscopy (FCS) which, in contrast to light scattering techniques, does not require filtration, was used as the main experimental technique for the characterization of non-aggregated micelles.

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EXPERIMENTAL STUDY OF AMPHIPHILIC BLOCK COPOLYMER MICELLES WITH HYDROPHOBICALLY MODIFIED SHELL-FORMING BLOCKS

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Symmetrical amphiphilic copolymers, e.g. polystyrene-*block*-poly(methacrylic acid), PS-PMA, associate when dissolved in organic selective solvents and form spontaneously spherical micelles. Polymeric micelles contain insoluble cores and protective soluble shells. High-molar-mass block polyelectrolyte, such as PS-PMA, are insoluble in water, but the aqueous solutions of micelles may be prepared indirectly, e.g., by step-wise dialysis into water.

The behavior of hydrophobically tagged PS-PMA micelles (with naphthalene and anthracene attached to polymeric chains) was studied in aqueous solutions by a combination of fluorescence correlation spectroscopy (FCS) and other fluorescence techniques, together with dynamic light-scattering and atomic force microscopy (AFM). The hydrophobic tags at the ends of PMA blocks do not like aqueous medium and try to bury back in the shell [1]. Their spatial distribution is a result of the enthalpy-to-entropy interplay. In this work, we used octadecylrhodamine B (ORB) as a micelle-specific label for FCS study [2]. Results of the latest studies for modified polyelectrolyte micelles will be presented and discussed.

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DEPLETION AND STRUCTURAL FORCES IN CONFINED POLYELECTROLYTE SOLUTIONS

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Monte Carlo simulations and density functional calculations have been performed for charged macromolecules confined to planar slits. The force between the confining walls has been evaluated as a function of separation, while keeping the chemical potential of the macromolecules constant. The electrostatic interactions have been approximated with a screened Coulomb potential, but have also been treated more explicitly within the framework of the primitive model of electrolyte solution. Highly charged spherical particles as well as flexible polyelectrolyte chains in confinement give rise to depletion and structural oscillatory forces as a function of surface separation. The sign and/or magnitude of the surface charge have no dramatic effect on the qualitative behaviour of the confined liquid. With neutral or oppositely charged surfaces an accumulation of charged aggregates is seen in the slit driven by the repulsive interaction between the aggregates, while equally charged surfaces give rise to a pure depletion. The net charge, the range of interaction as well as the particle density affect the details of the force curve. For spherical aggregates, the period of the oscillations scales approximately as the inverse cube root of the bulk aggregate concentration. Confined polyelectrolyte chains share some of these properties, but they do also display some different behaviour. One clear difference is that the polyelectrolyte net charge, that is the degree of polymerization, has no effect on the osmotic pressure. This is an indication that the polyelectrolyte chains do not pack as spheres but rather as cylindrical aggregates. Another difference is that the effective repulsive interaction between polyelectrolyte chains can be more long ranged and oscillatory forces appear more readily than for a corresponding solution of equally charged spherical macroions.

A STUDY ON FOAM FILMS STABILIZED BY A FLUORINATED SURFACTANT

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Foam films have been widely used to study the interaction of interfaces covered with adsorption layers of amphiphiles. Fluorinated surfactants have found application for some special purposes, for instance oil recovery, fire fighting and also in medicine. However, there are only few investigations of foam films with such surfactant [1, 2]. We have used the anionic surfactant tetraethyl ammonium perfluoro octane sulfonate for our investigations. Disjoining pressure isotherms of foam films have been measured. Also the dependence of the film thickness on concentration of electrolyte has been investigated. Newton black foam films (NBF) consisting of a surfactant bilayer are formed at 0.3 mol/dm^3 electrolyte (NH_4Cl) in the solution. The thickness of the NBF is about 6 nm. The mean lifetime of the NBF has been determined depending on surfactant concentration. From the disjoining pressure isotherms and the dependence of the thickness on salt concentration the potential of the electrical double layer can be estimated. The dependence of the mean lifetime on surfactant concentration allows the estimation of the so-called equilibrium concentration [3]. This concentration is the upper limit for the possible nucleation of holes in the NBF bilayer film and rupture.

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NEUTRAL AND IONIC AMPHIPHILIC POLYSACCHARIDES: DYNAMIC BEHAVIOUR AT INTERFACES AND EMULSIFYING PROPERTIES

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Dextran is a neutral polysaccharide consisting of α -1,6 glucopyranose units. Its biocompatibility makes it attractive as a raw material for the synthesis of surface active polymers. Hydrophobic derivatives of dextran have been shown to exhibit surface active properties with potential applications in drug delivery systems [1-2].

This work deals with the preparation of anionic amphiphilic derivatives of dextran obtained by reacting dextran with phenyl glycidyl ether and 1,3 propane sultone. Several dextran derivatives are obtained with varying degrees of substitution by phenoxy and sulfopropyl units. The water-soluble dextran derivatives described here have much higher hydrophobic degrees of substitution than those previously studied [1] thanks to the hydrophilic contribution of sulfopropyl groups.

The dynamic behavior of these polymers at interfaces is described through surface/interfacial tension measurements. The evolution of surface/interfacial tension with time can be described using the equations derived from diffusion-limiting models by Ward and Todai [3] or Hansen [4] depending on the concentration range. The dynamic behaviour is correlated to the structural characteristics of the polymers.

The emulsifying properties of the polymers are studied with hydrocarbon oils. The size of oil droplets is measured at the preparation and during emulsion ageing. Ostwald ripening is shown to induce the size increase with time. The cube of the mean radius of droplets increases linearly with time. The slope of this evolution is related to the surface active properties of the dextran derivatives. The experimental slopes are compared to the theoretical values calculated by the Lifshitz-Slyozov equation [5].

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*POLYANILINE CONTAINING INTERPOLYMER COMPLEXES SYNTHESIZED IN
LOW-POLAR ORGANIC MEDIA*

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In present work interpolymer complexes (IPC)s of polyaniline (PANI) emeraldine salt and poly(styrenesulfonate) (PSS) or DNA were prepared via interchange reaction between PANI protonated with dodecylbenzenesulfonic acid (DBSAH) and PSS or DNA complexed with dioctadecyldimethylammonium chloride (DODAC) proceeding in chloroform solution at ambient temperature.

Recently it was found that stoichiometric polymer-surfactant complexes (PSC) formed from PSS or DNA and DODAC dissolves in chloroform. Thus either polycations or polyanions can be transfered into low polar organic solvents in the form of corresponding PSCs.

It is known that PANI can be dissolved in chloroform upon its complexation (protonation) with strong amphiphilic acids such as dodecylbenzenesulfonic acid (DBSAH) or 10-camphorsulfonic acid. It was established that DODAC added to the chloroform solution of PANI oligomer (trimer) protonated with DBSAH displaces DBSAH from the complex to form DODA-DBSA salt and hydrogen chloride [1]. The latter is not able to protonate the trimer in low polar solvents. Therefore the trimer transformes from emeraldine salt to emeraldine base. The above observation suggests that PANI-DBSAH complex dissolved in chloroform may also participate in ion exchange reactions.

It was found that in the case of PANI-PSS IPC precipitation takes place at all PSS / PANI ratios. In the case of DNA-DODA at high DNA / PANI molar ratios complete precipitation does not occur. At DNA / (aniline unit) molar ratio ca. 1.5 the precipitate is not formed at all and the resulting product remains dissolved in the reaction mixture.

Thus, it was shown that PANI emeraldine salt can be coupled with PSS or DNA to form the IPCs via the interchange reaction proceeding between the PANI emeraldine salt and PSS or DNA complexes with the oppositely charged amphiphile in the organic solvent. These IPCs reveal a considerable conductivity, which seems to be dependant on conformational state of IPC components.

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FORMATION AND PROPERTIES OF MICELLAR INTERPOLYELECTROLYTE COMPLEXES

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The interaction of micelles of polyisobutylene-*block*-poly(sodium methacrylate) diblock copolymers, PIB(X)-b-PMANa(Y) (X = 20, Y = 100, 280, 425; X and Y are the number-average degrees of polymerization of the hydrophobic and the polyelectrolyte blocks, respectively), with strong cationic polyelectrolytes was examined by means of turbidimetry, analytical ultracentrifugation, and fluorescence spectroscopy (with the use of pyrene as a fluorescent probe). Water-soluble interpolyelectrolyte complexes (IPECs) were shown to be generated at pH > 6.5 if the interacting oppositely charged polymeric components are taken in a certain non-equivalent charge ratio $Z = [+] / [-]$, $Z < Z_{\max} < 1$. The results obtained by means of fluorescence spectroscopy and dynamic light scattering suggest that particles of such IPECs can be considered as onion-like micelles, each containing a hydrophobic PIB core surrounded by a water-insoluble complex shell assembled from coupled fragments of the oppositely charged polymeric components and an ionic corona built up from fragments of the PMANa blocks not involved in the interpolyelectrolyte complexation.

A response of the micellar IPECs to the variation of the ionic strength in the surrounding solution was examined. In the contrast to common non-stoichiometric water-soluble IPECs resulting from the interaction of PMANa with the corresponding cationic polyelectrolytes, an increase of the concentration of NaCl in solutions of such IPECs was not accompanied by a pronounced decrease of the values of Z_{\max} . This difference is hypothesized to be associated with peculiarities of the structure of the micellar IPECs, that is, with a considerably non-uniform distribution of cationic macromolecules in polyelectrolyte coronas of the copolymer micelles. At high ionic strengths of the surrounding solution ($[NaCl] > 0.5$ M), the micellar IPECs were found to dissociate to the individual copolymer micelles and cationic macromolecules due to screening effect of small ions.

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THE REACTION METHYL 4-NITROBENZENESULFONATE + Br⁻ IN CATIONIC AND ZWITTERIONIC MICELLAR SOLUTIONS

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Chemical reactions in micellar solutions are generally run under pseudo-first order conditions. For a process between a nucleophile, N, and an organic substrate, S, the observed rate constant can be written as [1]:

$$k_{obs} = \frac{k_2^w [N_w] + (k_2^m / V_m) [N_m] K_m}{1 + K_m [Surfactant_m]} \quad (1)$$

In this eq. square brackets indicate concentrations expressed in moles per liter of solution volume. Subscripts w and m stand for the aqueous and micellar pseudophases, respectively. $(k_2^m / V_m) = k_{2m}$ is the second order rate constant in the micellar pseudophase written with concentrations as a molar ratio, $[N_m] / [Surfactant_m]$. K_m is the equilibrium constant which describes the distribution of the S molecules between the aqueous and micellar pseudophases. Recently various authors have stressed the problem concerning the possible lack of meaning of the kinetic constants estimated from fittings of kinetic data by using equations such as eq. 1. In order to investigate this point the reaction methyl 4-nitrobenzenesulfonate + Br⁻ was studied in tetradecyltrimethylammonium bromide, TTAB, micellar solutions in the presence and in the absence of NaBr 0.1 M as well as in N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate, SB3-14, micellar solutions in the presence of NaBr 0.1 M. Discussion of kinetic results in cationic micellar solutions was used to show some problems concerning the estimation of the second order rate constants in the micellar pseudophase. The errors introduced by rationalizing the kinetic micellar effects in SB3-14 micellar solutions through pseudo-first order rate constants were also shown; the contribution of the reaction occurring in the aqueous phase and the binding of the bromide ions to the sulfobetaine micelles were the cause of such errors. To complete the work, the influence of the cation coming from the added bromides on the micellar effects observed in SB3-14 micellar solutions was investigated. Results give information about how cations influence the bromide association to the SB3-14 micellar aggregates.

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INVESTIGATING BILIQUID FOAMS

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Biliquid foams are unique and intriguing systems believed to be structurally similar to foams, although the actual structure is unknown. A distinction is that the gaseous phase is substituted by a liquid phase, and these systems were first reported by Sebba [1]. Potential uses of these biliquid foam systems include personal care products, soil remediation [2], and controlled release of actives [3]. However despite the broad range of potential applications, little has been done to clarify Sebba's proposed structure. Indeed authors have proposed that these systems are essentially high-internal-phase-ratio-emulsions (HIPRE) [4]. A variety of biliquid foams have been created to study affects such as surfactant identity and concentration on the system, and to map portions of the phase diagram for this complex system. Light scattering and optical microscopy have been used to study some structural details, and these techniques have been complemented with SANS, and PFG-NMR to attempt to test Sebba's proposed structure.

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REACTIONS IN MICROPHASE SEPARATING SURFACTANT SYSTEMS

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It is well known that fluorocarbon and hydrocarbon materials do not mix [1]. This demixing phenomenon (microphase separation) can be exploited in a system where there is a partially fluorinated structure, such as a micelle, and a solubilised hydrocarbon monomer [2]. The F-C within the micelle drives a local phase separation [3] and this can be used to effect the polymerisation of the monomer, leading to an interesting area of polymer templating.

Recent results will be reviewed and future prospects presented.

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ACTION OF FLUORO-SURFACTANTS IN ORGANIC SOLVENT

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Monodisperse non-ionic fluoro-surfactants have been synthesised and their interfacial adsorption and micellisation properties investigated in both aqueous and non-aqueous solvents. The compounds were perfluoroalkyl triethyleneoxide methyl ethers, with the structure, $X-(CF_2)_m-CH_2-O-(C_2H_4O)_3-CH_3$. Two of the surfactants were partially fluorinated (where $X = H$, and $m = 4$ or 6) and one fully fluorinated (where $X = F$, and $m = 6$). These compounds are abbreviated to H4EO3, H6EO3 and F6EO3 respectively. In water the fluorocarbon chains drive a strong solvophobicity, and the compounds behave like classic surfactants [1]. In an organic solvent (methyl ethyl ketone – MEK) a weak solvophobicity is evident due to fluorocarbon-hydrocarbon incompatibility; adsorption at the solvent-air interface can be detected by surface tension depression measurements. The results show that for fluorocarbon surfactants of this kind surfactant properties are not only limited to water-based systems.

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THE INTERACTION BETWEEN PEO-PPO-PEO TRIBLOCK COPOLYMERS AND IONIC SURFACTANTS IN AQUEOUS SOLUTION STUDIED USING LIGHT SCATTERING AND CALORIMETRY

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Properties of triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) ($\text{EO}_n\text{PO}_m\text{EO}_n$) in aqueous solution and their interaction with the ionic surfactants, sodium dodecyl sulfate (SDS) and hexadecyltrimethyl ammonium chloride (C_{16}TAC), have been investigated by dynamic (DLS) and static light scattering, differential scanning calorimetry and isothermal titration calorimetry. The studied copolymers (denoted P123 and F127) have the same hydrophobic PPO central block ($m=68$), but different length of the endblocks, $n=20$ and 97 , respectively. At $40\text{ }^\circ\text{C}$, the copolymers are associated into micelles composed of a hydrophobic PPO core and a water-swollen PEO corona with hydrodynamic radii of 9.8 nm (P123) and 12.1 nm (F127). The different copolymer/surfactant systems have been investigated at a constant copolymer concentration of $1\text{ wt } \%$ and with varying surfactant concentration. The total light scattering intensity as a function of surfactant concentration exhibits three distinct regimes where changes in the intensity occur. At low surfactant concentration ($<1\text{ mM}$), there is a strong intensity decrease, which is followed by an intermediate concentration regime, and thereafter a final decrease at high concentration ($\approx 15\text{ mM}$). These regimes may also be observed in DLS data. At low surfactant concentrations, the surfactants bind to the copolymer micelles forming a large copolymer-rich complex, and monomodal relaxation time distributions affected by electrostatic interaction are obtained. For both copolymers, the intermediate concentration regime is represented by bimodal distributions displaying the coexistence of two types of copolymer-surfactant complexes: one large copolymer-rich complex and one small surfactant-rich complex. Finally, at high surfactant concentrations where the scattering intensity is low, only the small surfactant-rich complex is present in the systems. Thus, the copolymer micelles are disrupted upon increasing surfactant concentration. When NaCl is added this process is shifted towards higher surfactant concentrations as the electrostatic interactions are screened. The light scattering results correspond well with the calorimetry results [1].

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AN INVESTIGATION INTO POLYMERIC EXCIPIENT-PARTICLE COMPATIBILITY IN SOLID-LIQUID FORMULATIONS

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The current strategy for choosing an appropriate polymer to stabilise a particulate dispersion is somewhat serendipitous. There is no current clear understanding as to why a particular polymer will adsorb and hence confer colloid stability onto a given material. Similarly, it is not understood why the same polymer whilst conferring good stabilisation properties on one compound totally fails when used on a different dispersion.

A number of water-soluble polymers were screened as potential stabilisers for a pharmaceutical dispersion including: methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, gum arabic, xanthan gum, gum guar, polyvinyl pyrrolidone and carrageenan.

Colloidally disperse samples of the particles were found to form upon the addition of the sulphated polysaccharide carrageenan in water at pH2 and pH7. Adsorption isotherms revealed adsorption maxima at 80mg/g and 90mg/g respectively. Dynamic light scattering measurements of the resultant carrageenan-particle complex showed a mean hydrodynamic size of 760nm which compared favourably with scanning electron micrographs of the powder 600-800nm, indicating that the system consisted of disperse unimeric particles. The particle-carrageenan suspension showed excellent dispersibility with the system remaining fully dispersed as monitored by turbidimetric measurements over 3 months.

Adsorption isotherms will be presented for a range of different particulate dispersions where the addition of a polymer clearly confers good stabilisation.

Particles chosen to carry out further polymer compatibility studies will include ionic compounds which are acidic e.g. ibuprofen in addition to basic compounds such as propranolol.

A SANS STUDY OF PROTEIN-SURFACTANT AGGREGATES

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Protein-surfactant aggregation in oppositely charged systems is a fascinating phenomena, among many things because of the delicate balance between the forces of interaction mainly stemming from electrostatic forces and hydrophobic interactions, the dispute about the complex structure and the practical importance of the gels.

Two interesting issues of protein aggregation are discussed based on small angle neutron scattering measurements (SANS) of the protein-surfactant system lysozyme-sodium dodecyl sulfate-water. First, a new set of data on the structure of the protein-surfactant complex in solution is added to the discussion of whether the model of “beads on a necklace”, “protein decorated micelles” or “flexible helix” is most appropriate. Second, the structure and formation of a homogeneous, transparent gel in room temperature is analyzed and put in its thermodynamical context, which has been recently presented [1, 2]. The gel structure in different ionic strengths, lower than the one caused by naturally occurring buffer salts has also been analyzed and it seems that a little salt render the system a more repulsive character than no-salt does. These SANS experiments have been carried out following a contrast variation method with three different contrasts. In addition samples have been studied over time.

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ENHANCED COLLOIDAL INTERACTIONS IN FOAM FILMS

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The adsorption density of surfactant molecules at the surface of a foam film depends on the thickness of the film and the interaction between the interfaces. Indications for this are given by measurements of the disjoining pressure isotherms of foam films, of their stability and of the gas-permeation through such films. If the film is compressed against repulsive electrical double layer forces, the adsorption density decreases. The adsorption density increases, however, if the film thins spontaneously under the effect of a negative disjoining pressure. This is due to a contribution of the interaction between the film interfaces to the chemical potential of the surfactant molecules in the adsorption layers. The free energy of the film contains a contribution from the adsorption density, which itself depends on the film thickness. Therefore, the external force, which has to be applied to decrease the film thickness is enhanced in comparison to the forces predicted by the classical DLVO theory. A theory of this enhanced colloidal interaction (ECI) is given, which quantitatively explains discrepancies between experimentally measured disjoining pressure isotherms and theoretical predictions by the DLVO theory. The change of the adsorption density in the film can be calculated from knowledge about the disjoining pressure isotherm or from the film interaction free energy. It also explains the dependence of the gas permeation through foam films and the stability of films on the film interaction free energy.

*KINETIC MICELLAR EFFECTS IN TETRADECYLTRIMETHYLAMMONIUM
BROMIDE-PENTANOL MICELLAR SOLUTIONS*

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The influence of alcohols on surfactant aqueous solution properties has been extensively studied in recent years [1]. The incorporation of linear alcohols into the micelles produces noticeable changes in micellar shape and in their transport properties. It also causes micelle swelling and a decrease of micelle charge density, thus increasing the degree of ionization. All these structural changes influence the reaction rates of micelle-modified processes. The goal of this work is to investigate the different factors influencing the reaction rate of two micelle modified processes in alcohol-surfactant solutions.

The reactions 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane + OH⁻ and 2-(p-nitrophenyl)ethyl bromide + OH⁻ were studied in tetradecyltrimethylammonium bromide, TTAB, and TTAB-pentanol micellar solutions. The influence of changes in the surfactant concentration as well as changes in the hydroxide ion concentration on the observed rate constant were investigated. If changes in the cmc and ionization degree provoked by the presence of the different amounts of n-pentanol in the micellar solutions are taken into account, the experimental kinetic data can be rationalized quantitatively by using the PIE model. Assuming that the ion-exchange equilibrium constant, $K_{\text{OH}^-/\text{Br}^-}$, for the competition between the bromide and the hydroxide ions in all TTAB and in TTAB-pentanol micellar solutions studied is the same, a good agreement between the theoretical and the experimental kinetic data was found in all the micellar media for the two processes studied. This assumption was checked by experimentally determining the ion-exchange equilibrium constant $K_{\text{OH}^-/\text{Br}^-}$ in TTAB and TTAB-pentanol micellar solutions through a spectroscopic method, results showing that the presence of n-pentanol does not affect substantially the value of $K_{\text{OH}^-/\text{Br}^-}$. The second order rate constants obtained from the fittings decrease slightly when the amount of pentanol increases, being greater than that in aqueous solution. This acceleration can be explained considering that micelles accelerate the reactions in which the charge is delocalized in the transition state.

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Micelles of amphiphilic block copolymers and their formation of water-soluble interpolyelectrolyte complexes

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Aqueous solutions of ionic amphiphilic diblock copolymers, polyisobutylene-*block*-poly(methacrylic acid) (PIB-PMA), were investigated with respect to their micellisation behaviour for various ratios between the hydrophilic PMA and the hydrophobic PIB block. The pH was varied systematically and the aggregation behaviour was studied by means of fluorescence spectroscopy, dynamic light scattering (DLS) and small-angle neutron scattering (SANS). The determined cmc is almost insensitive to pH and ionic strength and exclusively determined by the length of the hydrophobic block. SANS experiments show that the aggregation number of the formed copolymer micelles is sensitive to variations of pH and ionic strength: a decrease of pH or an increase of the concentration of NaCl leads to a rise of the aggregation number. DLS experiments show that hydrodynamic radii of the formed copolymer micelles increase with rising pH or decreasing ionic strength of the surrounding medium. Combination with the SANS results shows that the PMA polyelectrolyte chains of the hydrophilic corona are almost fully stretched [1].

By addition of an oppositely charged polyelectrolyte, poly(N-ethyl-4-vinylpyridinium bromide) (PEVP), to these micelles at charge ratios $Z = [+]/[-]$ smaller than 1 water-soluble interpolyelectrolyte complexes are formed. Analytical ultracentrifugation, fluorescence spectroscopy, SANS, and DLS show that complex onion-like species are formed. The nucleus consists of a PIB core and a shell assembled from the fragments of water-insoluble PEVP/PMA complex. The corona is formed by the excess fragments of PMA blocks that are not involved in the complexation with PEVP. It is interesting to note that the aggregation numbers of the copolymer micelles are not changed by the complexation process despite the fact that they are dynamic objects [1].

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EFFECTS OF HOFMEISTER ANIONS ON DPPC LANGMUIR MONOLAYERS

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In this work we try to understand the mechanism of operation of Hofmeister anions [1,2] using a model system: Langmuir monolayers of DPPC at the air-water interface, in the presence of Na-salts of Cl^- , Br^- , NO_3^- , BF_4^- , ClO_3^- , I^- , SCN^- , and ClO_4^- in the aqueous subphase. Our aim is to obtain dependable “thermodynamic” binding constants of the anions on the lipid headgroups and use these constants to evaluate older [1,2] and current [3] ideas about the Hofmeister effect. From our results (surface pressure vs. area per molecule at the surface) we have calculated the binding constants of anions on the phospholipid headgroups using a sequence of models to describe the charging of the monolayer due to anion adsorption [4,5]. The binding constants were found to follow the Hofmeister series. X-Ray diffraction experiments of the monolayers reveal that moderate concentrations of strongly-binding anions, such as I^- , disrupt the ordering of the monolayers even at high pressures, forcing the liquid-condensed and solid phases to disappear. Anions that bind less strongly, such as Br^- , affect the ordering of the lipids in the monolayer only at subphase concentrations higher than 1M.

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CHARACTERISTICS OF HETEROGENEOUS SURFACES BY ELECTROKINETIC MEASUREMENTS

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An efficient technique for characterizing electrokinetic properties of heterogeneous surfaces was presented [1-2]. The method is based on measurements of streaming potential or streaming current in the parallel-plate channel arrangement. The rectangular channel was assembled from two substrate plates to be studied, separated by a Teflon spacer. The performance of the technique in the case of heterogeneous surfaces was assessed in experiments involving monodisperse latex particles deposited on mica surface. The influence of particle coverage (measured directly by the optical microscope counting), suspension ionic strength and zeta potential ratio of the channel to particles on the apparent streaming potential was determined. The results were interpreted in terms of a theoretical model by considering quantitatively the hydrodynamic and electric field distributions around adsorbed particles. In this way a precise calibration of the channel was attained, allowing one to evaluate surface coverage and zeta potential of species adsorbed on the channel walls. It was demonstrated that due to the high sensitivity of the method, a presence of 0.5% of a monolayer (heterogeneity) at the surface could be detected including uncharged species that are not detectable by classical electrophoresis. These results were exploited as reference systems for studying multilayer formation of polyelectrolytes via the streaming potential measurements. Two types of polyelectrolytes were used in these studies: polyallylamine hydrochloride (PAH), of a cationic type and polysodium 4-styrenesulfonate (PSS) of an anionic type, both having molecular weight of about 70 000. A periodic oscillations of apparent zeta potential of surface was demonstrated, strictly correlated with the multilayer build up. These variations also were correlated with contact angle changes, measured independently. Kinetics of multilayer desorption (removal) also was determined. It was demonstrated that the PSS layer was considerably more resistant to washing out, compared to the PAH layer. Because of the high sensitivity, it was concluded that the electrokinetic method applied can be effectively used for quantitative studies of particle and polyelectrolyte adsorption and desorption.

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INCORPORATION OF POLY(N,N-DIMETHYLACRYLAMIDE) IN THE LAMELLAR PHASE OF AEROSOL OT-WATER

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The bilayer is the basic structural building block in various organized phases such as vesicles, lamellar phases or biological membranes. Such organized phases have found use in many applications related with several fields, for instance cosmetics, medicine, detergency or pharmacology. Most formulations also contain macromolecules added for specific purposes, i.e. for rheology or stability control.

From a compositional point of view, lamellar phases are simple and can be prepared with only two components. This paper focuses on effects of added polymers on the bilayers long range order arrangement, such as repeat distance. Incorporation of the water soluble uncharged polymer poly(N,N-dimethylacrylamide), into the Aerosol-OT/water lamellar phase was studied[1]. We find that the polymer and the surfactant do not show association in aqueous solution. Instead, when the macromolecular coils are larger than the thickness of the water layer between bilayers, two phases in equilibrium form: one rich in AOT and one rich in polymer. While the phase separation not is macroscopic the distance between bilayers is determined by the osmotic pressure in these two phases. Thus, it is possible to prepare samples with different global composition but with the same repeat distance of the lamella. Furthermore, it seems that this behaviour is obtained independent of whether the polymer coils were introduced by mixing or by polymerization *in situ*. In the first case the samples are prepared by weighing proper amounts of the three components while in the second case the initial mixture contains AOT, water, monomer (N,N-dimethylacrylamide) and α,α' -azobis(isobutyronitrile) as initiator and then the polymerization is carried out at temperatures somewhat above 60 °C. The evolution of the samples during the synthesis depends on the initial sample composition, while the properties of the final samples are in line with "mixed" samples. In addition, molecular weight and tacticity of the polymer chains were not influenced by being polymerised within the lamellar phase. Quite differently, coils with small dimensions are expected to have access to the water domains in between bilayers and no phase separation is expected.

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*A STUDY OF EFFECTS OF DISPERSE MEDIUM DENSITY ON COLLOIDAL
AGGREGATION KINETICS*

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Effects of the small difference in densities between disperse medium and polystyrene particles on the kinetics of fast or diffusion-limited cluster aggregation (DLCA) have been studied experimentally using small-angle light scattering (SALS). The density of the disperse medium was tuned by varying the volume fraction of D₂O from 0 to 80% so as to investigate the effects of both aggregates sedimentation and buoyancy. It is found that the time evolution of the average radius of gyration, $\langle R_g \rangle$ determined by SALS, initially follows well the usual DLCA kinetics, i.e., the power law. However, when $\langle R_g \rangle$ reaches a certain value the growth of $\langle R_g \rangle$ starts to accelerate. The onset of such acceleration shifts to a larger $\langle R_g \rangle$ value if the density difference between the disperse medium and the colloidal particles is smaller, indicating that the acceleration results from the sedimentation or buoyancy of aggregates when reaching a certain size. Numerical simulations using the population balance equations and accounting for the sedimentation effects are in good agreement with the experimental results. They are also confirmed by the measured dependences of the scattering intensity at zero angle and obscuration on $\langle R_g \rangle$, which deviate from the theoretical predictions when $\langle R_g \rangle$ reaches a certain value. On the other hand, the effects of the small difference in densities on the structure of aggregates are insignificant, because the difference in values of the fractal dimension, d_f estimated from the average structure factors measured either in the regime without the effects of the sedimentation (or buoyancy) or in the regime with such effects, are insignificant. Moreover, four different techniques for estimating d_f have been proposed, and the obtained d_f values are practically identical.

OSTWALD RIPENING OF ALKANE IN WATER EMULSIONS STABILIZED BY DIFFERENT SURFACTANTS

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The Ostwald ripening and solubilization rates of alkane in water emulsions stabilized by the non-ionic surfactants hexaethylene glycol n-dodecyl ether (C₁₂E₆), Tween20 and the ionic surfactant sodium dodecyl benzene sulfonate (SDBS) were investigated.

For emulsions prepared in one step under high shear conditions in a microfluidizer the ripening rates are almost independent on the surfactant concentration. For already formed emulsions to which extra surfactant solution is added the ripening rates increase with increasing added micellar surfactant concentration for the non-ionic surfactants: slightly for C₁₂E₆ and more for Tween20. With the ionic surfactant SDBS no increase is observed. The main aging process is due to the transport of alkane by molecular diffusion through the continuous phase. This mechanism is confirmed by the temperature dependence of the experimental rates. The measured solubilization rates are dependent on the ratio of the number of oil to surfactant molecules. The solubilization rates of different alkanes are approximately proportional to their solubility in micelles. An inverse relationship between solubilization rates and enhancement of the Ostwald ripening rates is observed. These results lead to the following conclusions about the effect of the presence of micelles on the ripening rate. This effect is different for micelles swollen by alkane and for surfactant micelles without alkanes. When an emulsion is prepared under high shear conditions with an excess of surfactant the alkane and surfactant molecules are distributed in a quasi-equilibrium state between large oil droplets and micelles swollen by oil. The Ostwald ripening process is not or hardly affected by the presence of the swollen micelles. When an already formed emulsion is diluted with a surfactant solution the quasi-equilibrium distribution of alkanes and surfactant is disturbed. During the evolution towards a new quasi-equilibrium distribution more alkane molecules are present in the continuous phase enhancing the Ostwald ripening process. Emulsions stabilized by surfactants with higher solubilization rates evolve faster to a new quasi-equilibrium state leaving on average less alkane molecules in the continuous phase and enhance therefore less the Ostwald ripening rate.

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*MICROSTRUCTURE CHARACTERIZATION OF AQUEOUS IONIC
PERFLUOROPOLYETHER MICELLAR SOLUTIONS BY SMALL-
ANGLE NEUTRON SCATTERING*

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The concentration and temperature effect on the microstructure of aqueous ionic chlorine – terminated perfluoropolyether micelles with N2 surfactant chain length and ammonium or potassium counterions were studied by SANS. Preliminary results are reported in [1]. The experimental spectra have been analyzed by a two-shell model for the micellar form factor and a screened Coulombic plus steric repulsion potential for the structure factor in the frame of the mean spherical approximation of a multi - ions system reduced to an effective one component macroions system (OCM). The charged micelles, surrounded by an ionic cloud of some counterions located in the region defined by the Debye's length, are dispersed in the continuous medium. At 28 C, in the surfactant concentration range .05 to .12 M, the micelles have a spherical shape with inner core radius of 1.5 nm for ammonium and potassium counterions, and interfacial layer thickness of 0.4 nm; at 0.2 M concentration, for both counterions, the shape is ellipsoidal, with axial ratio 2, the smaller axis is 1.5 nm as the core radius of the spherical micelles. Increasing the temperature up to 80 C the ellipsoidal shape of the 0.2 M ammonium sample becomes spherical whereas it remains ellipsoidal for the 0.2 M potassium sample. All the micelles are monodispersed. Average aggregation numbers and micellar surface charge differ for the counterions and change as a function of concentration and temperature leading to ionization degrees spanning from 0.3 to 0.5 for ammonium and from 0.4 to 0.45 for potassium micelles, respectively. The number of interfacial water molecules, the Debye's length, the surface potential and the area per polar head at the micellar surface are also known in details.

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PHOTOINDUCED ELECTRON TRANSFER BETWEEN CYTOCHROME *c* AND ANIONIC MICELLES CONTAINING A 1,4,5,8- NAPHTHALENE-DIIMIDE CHROMOPHORE

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1,4,5,8-Naphthalenediimides (NDI) are aromatic compounds with very interesting photophysical and electrochemical properties [1]. In this work, we describe the synthesis and characterization of a novel NDI with amphiphilic character, N-(2-phosphonoethyl)-N'-dodecyl-1,4,5,8-naphthalenediimide (compound 1). In aqueous alkaline solutions (pH > 8), 1 is negatively charged due to the dissociation of the phosphonate group, and forms anionic micelles. Micelles of 1 were capable of binding the cationic redox protein cytochrome c (cyt c). UV irradiation of the micelle-bound cyt c led to photochemical reduction of the protein from the Fe(III) to the Fe(II) state. Kinetic studies revealed that the photochemical reaction involves an electron-transfer from a photogenerated imide radical-anion ($I^{\cdot-}$) to the protein. Chemical reduction of 1 with aqueous sodium dithionite, on the other hand, generated radical-doped micelles, which were also able to reduce surface bound cyt c. Addition of α -cyclodextrin (α -CD) to a micellar solution of 1 resulted in micelle collapse, which is due to the formation of host-guest complexes, with the dodecyl chain of 1 included in the α -CD cavity. Compound 1 also reacts with zirconated silica gel, through zirconium phosphonate chemistry, generating particles coated with a monolayer of 1. In conclusion, our novel amphiphilic NDI is a rather versatile compound with great potential applications in surface science.

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DIELECTRIC SPECTROSCOPY OF MICELLAR SOLUTIONS OF SODIUM DODECYL SULFATE IN WATER BY DIFFERENTIAL MEASUREMENTS IN TRANSMISSION LINES

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The transmission line method is one of the simplest technique for the determination of complex permittivity of liquids and soft matter in wideband measurements from low frequencies up to several GHz. This work presents a "differential" procedure [1]. The measuring cell is built as a piece of coaxial line whose dielectric medium is sodium dodecyl sulfate. At high frequencies this cell cannot be described with lumped constants, but it must be represented by four distributed constants per unit of length, namely a shunt capacitance and conductance and a series inductance and resistance. The characteristic impedance and the propagation constant of the cell are functions of the four parameters. This differential method consists in the use of a network analyzer and two measuring cells identical but for the length of the central segment of uniform cross section. The network analyzer sends an electrical signal to a cell and measures the reflected and the transmitted parts, from which the scattering matrix and the cascade matrix are determined. Making two different measurements, with the two cells of different length, and using cascade matrices properties, the propagation constant of the central segment of uniform cross section of the two cells is obtained. The uniformity and regularity of the central segments are required, however no other information or hypothesis are required about the actual geometry of the cells or their terminations and connections to the measuring instrument. The complex dielectric permittivity of the sample is obtained from the propagation constant by repeating the measure on the same cells both empty and filled with the sample. This technique was used to measure the dielectric constant of a ionic micellar solutions of sodium dodecyl sulfate in water in the frequency range 100KHz-3GHz. Experimental data were investigated by use of three different models. The simplest one make use of two Debye relaxation processes, one for micelles and one for water [2]. The second model uses a Debye relaxation for water and a Cole-Cole relaxation for micelles [3]. Finally the Cole-Cole relaxation was substituted with two Debye relaxations [4].

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CHARGE REVERSAL OF COLLOIDAL PARTICLES BY POLYELECTROLYTES

(POTENTIOMETRIC TITRATION AND MODELING)

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Titration experiments were performed on well-characterized sulfate and carboxylate latex particles, at various ionic strengths and added oppositely charged polyelectrolytes.

The surface charge of the bare particles as a function of pH could be analysed in terms of a well-established model including dissociation of the surface functional groups.

When polyelectrolyte is added, the titration curves for all ionic strengths investigated show a charge reversal occurring at the same pH value. This behavior could be predicted with a simple model including two types of surface groups: one corresponding to the functional group grafted onto the particle, the other one corresponding to the adsorbed polyelectrolyte, supposed to be acting like a fully dissociated group, evenly spread onto the surface.

GLASSY LIQUID CRYSTALLINE STATE AND WATER SORPTION OF ALKYL

MALTOSIDES

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A DSC and sorption calorimetric study of two maltosides (C_8G_2 and $C_{10}G_2$) was performed. In the dry state both surfactants show the absence of the main transition corresponding to the melting from crystalline to the liquid crystalline state. Instead, a glass transition at about 55 °C was observed. SAXS experiments show that below the glass transition temperature (in the glassy state), the studied surfactants have the same lamellar structure as in the liquid crystalline state. Nevertheless, the presence of the glass transition shows that the structure of the glassy state is “frozen”, i.e. molecules perform thermal motion in a lesser degree than in the liquid crystal. Since the structure of this glassy state is the same as in liquid crystals, it can be called “glassy liquid crystalline state”.

A sorption calorimetry study showed that during sorption of water by the glassy liquid crystals an exothermic enthalpy of mixing is observed while mixing of water with liquid crystals is accompanied by a small endothermic heat effect. The explanation of the exothermic heat effect deals with the fact that during the mixing the water molecules have a transition from a liquid state to a “frozen” state.

Possible mechanisms of relaxation of the glassy liquid crystals are also discussed.

STRUCTURAL STUDY OF POLY(N-ISOPROPYLACRYLAMIDE) MICROGELS

INTERPENETRATED WITH POLYPYRROLE

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Thermo-sensitive cross-linked poly(N-isopropylacrylamide) [poly(NIPAM)] microgels present a continuous volume transition from swollen to collapsed states at $T \approx 307\text{K}$. The structural changes dealing with the swelling of highly cross-linked poly(NIPAM)] microgels in D_2O have been recently studied by light and neutron scattering with a core-shell model proposed [1]. The present work deals with the swelling of poly(NIPAM) microgels interpenetrated with polypyrrole molecules. The possible modifications on the structure of the polymer network induced by the presence of polypyrrole are investigated prior to tackle the study of the electrical properties. Pyrrole was dissolved in the microgel dispersion and polymerization was induced at three selected temperatures; 293K for microgels at the swollen state, 310 K at the collapsed state and 306 K for the state where swelling starts. Small angle neutron scattering and scanning electron microscopy were used for studying poly(NIPAM)] microgels with 0.25% (w/w) and 10% (w/w) bisacrylamide cross-linker content. High contrast was found for non-gold-covered samples in scanning electron microscopy which clearly indicates that the interpenetration with polypyrrole is effective. The small angle neutron scattering patterns consists of solution-like concentration fluctuations given by a Lorentz (Orstein-Zernike) type function and solid-like concentration fluctuations with Gaussian profile. Comparison of the microgels interpenetrated at 293K and at 310K shows no significant differences in the scattering functions.

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*THE RADIAL DISTRIBUTION FUNCTION IN COLLOIDAL DISPERSIONS WITH
LONG-RANGE INTERACTIONS VIA CONFOCAL MICROSCOPY*

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Charged colloidal systems have received a great deal of attention, owing to their technological importance and fundamental relevance as a model system. Our aim is to identify, and address, the controversy surrounding the effective pair interaction, and investigate the possibility of many-body effects.

We use confocal microscopy to determine the colloid-colloid radial distribution function (RDF) of a colloidal liquid in 3D. Monte-Carlo simulation is then used to model the RDFs, and colloid-colloid pair potentials are chosen to fit the experimental data.

Our results agree with the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory, with no evidence for many-body effects nor effective colloid-colloid attractions, at high volume fractions, close to freezing (0.13). Ongoing work at low volume fractions (0.003) suggests the possibility of some deviation, hinting towards reentrant melting.

*COLLOIDAL SYSTEMS WITH ATTRACTIVE INTERACTION: EVALUATION OF
SCATTERING DATA USING THE GENERALIZED INDIRECT FOURIER
TRANSFORMATION METHOD*

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The evaluation of scattering data from attractive interacting systems is still a challenging problem. In our approach we used the generalized indirect Fourier transformation technique [1] in combination with various structure factor models for attractive interactions.

We adapted a routine from J. Bergenholtz [2], which is capable of calculating attractive structure factors, for our software. It now allows us to use the SMSA, the HMSA and the Percus-Yevick closure relations for attractive systems. The potential can be a square well or a depletion potential. Sometimes the separation of the scattering curve into a completely free form factor and a structure factor for attractive interaction is not possible. So we also added the possibility to keep the form factor fixed during the calculations.

The static light scattering data of different systems was evaluated using this new possibility: Dense suspensions of silica, where van-der-Waals forces cause attraction and concentrated o/w emulsions with added polymer, which results in depletion interaction.

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LIQUID-LIKE STRUCTURES AND DIFFUSION USING OF LIPOSOMES

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Lipids form vesicles that are extensively used as vehicles for the targeted delivery of drugs. However, in Colloidal Science, their potential value lies in the relative easiness with which their surfaces can be manipulated, either by choice of the bilayer lipid composition, or by chemical modification to incorporate different molecules. In this work, liposomes were prepared by the extrusion technique. The vesicles were made both Egg phosphatidylcholine and phosphatidylserine. The size distribution was determined by photon correlation spectroscopy. Static and dynamic light scattering were the experimental techniques. It is well known that a crucial feature in light scattering experiments is to avoid the effects of multiple scattering (MS). In this sense, liposomes present certain advantage, since they consist in an aqueous volume entirely enclosed by a thin layer of lipid molecules. Thus, from an optical viewpoint, liposomes can be considered as colloids with an *effective* refractive index slightly different from that of the solvent and concentrated but relatively transparent colloidal dispersions can be prepared. In our case, liposomes allowed us to explore moderate particle volume fractions (up to 10%). The knowledge of surface electrical properties of liposomes presents a great interest. Among others, we focus on the effective charge of particle [1]. It is a useful parameter in the study of interactions between particles and its link with the bare charge is still an open question today. Usually, the surface charge density of liposomes has been investigated from electrophoretic mobility measurements and, as it is well known, this method is rather controversial. In this work, we apply two different ways of measuring the effective charge of these lipid structures: a) On the one hand, liquidlike structures are formed for a set of liposomes with different surface charges. Effective charges are determined from experimental structure factors $S(q)$ using a Derjaguin-Landau-Verwey-Overbeek potential and an Ornstein-Zernike scheme [2]. b) On the other hand, via the measure of the collective diffusion coefficient of particles [3]. Also, we consider the relationship between hydrodynamic interactions (HI) and electrostatic repulsion. For this purpose, the hydrodynamic function $H(q)$ was obtained at different liposome concentrations.

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HOW POLYMER ARCHITECTURE AFFECTS TRANSIENT NETWORK

FORMATION IN OIL –CONTINUOUS MICROEMULSIONS: A COMPARISON OF COMPOSITIONALLY SIMILAR BLOCK- AND GRAFT- COPOLYMERS

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Transient network formation involves the formation and dissolution of crosslinking points between segments of polymers which are not soluble in the bulk solution, for example between hydrophobic segments of hydrophobically modified water soluble polymers in aqueous solution.[1] The same concept has been used to explain the viscosity enhancement caused by hydrophobically modified block copolymers in water-continuous microemulsions.[2] In this case the oil droplets act as crosslinking points when two polymers place their hydrophobic chains into the same droplet.[3] More recently, the opposite case, of hydrophilically modified hydrophobic polymers in oil-continuous microemulsions, has been investigated,[4, 5] and in this case the polymers used were graft, rather than block copolymers. However, to date the majority of the work on oil-continuous microemulsions has involved end-modified or tri-block copolymers, and a systematic comparison of graft- and block copolymers of similar composition was lacking. In this work the transient network forming abilities of polystyrenes modified with hydrophilic poly(ethylene oxide) chains was investigated as a function of the copolymer architecture. Tri-block (PEO-PS-PEO) and graft- (PS-g-PEO) copolymers were prepared, varying both the PS and the PEO chain lengths. The effect of the different polymers in AOT oil-continuous microemulsions was determined as a function of the droplet concentration and the droplet size. Viscosity enhancement in all cases was due to the hydrophilic side chains being dissolved into the water droplets. However, significantly different degrees of viscosity enhancement were observed with the different polymer architectures as well as different trends with increasing droplet concentration or droplet size.

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*POLARITY EFFECTS AND COSURFACTANT / SURFACTANT INTERACTIONS IN
CONCENTRATED SURFACTANT BILAYERS*

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The partitioning behaviour of a muonium substituted cyclohexadienyl radical derived from 2-phenylethanol (PEA) adsorbed at the water/surfactant interface in lamellar phase dispersions prepared from dichain cationic surfactant (e.g., DHTAC) has been reported [1]. Recently we have collected more evidence to support the partitioning hypothesis and have shown that the tracer molecule's occupancy at the interface is quite dynamic. This is on the basis of extension to other systems (e.g., hexenol), para-magnetic quenching in the aqueous subphase and further investigations of the variation of resonance peak position with solvent polarity. Finally, we speculate on the conformation of radicals derived from cosurfactants in partial-solvents.

Avoided-level-crossing muon spin resonance (ALC- μ SR) is a sensitive magnetic resonance type technique which can probe the local environment of a muon spin labeled free radical when formed by muonium addition to an unsaturated chemical bond. In high magnetic fields the coupling of the muon, proton and electron spins leads to characteristic sharp peaks in the field dependence of the observed muon spin polarization at avoided crossings of magnetic energy levels. Tracer molecules thus formed require no special chemistry other than a C=C bond. When such radicals are resident in an isotropic environment they display only muon-proton spin flip-flop transitions (Δ_0). When the radical resides in an anisotropic environment the hyperfine anisotropy is not dynamically averaged and an additional type of resonance (muon spin flip transition, Δ_1) appears at a lower field. The centroid positions of the resonances of a muonated radical are characteristic for the polarity of its environment. This, together with the temperature dependence of the resonance fields, facilitates the construction of a polarity scale based on the affinity of the radical for an aqueous or non-aqueous environment, calibrated by measurements on water and, e.g., molten octadecane.

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INTERMOLECULAR FORCES BETWEEN HYDROCARBONS ADSORBED AT LIQUID/VAPOR INTERFACES

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Experimental data on the dependence of the surface tension of water or mercury on the adsorption of n-alkanes and benzene from the vapor phase over a range of temperatures are interpreted to obtain the two-dimensional second virial coefficients for the adsorbed molecules. The virial coefficients are compared with calculations based on the Lennard-Jones (L-J) formalism in two dimensions, using the L-J parameters as known for the three-dimensional gases. Good agreement is found between the experimental and calculated two-dimensional virial coefficients for methane, ethane and propane on water. For these weakly physisorbed molecules on water, corrections to the attractive component of the L-J interaction potential arising from either the frequency-dependent interaction with their electrostatic images in the bulk aqueous phase, as described by McLachlan, or from polarization of the adsorbates by a surface electric field are minor. For butane, these effects may become significant but possible changes in conformation on adsorption weaken the validity of using the gas-phase L-J parameters in estimating the two-dimensional virial coefficients. With benzene, the surface second virial coefficient on water is significantly less negative than the L-J predictions, corresponding with a reduction of ~30% in the attractive term. The enthalpy of adsorption of benzene is twice that of butane, indicating a closer binding to the water and increased susceptibility to the McLachlan and surface polarisation effects.

For adsorption of the alkanes and benzene on mercury, the calculated L-J second virial coefficients are all very different from the experimental values. The attractive term in the L-J potential of mean force is virtually abolished for all these adsorbates, indicating that the McLachlan effect and/or polarisation in the surface field are important aspects of the non-localised physisorption on mercury. Significant reduction in the attractive term has also been observed for adsorption on solid metals, for which localised adsorption is probable.

Analysis of the standard entropies of adsorption indicate that no significant structuring of the surface of water or mercury occurs on adsorption of small n-alkanes or benzene.

INTERMOLECULAR FORCES BETWEEN ADSORBED MOLECULES:

1,2 DIPALMITIN AT THE HEPTANE/WATER INTERFACE

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Understanding the intermolecular forces in the adsorbed state at A/W and O/W interfaces is fundamental to much of surface and colloid chemistry and to a number of biological structures, notably membranes. Surprisingly little direct data is available. Much discussion has been on the interpretation of equations of state derived from data at rather high surface pressures, with more recent interest focussing on two-dimensional second virial coefficients as a route to estimating intermolecular pair-potentials. This study is of the adsorption of a well-characterized 1,2 dipalmitin at the n-heptane/water interface at 25°C from dilute solution (low surface pressures) to near saturation in the heptane, using a sensitive drop-shape method and good system reproducibility. Possible dimerization of the diglyceride in heptane was checked by infra-red absorption. This system was chosen, in part, as contributing to our understanding of the large positive second virial coefficients measured in spread phospholipid monolayers at this interface. The second virial coefficient for dipalmitin is positive, but much smaller than for the corresponding phospholipid. This finding does not match the suggestion that the normal components of the ester carbonyl dipoles contribute to the repulsive force between phospholipid molecules in dilute monolayers. The magnitude of the dipalmitin second virial coefficient indicates an attractive component in the pair potential, raising questions on the common assumption that the van der Waals attractive forces at the oil/water interface are screened out by the liquid paraffin, and directing attention to the head-group interactions.

PEP-PEO COPOLYMER MICELLES: AN IDEAL COLLOIDAL MODEL SYSTEM

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The diblock copolymer poly(ethylenpropylene) PEP poly(ethylene oxide) PEO has a pronounced tendency of forming micelles in water, due to the exceptionally high interfacial tension between the hydrophobic PEP core and water. The micelles are frozen since no unimer exchange was observed by time resolved Small Angle Neutron Scattering (SANS) measurements and can be regarded as form stable colloidal entities.

Changing block composition the morphology of the micelles can be completely changed. Architecture and size can be adjusted by chemistry in order to be suitable to investigate the underlying physical problems. Therefore we propose PEP-PEO micelles as an ideal colloidal model system.

We selected two different architectures: PEP1k-PEO20k copolymer micelles, which can be seen as *tunable* analogs of unimolecular star polymers (= *ultrasoft* colloids [1]); PEP4k-PEO4k copolymer micelles, which can be seen as hard sphere-like system.

The micellar arm number of PEP1k-PEO20k micelles is approximately 120 in pure water and can be reduced up to 60 by addition of DMF, which is also a selective solvent for PEO but less incompatible with PEP. The form keeps stable up to 20% DMF molar fraction. This feature makes these micelles particularly useful to investigate the phase diagram of star polymers, which has been calculated by theory as a function of concentration and arm number [2].

SANS measurements of PEP1k-PEO20k micelles in water show a liquid to gel transition crossing the overlap concentration c^* . The gelation phenomenon is temperature dependent. The addition of PEO160k homopolymer as a depletion agent induces a melting of the system with increasing homopolymer content, as we observed by Small Angle X-Ray Scattering measurements.

On the other hand PEP4k-PEO4k micelles are characterized by an arm number of approximately 1500 and a correspondent core radius of 15 nm.

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WATER IN WATER EMULSIONS FROM DHBC AND OPPOSITELY CHARGED SURFACTANT COMPLEXES

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Electrostatic complexation of double hydrophilic block copolymers (DHBC), (PAANa-*b*-PVA), with oppositely charged dodecyltrimethylammonium bromide (DTAB) in water, leads to an associative phase separation (coacervation). Potentiometric measurements with DTAB specific electrodes indicate that the binding of DTAB to oppositely charged DHBC is highly cooperative as opposed to the case of random copolymers. Considering the composition triangle water-DTAB-DHBC, the extension of the diphasic region as well as its shape, are tunable through the polyelectrolyte copolymer composition. For instance, the extension of the two-phase region increases with PAANa content. As compared to homopolymer PAANa/DTAB phase diagrams, the two-phase region with DHBC is rotated around the water corner, following the line of charge stoichiometry. Along the water-DTAB axis of the composition triangle, the minimum DTAB concentration, for which phase separation no longer occurs in the presence of copolymers, increases as the polymerization degree of the polyelectrolyte PAANa block increases. On the water-DHBC axis, the minimum concentration of copolymer for which no coacervation occurs as surfactant is added, decreases as the neutral block length increases. All the observations confirm that coacervation results from a balance between counter-ion release and conformational entropy loss of the polymer upon electrostatic complexation with oppositely charged surfactant. Using copolymers allows tuning these two contributions by introducing more conformational entropy constraint without adding more ionisable groups. The presence of a second neutral (non-complexing) block induces the swelling of the coacervate and thus reduces the extension of the two-phase region. By increasing the length of the neutral block or by increasing its solubility highly swollen surfactant-copolymer complexes are obtained, which do not macroscopically phase separate. Water in water emulsions are obtained with promising application potential.

*CHARGED POLYMER STABILISED SURFACES: AN EXAMINATION OF
INTERACTION FORCES MEASURED BY AFM*

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The interaction forces between polyelectrolyte covered particles or the adhesion between colloidal particles and surfaces mediated by polyelectrolytes are of great interest due to the wide application of polyelectrolytes as dispersion stabilizers or surface modification agents. Here polyethyleneimine (PEI) or polystyrenesulfonate (PSS) have been adsorbed on solid substrates and colloidal particles attached to AFM cantilevers allowing the direct measurement of interaction forces and adhesion. The long-range electrostatic forces have been shown to agree with DLVO-theory at different salt conditions. However in contrast to unmodified surfaces the adhesion behaviour can not be described in simple terms especially due to the occurrence of adhesion events on the single molecule level. First results indicate a strong dependence on salt concentration. Besides surface modification with polyelectrolytes, Au-coated AFM tips modified with different alkyl thiols can also be employed to study the above effects. For instance, the interaction forces between COOH-terminated AFM-tips and a PSS-coated surface show a strong dependence on solution pH.

ADSORPTION OF PAMAM DENDRIMERS TO PLANAR MICA SURFACES

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The adsorption process of nanoparticles or polyelectrolytes on oppositely charged surfaces is of great importance in many industrial, environmental or biological processes. Simple nm-sized model systems like dendrimers, which allow for a well defined variation of different parameters such as size, charge and chemical composition are especially well suited to further elucidate the main driving forces involved in adsorption kinetics and steady state configurations. First results on the adsorption of high generation Poly(amidoamine) (PAMAM) dendrimers onto mica surfaces are presented. The lateral distributions of PAMAM-dendrimers were obtained by *ex-situ* measurements with Tapping Mode AFM. Besides adsorption kinetics for different bulk concentrations, the influence of ionic strength and dendrimer generation were examined. A preliminary quantitative description in the framework of random sequential adsorption (RSA) model reproduces the experimental data. The main conclusions are as follows. The amount of dendrimers adsorbed is diffusion limited and the surface coverage for long adsorption times does not depend on the dendrimer concentration. Surface coverage and interparticle distance (as determined by the pair-distribution functions) can be regulated by the ionic strength of the solutions.

ROTATIONAL DIFFUSION OF MAGNETIC AGGREGATES IN IRON

FERROFLUIDS

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Recently, the first direct images of magnetic aggregates in a ferrofluid in zero external magnetic field were obtained using cryogenic transmission electron microscopy (cryo-TEM) [1]. Relatively monodisperse ferrofluids were synthesized with different average sizes of the iron particles (all with a 7 nm thick organic surface layer and dispersed in decalin). Aggregates were found when the iron cores of the particles had a radius above 7 nm, and larger iron particles led to larger aggregates.

Now, we have studied the same ferrofluids by measuring the dynamic magnetic susceptibility in the 1 Hz to 100 kHz range. Fannin [2] reviewed the theory of this technique, which allows the study of the rotational diffusion of magnetic particles if their magnetic dipole moments have a fixed orientation within the particles. A clear correlation is found between the size of the magnetic aggregates observed by cryo-TEM and the rotational diffusion rate derived from the dynamic magnetic susceptibility spectrum. In the absence of aggregates, the measured Brownian rotation rate is as expected for single spherical particles. As soon as aggregates appear, the rotational diffusion rate drops by more than one order of magnitude. Upon dilution, the rotational diffusion rate goes up again, which suggests that the average aggregate size decreases because it results from a dynamic equilibrium.

The measurements give new insight into the interpretation of dynamic susceptibility measurements on ferrofluids and into the concentration dependence of magnetic aggregate formation in ferrofluids.

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*DEPLETION ATTRACTION IN MIXTURES OF MULTIARM STARS AND LINEAR
POLYMERS IN SOLUTION*

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The dynamics in solutions of multi-arm stars (with 128 arms) are studied in the presence of linear homo-polymer chains of the same kind (polybutadiene) by dynamic light scattering. The former can be described well as a soft spherical particle with repulsive inter-particle potential while the latter act as a depletant of the soft spheres. The depletion interaction induced by the presence of the linear polymer chains leads to the formation of clusters of the multi-arm stars in dilute solutions of the latter and close to the overlap concentration of the former. These finding directly suggests that due to the depletion interaction the inter-particle potential between two stars should have an attractive part. Moreover, at high star volume fractions, where in the absence of linear polymer chains a thermo-reversible gel has been observed in good solvents, the addition of small amounts of linear chains leads to a liquidification of the gel [1]. Such phenomena, at low and high particle volume fractions reveal the colloidal character of the multi-arm star polymer and resemble both the well known depletion induced phase separation in colloid-polymer mixtures [2] as well recent reentrant phenomena observed in colloidal systems in the glass regime [3].

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POSSIBLE INDUCED ENHANCEMENT OF DISPERSION FORCES BY CELLULAR PHONES

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We have made a simple model calculation of the dispersion forces between two human blood cells in blood. By focusing the same radiation density, as in room-temperature thermal radiation, in the microwave region we find a huge enhancement of the attractive force [1]. Related effects are predicted to occur also in other types of biological tissue. The quantitative results should not be taken at face value, since the model is crude. The effects are so large though, that further investigation is motivated. The origin of the effects lies in the variation of water and/or ion content. In the microwave region of the spectrum both the dipolar contributions from the water-molecules, and the mobile-ion contributions are important parts of the dielectric function, and cause the enhancement.

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THEORETICAL EXCESS POLARIZABILITIES FOR CLOSED SHELL IONS IN WATER

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We report preliminary results from quantum-chemistry calculations of the excess polarizabilities for ions in solution. So far we have studied closed shell ions in water. These excess polarizabilities are very important for the theory of colloids. They are needed for better understanding of Hofmeister effects. The goal is to find quantitative results of, e.g., ion specific surface tension of salt solutions [1], double layer forces [2], and pH measurements [3]. The DLVO-theory is known to be incomplete and the excess polarizabilities are needed as inputs to calculations of the missing effects coming from dispersion forces. We use polarization propagator calculations of the polarizability tensor at imaginary frequencies. Calculations within our formalism have previously been successfully applied to the noble gases and *n*-alkanes [4].

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DENSITY FUNCTIONAL THEORY CALCULATION OF INCLUSION COMPLEXES OF BINAPHTHYL DERIVATIVES AND BETA-CYCLODEXTRINS

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We investigated the interaction of the host-guest beta-cyclodextrin-2,2'-Dihydroxy-1,1'-binaphthyl complex by means of molecular dynamics simulation using a density functional based tight-binding code [1]. We focused in particular on the investigation of the most stable conformation of this complex by looking at some of the structural properties that change with the time. This includes the hydrogen bonding formation of the active agent guest molecule with the torus-like macro ring of the host beta-cyclodextrin leading to the formation of the stable adduct in the lipophilic cavity of the biopolimeric matrix [2]. The role of the solvent water, in stabilizing the complex was also discussed. The chiral separation ability of beta-cyclodextrin on the (R) and (S) enantiomeric pair of binaphthyl was also investigated. We relate our results of the final stable optimized geometry of the complex to the UV/Vis and circular dichroism spectral study.

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THERMODYNAMIC STUDY OF THE INTERACTION BETWEEN HYDROXYPROPYL CYCLODEXTRINS AND *n*- OCTYL- β -D-GLUCOPYRANOSIDE

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The interactions of α , β and γ hydroxypropyl-cyclodextrins with the non ionic surfactant *n*-octyl- β -D-glucopyranoside in aqueous solution have been investigated by isothermal titration microcalorimetry at 298.15 K. Enthalpies and apparent equilibrium constants for the inclusion complexes formation process were calculated from the calorimetric measurements. Both, endothermic and exothermic interactions have been found depending on the cyclodextrin involved in each experiment. Gibbs energies and entropies were calculated by using the classical thermodynamics relationships. Different concentrations of cyclodextrin and surfactant were used in order to investigate the stoichiometry of the complexes as well as the interaction of micelles with the cyclodextrins.

EFFECT OF CHITOSAN ON STABILITY OF OIL-IN-WATER EMULSIONS

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Removal of emulsified petroleum products is a major challenge in processing oily wastes coming from oil-production and oil-refining, machining industries, surface and water transport, gasoline stations and so on. Conventionally used methods, e.g. flocculation, coagulation, air flotation, cannot provide desirably low effluent concentration. At the same time, adsorption remains effective but a very expensive method. One of the promising solutions for bringing together high efficiency and low cost is development of more effective polymeric flocculents and use of specially designed polymers to enhance phase separation, coalescence and demulsification of oil-in-water emulsions [1].

Owing to unique combination of properties – positive charge in a wide pH range and ability for hydrophobic interactions - aminopolysaccharide chitosan is a very promising candidate for treatment of negatively charged [2] oil-in-water emulsions. In this work the effect of chitosan and its hydrophobically modified derivatives on stability of diesel oil-in-water emulsions has been studied for emulsions with oil content from 0.01 to 0.1%, in wide pH range, and at various ionic strengths, including natural seawater. Special attention was given to feasibility of oily wastes deep cleaning by filtration of chitosan treated emulsions through various filter-beds. The best results were obtained for chitosan to oil mass ratio from 20 to 40, in pH range from 6 to 10. Further increase of chitosan concentration and pH resulted in lower efficiency of oil removal.

Although stability of emulsions under study did not change significantly in the presence of cationic surfactant CTAB up to concentration 10^{-4} M, the addition of chitosan doses as low as 1/75 (polymer/oil ratio) led to a fast phase separation due to the synergetic effect. Effect of SDS was more complicated as a result of insoluble chitosan/SDS complex formation, nevertheless, there was no linear correlation between SDS concentration and chitosan demand for effective emulsion flocculation, as it was found in [3]. Analysis of all experimental data has enabled us to conclude that both mechanisms - flocculation and coalescence are involved in destabilization of the diesel oil-in- water emulsions in the presence of chitosan and its hydrophobic derivatives.

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MICROEMULSIONS IMMOBILIZED ON ORGANOGELS: AN ALTERNATIVE METHOD FOR ENVIRONMENTAL BIOREMEDIATION

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Reverse micelles are formed when surfactants are dissolved in neat organic solvents or in organic phases containing small amounts of water. In the latter case the reverse micelles comprise roughly spherical pools of water surrounded by polar head groups of surfactant molecules. Micelles with different sizes and properties can be obtained by changing the water/surfactant ratio in the solution [1]. Reverse micelles of this type have been widely studied because of their usefulness as microreactors for chemical and biochemical reactions. Not only can one carry out chemical reactions in a confined environment but also, since polar and non-polar environment are brought into close proximity, one may efficiently carry out reactions that are difficult to achieve in bulk homogeneous environment [2].

Enzymes are efficient catalysts, however they are not used extensively in the chemical manufacturing industry because of problems related to long-term stability and the belief that biological molecules will not function in anhydrous environments [3].

The purpose of this study is seeking to enhance enzyme stability and activity in the presence of organic solvents. In particular, a laccase, initially encapsulated in microemulsions of AOT/isooctane/water, is immobilised on an organogel and used to oxidize polyphenol compounds. This method differs from the covalent binding and cross linking in that the enzyme itself does not bind to the gel matrix.

The reaction is studied analysing both continuous and discontinues process.

The procedure is used as a model of environmental bioremediation to decontaminate ground water from pesticides. The kinetics behaviour of the “bound” enzyme is studied in details.

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GROUND WATER REMEDIATION AND SURFACTANT RECOVERY THROUGH MICELLAR SOLUTION

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Surfactant micelles have attracted considerable attention in many industrial applications such as cosmetics, foods, pharmaceuticals, pesticides and coating materials in the last decades. One of the most important properties of aqueous micellar solutions is their ability to enhance the solubility of otherwise sparingly soluble substances [1]. The important characteristic of micelles is that the hydrocarbon chain constitute the inner part of the micelles. Here the water concentration is low or negligible, and the concentration of ionic head groups in this region is also negligible. The inner hydrocarbon region thus consists of randomly oriented hydrocarbon chains forming a liquid-like region. The ionic head group, counterions, water, and part of the hydrocarbon chain are positioned in a thin layer surrounding the micelle. The solubilizing power of micelles is associated with the hydrocarbon core and it is then not surprising that apolar molecules appear to solubilize in the micellar core.

Here we take advantage of these micellar properties to extract aromatic compounds from water and also to recovery the surfactant.

Chlorinated aromatic compounds, owing to their high hydrophobicity, represent a dangerous class of ground water pollutants. In particular, 2,4,5 trichlorophenol (tcf) is an important herbicide and is used as intermediate in the pesticides production. For this reason various techniques have been used to remove the contaminants from the soil. An innovative method is called *in situ flushing* and consists of an injection of fluid and additives that increases the pollutants solubility [2]. In this work, a plant for ground water remediation, with recovery of the surfactant, is described. The contaminants are extracted in micellar solutions. The behaviour of cationic, anionic and zwitterionic surfactants has been analysed.

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STRUCTURE AND REACTIVITY OF W/EXTRA VIRGIN OLIVE OIL EMULSIONS

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It is common knowledge that extra virgin olive oil has particular nutritional qualities [1]. These properties are largely due to its high content of antioxidants that can scavenge free radicals. The concentrations of these substances depends on different parameters and also on the production method [2]. Olive oil is a natural product and the chemical composition of its nonpolar part and the liposoluble antioxidants may differ significantly from oil to oil. Recently, some authors have shown that dispersed water and suspended particles act as antioxidants then protecting olive oil from oxidative damage [3]. In this study we emphasize the role of dispersed water as a stabilizing agent against oxidation. For this aim, we dispersed the water directly in extra-virgin olive oil and we homogenized the mixture with ultraturrax. The emulsions were oxidized with UV light and the extent of oxidation was monitored by measuring the peroxide value (PV). The evolution of emulsion structure was followed calculating the size distribution at different times. In addition, sedimentation measurements were carried out both on oxidized and non-oxidized emulsions to check the influence of oxidation on emulsion stability. The experimental results indicate that oxidation capability of extravirgin olive oil depends on the quantity of dispersed water and on the “polydispersity degree” of the water droplets.

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WATER OF HYDRATION IN COAGELS

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Alkanoyl-6-O-ascorbic acid esters, ASC_{*n*}, are vitamin C-based anionic surfactants. When dispersed in water at room or lower temperatures and above a *ca.* 5% concentration, these derivatives form coagels, which, at higher temperatures, turn into either micellar solutions or gel phases, depending on the length of the hydrophobic tail[1]. The coagel-micelle and coagel-gel transitions have been accurately studied by DSC. It has been shown that while the transition enthalpy is mainly ruled by the hydrophobic chains' packing, the Krafft point seems to be mainly related to the interactions between the polar headgroups and the solvent. In previous studies, we investigated the effect of water structure modifiers, such as sucrose and urea, salts and salt concentration. The results indicate that hydrogen bonds between the polar headgroups and water plays a significant role in the coagel transition. Moreover, strong anion specificity was observed, following a Hofmeister series[2]. The coagel phase is usually thought as formed of surfactant lamellae separated by thin interlayers of strongly bound water molecules essentially "frozen". DSC measurements were performed in order to determine the types of water present in the system and the relative amounts. Two kinds of water were detected: hydration water and bulk water, where lamellae "islands" could be hypothesized to be dispersed. The number of hydration water molecules per polar headgroup decreases linearly with increasing [ASC_{*n*}]. Values of the interlayer thickness derived assuming a model are in agreement with those reported so far. The effects of glycerin, propylene glycol, PG, and poly(ethylene glycol), PEG, as co-solvents were also investigated by DSC. While glycerin seems to stabilize the coagel, PG and PEG decrease the compactness of the lamellar structure. Both PG and PEG are probably able to penetrate into the lipid portion of the lamellae.

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MOLECULAR SELF-DIFFUSION IN A MICELLAR CUBIC PHASE OF AN IONIC SURFACTANT WITH MIXED MONOVALENT/POLYMERIC COUNTERIONS

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The molecular self-diffusion in concentrated aqueous mixtures has been investigated by NMR pulsed field gradient techniques. The investigated structures were an ordered cubic Pm3n phase (ca. 50 wt% water) and a disordered micellar phase, both containing cetyltrimethylammonium (CTA⁺) micelles with mixed acetate (Ac⁻) and polyacrylate (PA⁻) counterions. [1] The system studied is unique since the proportions of the ions can be varied continuously within a single phase. It is the result of a novel approach to the phase behavior of oppositely charged polymer-surfactant systems presented previously. [2,3] The strategy has been to synthesize the polyion-surfactant ion complex salt and use it as point of departure. By mixing the complex salt with the simple surfactant in water, truly ternary systems are obtained in which the counterion composition of the surfactant aggregates can be varied from polymeric to monovalent.

The observed diffusion coefficients for the four different molecular species in the cubic Pm3n phase covered four orders of magnitude with the rate of diffusion decreasing in the order water > Ac⁻ > PA⁻ > CTA⁺. As the CTA⁺ gave broad lines in the ¹H-NMR spectrum, it was possible to use the PFG STE technique to measure the PA⁻ diffusion. For all species, the diffusion coefficients were largely insensitive to the counterion composition, both in the cubic and the micellar phase. A model considering obstruction effects and binding to the micelles could account for the reduced diffusion of Ac⁻ and CTA⁺, compared to dilute reference solutions. For water, the reduction of the diffusion was mainly due to obstruction effects. The PA⁻ diffusion was much more retarded than the Ac⁻ diffusion in the cubic phase; moreover, the molecular weight dependence of the diffusion was dramatically enhanced for the polydisperse polyion. Both effects are attributed to electrostatic attractions and obstruction effects experienced by polyions diffusing in a concentrated matrix of stationary micelles.

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COMPLEX FORMATION BETWEEN ANIONIC POLYSACCHARIDES AND BASIC PROTEINS

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Natural polyelectrolytes such as anionic polysaccharides interact strongly with oppositely charged proteins which leads to three different types of phases: soluble complexes, complex coacervates and amorphous precipitates[1]. The knowledge of these interactions is of considerable importance in many biological systems and for the control of the stability and texture of processed foods [2].

We have been investigating by turbidity measurements and by confocal scanning laser microscopy the interaction between pectins, plant cell wall polycarboxylates, and two basic globular proteins, lysozyme and 2S protein from rapeseeds called napin. The effect of the pectins linear charge densities ($\xi = 0.42, 0.92, 1.17$) and the ionic strength on the protein-pectin phase behaviour have been studied. The pH was 7 such that the carboxylic groups are completely dissociated and the charge density of the protein remains constant. Particular attention was given to the boundary between the precipitation and complex coacervation.

By small angle neutron scattering the structure of the three types of complexes has been determined. By contrast matching, the signal of the polyelectrolyte can be cancelled such that the spatial organisation of the proteins over a few hundred Å inside the complexes can be visualized.

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*SELF ASSEMBLY STRESS IN A BIPOLAR PHOSPHOCHOLINE - WATER SYSTEM:
FIBRILS AND NANOPARTICLES*

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The bipolar compound dotriacontan-1,1'-diyl-bis-[2-(trimethylammonio)-ethylphosphat] (PC-C32-PC) in water forms novel types of aggregate structures due to the long alkyl chain and the large polar headgroups at both chain ends a mismatch between polar and non-polar parts. In diluted samples (< 99.5 wt% water) a highly viscous almost transparent gel is observed. At temperatures above 70 °C the gel disappears and a fluid solution is obtained with low surface tension and extreme wetting behavior.

DSC measurements revealed different endothermic peaks upon heating and a strong hysteresis in the transition behavior. A peak at 50°C is probably caused by a transition in the chain region. FT-IR measurements confirm this assumption. An attempt was made to characterize the particles at high temperature and in supercooled solutions with DLS measurements. The main fraction of the sample consists of small mono-dispersed nanoparticles. With AFM we detected lamellae, fibrils, or particles in the suspension. Estimates of step heights showed steps corresponding to the length of the molecule (6 nm). With freeze fracture EM parallel stripes were seen as well as mono-disperse nanoparticles. Negative staining and cryo EM of diluted suspensions revealed a network of stiff fibers. It can be concluded that the bola compound cannot form lamellae. Fibrils with rigid chain packing appear at low temperature. At the transition at higher temperature the aggregate size and morphology changes dramatically. Mono-disperse nanoparticles are formed.

INTERPARTICLE FORCES GENERATED BY TOPOLOGICAL DEFECTS IN NEMATIC LIQUID CRYSTALS

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Using an appropriate iron surface treatment, we successfully realize the alignment of iron micro-spheres in a nematic liquid crystal (NLC) matrix without applying any external field. We have used the anisotropic elastic properties of the liquid crystalline solvent to control the spatial organization of the particles. In such a solvent, the interactions, leading to the formation of chainlike structures by the micro-spheres, include a short-range repulsion and a long-range dipolar attraction. We present a new method to measure repulsive interactions between colloidal particles [1][2].

The equilibrium interparticle distance is determined from the observation with a microscope of a large set of pair particles. This average equilibrium distance is similar to the one previously observed on droplets in NLC. Next we have placed the particles in a weak magnetic field ($0 < H < 50$ Oersted) and observed the change of interparticle distance with the magnetic field. From the knowledge of magnetization curve of iron, the magnetic force between two particles can be calculated for different separations with a finite element method. Equating the magnetic and elastic force we obtain the elastic force between two particles in a NLC as a function of the interparticle distance. This force is compared with some theoretical predictions.

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FORMATION OF MULTILAYER COATED COLLOIDS FROM THERMOREVERSIBLE GRAFT-COPOLYMERS

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Multilayers can be formed by consecutive self-assembly of polyelectrolytes of alternating charge, where a large variety of charged molecules can be employed as building blocks. Thermoreversible polymers in solution undergo a transition from a water-soluble to an insoluble state with increasing temperature, and are therefore promising compounds to develop temperature-controllable layered materials. Previous investigations showed that the presence of an interface and of charged groups on the thermoreversible chain affect the phase transition, in particular a minimum density of thermoreversible loops is required in order to achieve a complete phase transition. [1]

Here, an improved polymer architecture is synthesized, consisting of a thermosensitive backbone of poly (N-isopropylacrylamide) (PNIPAAm) and charged side chains of P2VP. [2] These co-polymers provide properties of polyelectrolytes and of classical thermosensitive polymers, which are necessary for the formation of thermoreversible polyelectrolyte multilayers.

The adsorption properties of graft-copolymers of different grafting density are studied on planar surfaces and on colloidal particles. X-ray reflectivity, AFM, ζ potential, and SPLS measurements monitor the adsorption of the thermoreversible polyelectrolyte either on planar support or colloidal particles, and the adsorption isotherms are established. The results show a more stable adsorption for a larger density of side chains.

Conditions have been developed for the multilayer formation from these copolymers, where a low pH value provides sufficient charge density of the side chains to achieve charge reversal on adsorption. Multilayer-coated colloids were prepared and investigated by ²H NMR relaxation of the water, which monitors the water mobility. Furthermore, the phase transition is studied by X-ray reflectivity of planar multilayers.

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PROTEIN CONCENTRATED SOLUTIONS

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In this study we investigated Cytochrome C solutions at high concentration. Horse heart Cytochrome C is a globular protein consisting of 104 amino acids, 12 negatively charged (Glu, Asp) and 21 positively charged (Lys, Arg) and characterized by a pI=10.2. Its molecular weight is 12384 Dalton and its shape in aqueous solutions is approximately spherical ($a \times b \times b = 15 \times 17 \times 17 \text{ \AA}^3$).

It is well known that with protein solutions the inter-molecular interaction can be tuned to some extent varying the protein volume fractions, ϕ , and the content of salt. Therefore we want to investigate the effect of the protein volume fractions, pH, ionic strength and salt nature on the properties of Cytochrome C concentrated solutions ($\phi=0.10-0.50$). Rheological measurements and Small Angle Neutron Scattering are useful tools to describe the macro and microscopic properties of complex fluid systems. Both SANS spectra and viscosity curves show a very intriguing salt dependence. In particular, NaSCN results more effective than NaCl in screening the repulsive interactions among protein molecules. This is a proof that the co-ion nature influences the macroion-macroion interactions in agreement with the Hofmeister series.

POLYALLYLAMINE POLYALLYLAMMONIUM-CARBAMATE BASED GELS: PROPERTIES AND POSSIBLE APPLICATIONS

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The synthesis and characterization of a novel series of polymer gels have been studied. They are formed at ambient temperatures by bubbling CO₂ [1] through solutions of polyallylamine (PAA; a latent gellant) in several organic liquids, including aliphatic primary alcohols, 1-methyl-2-pyrrolidone, dichloromethane etc. The stabilities of the alcohol gels, as indicated by the (irreversible) degelation temperature, T_g^{dt} , were strongly dependent on the number of carbon atoms (C_n) in the alkyl chains of the alcohol liquids: this value increases increasing C_n . The mechanism of formation and the microenvironmental properties of PAA-based gels containing a small amount of a pH-sensitive probe, 2,6-naphthalenedicarboxylic acid (2,6-NDCA), have been probed using static and dynamic fluorescence measurements. A measurable pH change and significant alterations to the fluorescence spectra were coincident with gelation of PAA solutions in 1-butanol as CO₂ was bubbled through, and the fluorescence spectra were monitored over several hours until no further changes were detected. Analyses of dynamic fluorescence decay histograms indicate the presence of three decay times due to different microenvironments where the 2,6-NDCA molecules are located when the gelation occurs. These gels, especially the ones made by 1-methyl-2-pyrrolidone and 1-pentanol have been successfully tested as cleaning agents for painted surfaces and they can be purposed as a new tool in cultural heritage conservation technology.

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DEMIXING TRANSITIONS IN MICROEMULSIONS FORMED BY MIXTURES OF DDAB, WATER AND THERMOTROPIC LIQUID CRYSTALS

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Water in oil microemulsions, in which the oil component is the isotropic phase of a thermotropic liquid crystal (LC) [1], display demixing transitions of various nature in the proximity of the nematic transition of the pure LC compound. The coexisting phases are either both isotropic, and differing in the concentration of water-surfactant droplets, or one of them is nematic. The phase behavior of a DDAB-water-5CB mixture, which we have studied with various techniques, is very rich and combines features of the lyotropic systems with those of the isotropic-nematic transition of thermotropic LC. We find that the demixing transitions are anticipated, in the high T side, by increase of droplets density fluctuations and decrease of their collective diffusion, indicating the presence of attractive interactions mediated by growing paranematic fluctuations. Such a behavior, together with the topology of the resulting phase diagram, can be understood on the basis of a diluted Lebwohl-Lasher model.

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MICELLAR AGGREGATES FORMED BY DILAUROYL PHOSPHATYLNUCLEOSIDES: STRUCTURAL INVESTIGATION OF THE L₁ CORNER OF THE SYSTEM DI-C₁₂P-NUCLEOSIDE / WATER / CYCLOHEXANE

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Di-C₁₂P-nucleosides, double chain phospholipids with a nucleosidic polar head, are synthetic surfactant molecules that merge the self-assembling properties of the lecithin to the molecular recognition characteristic of the nucleic basis. We are interested in the expression of molecular recognition in self-organized systems, where the driving force of the aggregation is the exclusion of hydrocarbon chains from contact with the aqueous medium. Di-lauroyl-derivates form semi-flexible elongated aggregates in 0.1M phosphate buffer solutions, also called polymerlike micelles. This study is focused on two representative members of this class of compounds: di-C₁₂P-uridine (dlpu) and di-C₁₂P-adenosine (dlpa). These bases have different π -stacking attitudes, because uridine is poor homo-stacker while adenosine has high stacking tendency. A modulation of the recognition pattern between complementary bases can be achieved by control of the orientation and the distance between nucleoside groups at the aggregate interface. This can be accomplished by introducing a third component (oil) to previously studied binary systems [1,2]. This is extremely important for understanding of the recognition process in the living systems. The effect of added oil on the local structure of oil-swollen cylindrical micelles in the ternary systems has been investigated by Small Angle Neutron Scattering (SANS), Static Light Scattering (SLS), Quasi Elastic Light Scattering (QELS) and Small angle X-ray Scattering (SAXS). Circular Dichroism experiments have provided a correlation of the structural features of the micelles with electronic properties and molecular recognition of the bases present in the polar head of the surfactant. A cylindrical local structure is preserved up to 0.4% oil volume fractions for both derivatives, but for higher oil fractions, base specificity starts to emerge. Dlpa aggregates undergo in fact a structural transition that affects base conformation as well, like confirmed by CD spectra. These findings substantiate the importance and specificity of base presence on the polar head of such derivatives and how interfacial curvature is critical for base-base interactions

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*PHASE BEHAVIOR OF SURFACTANT-POLYMER MIXTURES IN RELATION TO
POLYMER CHARGE*

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The phase behavior of dodecylammonium chloride (DDACl) and differently charged carrageenans (CAR) was examined at 303K by conductometry, potentiometry, surface tension, static light scattering and microelectrophoretic measurements. The complex interactions between DDACl and CAR starting at very low concentration are accompanied by the formation of single and coexisting phases, differently structured soluble polymer-surfactant monomer complexes, surfactant micelles, polymer-micelle complexes, and solid crystalline and gel phases. The multistep mechanism of DDACl and CAR interactions was discussed in terms of successive electrostatic, hydrophobic, and intra- and interpolymer interactions. It was shown how the increase of carrageenans charge density (the three main forms of carrageenans differ in the number of sulfate groups per disaccharide; κ -CAR has one, ι -CAR has two, and λ -CAR has three, respectively) lead to a wide variation in surfactant monomers adsorption to polymer chains and phase separation properties. The increase of CAR charge density improved the degree of ordering in various carrageenan-surfactant species. Giant vesicles were found as single and/or coexisting phases.

MICELLAR AGGREGATION OF ALKYLTRIMETHYLAMMONIUM BROMIDE SURFACTANTS STUDIED BY EPR OF AN ANIONIC NITROXIDE. A COMBINED EXPERIMENTAL/COMPUTATIONAL APPROACH

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Electron Paramagnetic Resonance (EPR) of spin-probes is a technique that lends itself well to the physico-chemical characterization of multi-domain systems, allowing the simultaneous study of structural and dynamic properties of the various domains. Spin-probes can be tailored in such a way that they either solubilize in one kind of micro-domains or, alternatively, partition and exchange between different compartments.

The micellization process of five alkyltrimethylammonium bromide surfactants [$\text{CH}_3(\text{CH}_2)_{n-1}\text{N}(\text{CH}_3)_3\text{Br}$ ($n=6,8,10,12,16$), C_nTAB] in aqueous solution has been studied by Electron Paramagnetic Resonance (EPR) spectroscopy by employing 3-Carboxy-Proxyl [2,2,5,5-tetramethyl-3-carboxypyrrolidinyloxy, CP] as spin-probe. The change of the nitrogen isotropic hyperfine coupling constant (A_N) of CP in different environmental polarities and the influence of H-bonds on NO moiety have been quantitatively analysed by an *ab initio* computational approach.

The dependence of both A_N and the correlation time (τ_c) of the spin probe on the surfactant molality, m , have been analysed. With increasing m , A_N decreases while τ_c increases. Particularly, in the case of C_nTAB with $n \leq 8$, both A_N and τ_c change regularly without any abrupt slope change. In contrast, in the case of C_nTAB with $n > 8$, both A_N and τ_c of CP show a slope change at a concentration corresponding to the critical micellar composition (cmc) of the surfactant; the variation of both A_N and τ_c upon micellization becomes more marked with increasing the surfactant chain length. The A_N decrease can be ascribed to the embedding of the NO moiety of CP in the outer part of the micellar hydrophobic core. The τ_c increase can be interpreted in terms of a reduction of the probe mobility determined by the strong electrostatic interaction between the CP negative charge and the cationic micelles' surface. The CP affinity for the micellar pseudo-phase has been estimated by evaluating the distribution coefficient, K_d of the spin-label between the micelles and the aqueous medium. The K_d value increases with increasing the length of the surfactant hydrophobic chain. Above the cmc, also in very concentrated solutions, A_N decreases and τ_c increases without approaching a constant value. The increasing hydrophobicity of the TC solubilization site could be related to changes in the micellar structure, such as an increase in the surfactant aggregation number and counter ions condensation.

EMULSION FROM BY-PRODUCTS OF MILK PROCESSING.

A SELF-DIFFUSION NMR CHARACTERIZATION

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The final by-product of milk processing, that is a kind of whey obtained after extraction of a whey protein based fresh cheese (a sort of cottage cheese), is actually used as animal feed. However this whey still contains little amounts of proteins and phospholipids together with a large amount of lactose.

The powder obtained from freeze-drying this residue was ultrafiltrated through a 10000 D membrane. The protein fraction was then used to emulsify triolein in water. Stable emulsions were obtained and characterized through optical microscopy and self-diffusion NMR measurements. Time dependent self-diffusion coefficients were measured for the oil component. The effect of lactose addition on the emulsion stability was also investigated.

INTERACTIONS OF LOW MOLECULAR-WEIGHT MOLECULES WITH WATER-SOLUBLE POLYMERS: ULTRAFILTRATION AND SPECTROSCOPIC STUDIES

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Interactions of low molecular-weight molecules with polymers are interesting in order to understand biological processes from both the structural and the functional point of view. Charged macromolecules (polyelectrolytes and polyampholytes) constitute a large class of materials that are particularly important for biological systems. In polyelectrolyte theory [1,2], when long range electrostatic interactions are dominant, polyelectrolytes are assumed to bind counterions nonspecifically, and they are considered to move freely around the axis of the polymer chain. Thus, the electrostatic water-soluble polymer counterion interaction may be regarded as an adsorption phenomenon of counterions on the surface of the polymer domain. Due to the hydrocarbon nature of some water-soluble polyelectrolytes, they can also undergo hydrophobic interactions with other low molecular-weight species. Other interactions such as electron transfer or hydrogen bonding may also be present in multicomponent aqueous systems containing these polymers. Due to these interactions, macromolecules in solution exhibit, beyond their chemical structure, different properties as conformation of the polymer chains, excluded volume, surface activity, or formation of higher-order structures as aggregates, gels, *etc.* The conjunction of all these features determines the properties and behavior of the system.

Ultrafiltration has emerged as a useful technique to detect and quantify these interactions [3]. This technique is based on the separation of particles whose size is greater than the ultrafiltration membrane pores (as water-soluble polymers) from smaller molecules (as counterions). The rate of filtration of counterions is strongly influenced by their interactions with the polyelectrolyte. Different spectroscopic techniques may provide information about the nature of such interactions. Poly(sodium 4-styrenesulfonate) (PSS), and poly(acrylic acid) (PAA) are subject of study along with L-tryptophan, L-phenylalanine, salicylic acid, methylene blue, rhodamin-B, and 2,3,5-triphenyltetrazolium chloride.

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COMPLEXATION OF ANIONIC POLYELECTROLYTES WITH CATIONIC LIPOSOMES: EVIDENCE OF REENTRANT CONDENSATION AND LIPOPLEX FORMATION

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The complexation between a flexible polyelectrolyte and a charged colloidal particle of opposite sign represents a fundamental problem for the knowledge of complex systems. It has been studied both experimentally and theoretically by various authors, owing to its importance in different fields and the potential applications in both chemical and biological realms. The theory of this phenomenon is attractive, as it presents many parallels with other areas of physics; moreover, the mechanism underlying this process is rather complex, resulting in two important effects: "charge inversion" and the presence of a short distance, attractive potential between polyelectrolyte-coated liposomes. The purpose of this work is to present a rather unexpected phenomenon manifested in the complexation between cationic liposomes (DOTAP) and an oppositely charged polyion (NaPAA). The formation of polyion-liposome complexes has been directly monitored in terms of the apparent hydrodynamic radius R_H as determined by dynamic light scattering (DLS) and by transmission electron microscopy (TEM) measurements. The main findings can be summarized in a charge ratio-dependent scenario. The size of complexes of DOTAP with NaPAA remains fairly constant (of the order of 200 nm) until a charge ratio $\text{NaPAA}/\text{DOTAP}=0.5$ is reached, at which point a gradual increase in size is observed up to the charge neutralization, where the complexes condense in macroscopic aggregates with peculiar molecular assembling. As the charge ratio is further increased (at moderate excess NaPAA), a sharp transition towards lower sizes is observed corresponding to a structural rearrangement that provides a pathway for their subsequent break-up into smaller size lipoplexes. Moreover, completely unusual in the aggregation of charged colloidal suspensions, for polyions of higher molecular weights, a charge ratio more than 10 lead to a different growing kinetic regime in which two separate populations appear with two distinct time evolution regime. This size increase appears to occur in two coexisting phases. First, for each polyion concentration, the initially formed lipoplexes undergo a further aggregation forming even larger structures whose average size

continuously increases with time. We have measured complexes with an estimated size larger than 1-5 μm at time of the order of 10^3 min from the beginning. Second, an essentially static regime coexists in which the lipoplexes (of size of the order of 150 nm) are stable and do not undergo further aggregation.

This complex phenomenology has been discussed in light of scaling theories of polyelectrolyte adsorption at an oppositely charged surface recently developed by Dobrynin and Rubinstein.

SELF-ASSEMBLING AND DYNAMICS IN ION-CONTAINING POLYMERS BASED ON PARAMAGNETIC AND FLUORESCENT PROBES

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The phase-separated morphology and the effect of ionic aggregation on the backbone chain mobility in poly(ethylene-*co*-methacrylic acid) (EMAA), Nafion and sulfonated polyimide (SPI) ionomers were investigated by spin probe electron spin resonance (ESR) and fluorescence spectroscopies [1-4]. The spin probes differed in their hydrophobicity and in the position of the nitroxide group with respect to the ionic head. The fluorescent probes were pyrene (P) and 1,3-bis(1-pyrene) propane (P3P). In EMAA dispersions in water, the fluorescence and ESR spectra of hydrophobic probes suggested a probe environment of low polarity and high viscosity that was identified as the micellar core. The critical micellar concentration (CMC) of the ionomer was estimated as 0.02 % wt EMAA, and was deduced from the concentration dependence of the intensity ratio of the first to the third vibronic peak in the fluorescence spectrum of P. In Nafion the probes prefer hydrated sites just below the interface, rather than the hydrophobic microenvironment of perfluorinated chains. The effect of ionic aggregation on the backbone chain mobility was determined from the ESR spectra, which clearly indicated the highly restricted mobility of the chain segments in the hydrocarbon shell surrounding the ionic aggregates. In the most recent studies we have detected the presence of an ion-depleted zone in the swollen EMAA membranes, surrounding the ionic clusters [3]. In addition, the use of perfluorinated nitroxide probes for the study of Nafion membranes and solutions has been recently introduced [4].

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*SPATIAL EFFECTS IN THE DEGRADATION OF POLYMERS BY ESR IMAGING:
CRYSTALLINE, AMORPHOUS AND RIGID AMORPHOUS PHASES IN
HETEROPHASIC PROPYLENE-ETHYLENE COPOLYMERS*

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We present a study of thermal degradation in two heterophasic propylene-ethylene copolymer (HPEC) samples containing respectively 12 and 25 % wt ethylene (E) in the ethylene-propylene rubber (EPR) component. The polymers contained Tinuvin 770 as a hindered amine stabilizer (HAS). The formation of nitroxide radicals from HAS during heat treatment at 120 and 160°C provided the contrast in the electron spin resonance imaging (ESRI) experiments. Additional details were obtained by spin probe ESR, DSC, and FTIR [1-2]. ESR spectra of the thermally treated polymers indicated the presence of radicals in two environments differing in their dynamics: The fast component was assigned to nitroxides located in the rubber domains; and the slow component to nitroxides in the rigid amorphous phase, where the local mobility is restricted due to the proximity to crystalline domains. The results from the spin probe study confirmed the conclusion that nitroxides located in amorphous domains are sensitive to the degree of crystallinity. This study detected the presence of an interphase where the dynamics of the probes is restricted due to their proximity to crystalline domains. The radical distribution was deduced from 1D ESRI and the variation of the ESR line shapes along the sample depth was determined from 2D spectral-spatial ESRI. The spatial and morphological variation of the degradation processes during thermal treatment was deduced from the ESR imaging experiments.

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MEASUREMENTS OF DRYING STRESS IN COATING LAYERS

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In any coating process with granular precursors in a liquid medium, there will be a drying step. This step will greatly influence the quality of the finished product. If the coating is not properly dried, defects may be introduced or the product may be deformed. Often, these defects and deformations may be attributed to stresses induced in the drying step.

Previous work on drying in other fields has already gives us a rather consistent picture of the important parameters controlling the drying behaviour of granular materials, mainly ceramic and sol-gel systems. Drying rate, particle size and liquid surface tension are the parameters that affect the drying stress evolution the most.

We have made drying stress measurements of various model paper-coating formulations to elucidate how the paper coating composition will affect the drying stress evolution. The model systems included pigment (precipitated calcium carbonate), a soluble polymer (carboxy-methyl cellulose), and latex binders of varying glass transition temperature (styrene-butadiene latex), all commonly used in the paper coating industry.

The stress development during drying was studied using a controlled environment stress apparatus that simultaneously monitors drying stress, weight loss, and relative humidity. Their stress histories exhibited three distinct regions. First, a period of stress rise was observed, which reflected the capillary tension exerted by the liquid on the particle network. Second, a maximum stress was observed that was followed either by a period of stress decay or rise depending on the organic species present. Significant differences in stress histories were observed between coatings containing soluble and non-soluble binders.

Maximum drying stresses (σ_{\max}) of 0.2–0.5 MPa were observed for coatings produced from pure calcium carbonate or calcium carbonate-latex suspensions, whereas coatings with carboxymethylcellulose exhibited substantially higher σ_{\max} values of 1–2 MPa. Upon drying, these coatings were quite hygroscopic, such that cyclic variations in relative humidity induced large cyclic changes in residual stress.

*WATER TRANSPORT IN DOUBLE EMULSIONS: THE EFFECT OF THE
OSMOTIC PRESSURE*

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Double emulsions are a potential structure for food applications. Not only can the fat content be reduced but also improved scattering properties and the possibility to separate components make these structures very promising. However, in order to control the release of encapsulated components and to prevent the structure from phase inverting and creaming, one needs to be able to control the diffusion between the two water phases.

In the present study the diffusion properties between the two water phases are studied. NMR self diffusion is used to show the different water phases, i.e. free water, encapsulated water and water solubilised in reversed micelles in the oil. Furthermore, altering the chemical potential of the external and internal water phases by dissolving neutral linear polysaccharides of suitable molecular weights controls the internal particles size. In order to quantitatively control this change, a numerical model was developed allowing the prediction of the swelling/shrinking behavior of W/O/W double emulsions.

***STUDY OF PERFLUOROPOLYETHER WATER IN OIL
MICROEMULSIONS BY SMALL-ANGLE NEUTRON SCATTERING***

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Ternary water-in-oil microemulsions formed from an ammonium carboxylate PFPE surfactant of molecular weight 710 and a PFPE oil of molecular weight 900, leading to microemulsions that show a dynamic percolation phenomenon [1,2], were investigated by SANS to characterize the microstructure. Hard sphere and adhesive hard sphere potentials were used to model the droplet - droplet interactions assuming polydispersed droplets with a Schultz distribution of sizes. In [3] a preliminary analysis is performed on microemulsion samples with a water/surfactant molar ratio of 15 and 20, at a temperature of 20 C. For volume fractions less than 0.22, the microemulsions are composed of polydispersed spheres with an aqueous hard core of average diameter 6-7 nm with a polydispersity of 20%. Excluding the most diluted sample at W/S=20 that does not show adhesion, all the other samples are adhesive with the following values of the square-well potential parameters, width 0.7 nm and depth of few $K_B T$ units. In this work we report on a larger number of samples studied with the same procedure.

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EFFECT OF THE IONIC SURFACTANT CONCENTRATION ON THE STABILIZATION/DESTABILIZATION OF LATEX PARTICLES

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There exist many industrial processes that require the utilization of colloidal dispersions. These dispersions are usually unable to maintain their dispersed state by their own. Surface properties of these colloids can change by adsorbing some molecular chains. By controlling the main mechanisms of this phenomenon, dispersions can be stabilized/destabilized, so that these ones perform in the process correctly. This work was focused on analyzing the stability of latex dispersions under a wide range of ionic surfactant concentrations. Concentrations well above the critical micelle concentration were reached. The effects of surface charge sign, its value and the type of surfactant were examined. Complementary data about the complexes formed below the CMC were obtained by means of electrophoretic mobility. Complex aggregation studies by adding NaCl were carried out using a low-angle light scattering technique. The critical coagulation concentration was obtained at different complex coverage. Below the CMC, different behaviours can be observed when surfactant and surface have the same or opposite sign. A wide stability region at concentrations around the CMC was found. This stability is independent of the surface, but it depends on the type of surfactant adsorbed. Well above the CMC (at high micelle concentration), the flocculation of the system takes place. This process is reversible by dilution. Different interaction contributions can be assigned to the different stability regimes. Below the CMC, the electrostatic repulsion potential, the London van der Waals one and the steric contribution should be considered. However, above the CMC a new contribution must be included to take into account the interaction between micelles and complexes. Flocculation at very high surfactant concentrations can be due to the fact that micelle depletion provokes particle attraction. The electrostatic repulsion among the charged micelles and the complexes enhances that flocculation mechanism.

SPINODAL DECOMPOSITION AND INTERNAL CLUSTER STRUCTURE IN COLLOIDAL CHARGE HETEROAGGREGATION

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Aggregation in colloidal systems was shown to produce clusters with internal uniform structure, which can be characterized by a fractal dimension, d_f . Whereas diffusive aggregation yields $d_f=1.7-1.8$, regardless the system, aggregation with a repulsive interaction between particles produces clusters with $d_f=2.0-2.1$. Previously, we have shown that the fractal dimension of clusters formed in charge heteroaggregation is much lower the diffusive aggregation value, caused by the attraction between particles [1]. Here, by means of Brownian dynamics simulation we study: *i*) the distribution of positive and negative particles inside the cluster and *ii*) the spatial ordering of heteroclusters. The radial distribution function shows that the particles inside clusters are surrounded by a layer of particles of opposite charge. At high interaction strength or range, this layering effect can be observed up to distances corresponding to 6-7 radii. For the analysis of the spatial distribution of clusters, the pair distribution function was studied at distances larger than the average cluster radius. A minimum in this region reveals a depletion layer around the aggregates, which is shown to grow at the same rate as the aggregate, thus producing a single peak in the structure factor, $S(q)$. The structure factor at different times in the aggregation progress can be re-scaled onto a time-independent master curve, $F(q)$. The radius of the aggregate, R , and its fractal dimension are used in the re-scaling, following the spinodal decomposition re-scaling: $S(qR,t)=R^{d_f} F(qR)$ that was shown to work in diffusive aggregation [2].

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SURFACE ACTIVITY OF β -CYCLODEXTRIN IN AQUEOUS SOLUTIONS OF HYDROPHOBIC ORGANIC COMPOUNDS

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Hydrocarbons encountered in the environment are usually adsorbed on the solid particles or on the organic matter. It is known, that β -cyclodextrin may enhance the biodegradation of hydrocarbons using microbial colonies isolated from a petroleum polluted soil and effects on photodegradation of organophorus pesticides in humic waters. β -Cyclodextrin, environmentally inoffensive compound, increases the solubilization and the removal of contaminants from surfaces. However, complexation constants of polyaromatic hydrocarbons and β -cyclodextrin in aqueous environment are not favourable and only a small part of cyclodextrin molecules contain complexed hydrocarbons. Thus, an increase of the hydrocarbon solubilization using β -cyclodextrin may be obtained only by modifying the complexation equilibrium. It was recently suggested [1-3] that ternary complexes $\{\beta\text{-Cyclodextrin} + \text{Hydrocarbon} + M^{Z+}\}$ makes it possible not only enhancing hydrocarbon solubility but also its reactivity. The knowledge of the surface properties of these complexes is essential for the comprehension of the mechanism of pollutant solubilization and degradation. In this work we are dealing with the surface properties of β -cyclodextrin and its binary and ternary complexes. The air/aqueous solution surface tension were measured in function of β -cyclodextrin concentration for a series of solutions containing ionic and non-ionic species. At first complexes $\{\beta\text{-Cyclodextrin} + \text{Anthracene or Behenic Acid} + \text{Silica}\}$ were studied. Next, complexes $\{\beta\text{-Cyclodextrin} + \text{Anthracene} + M^{Z+}\}$ with Pb^{2+} , Fe^{2+} and Fe^{3+} were investigated. It was observed that the surface activity as well of β -cyclodextrin as of its complexes is weak. Nevertheless, it was found that the surface behaviour allows to differentiate all binary or ternary complexes studied.

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EFFECT OF ELECTROSTATICS ON THE PROPERTIES OF POLYELECTROLYTE MULTILAYERS

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Thin adsorbed polymer films are the topic of many recent studies due to their variety of technical applications (e.g. coating) and the interesting properties arising from their confined geometry. The polymer films presented in this study were prepared by alternate adsorption of polyanions and polycations from aqueous solution onto solid substrates (silicon, glass) [1]. In general, the formation of polyanion/polycation complexes is assumed to be the driving force for the multilayer formation. With increasing salt concentration the film thickness increases due to electrostatic intra- and interchain screening of charges. Multilayer build-up occurs up to high ionic strength (above 1 mol/L) although the charges are totally screened in this regime [2]. This rises the question to which extend electrostatic attraction is required for the formation of the multilayers and non-electrostatic contributions will be discussed. The influence of ionic strength, polymer charge density and charge distribution on multilayer formation is investigated by ellipsometry, AFM and reflectometry methods [3]. Recently, we also started studying the film internal structure of partly deuterated polyelectrolyte multilayers as a function of above control parameters and subsequent changes of film structure by ex-situ manipulations of environmental conditions (e.g. hydration, temperature and ionic strength).

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*HYDRATION OF ADSORBED POLYELECTROLYTE MULTILAYERS: TOWARDS A
BETTER UNDERSTANDING OF THE INTERNAL STRUCTURE*

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The polymer films presented in this study were made by alternate adsorption of polyanions and polycations from aqueous solution onto solid substrates (Silicon, glass) using the layer-by-layer method developed in the early 1990s by Decher et al.[1]. In the present work the effect of electrostatics on the formation and hydration of the polyelectrolyte multilayers is investigated. Therefore the multilayers are prepared at different salt concentrations and with different polymer charge densities [2]-[4]. The equilibrium film thickness is measured by ellipsometry and X-ray reflectometry at different relative atmospheric humidities. We found that the amount of water absorbed by the polymer film increases with increasing film thickness, but the net percentage of water absorbed decreases after reaching a maximum for a certain number of layers. These findings enable us to have a better understanding of the internal structure of the polyelectrolyte multilayers as we shall attempt to explain our results.

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IDENTIFICATION OF OPTIMUM FORMULATION (HLD=0) BY TURBISCAN

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The phase behaviour of surfactant/water/oil systems (S/W/O) is dependent on surfactant affinity for water and oil [1]. The *optimum formulation*, defined as the formulation in which surfactant has the same affinity for water and oil, has been expressed as a numerical function (HLD, hydrophilic-lipophilic difference) of formulation variables [2]. The identification of *optimum formulation* (HLD=0) is generally performed by looking for the minimum of stability and/or interfacial tension, which very often are not easy to determine (very low interfacial tension values are difficult to measure and very stable emulsion are difficult to separate). In this work a new method to determine the *optimum formulation* by using Turbiscan MA 2000 (a multiple light scattering analyzer) has been developed. The emulsion stability has been determined by following the profile of the transmission and/or back scattering along the test tube length as a function of time. Turbiscan measurements of phase separation for Tween 80-Span 80/Water/Dodecane systems, at water oil ratio equal to one and in function of HLB (from 10.2 to 10.7), are performed at room temperature. Samples are monitored, after a vigorous mixing, during 24 hours and until full phase separation. Results show an easy identification of HLD=0. Kinetics studies have also been made in order to predict the *optimum formulation*.

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EFFECT OF SODIUM DODECYL SULFATE ON THE PROPERTIES OF DIOCTADECYLDIMETHYLAMMONIUM CHLORIDE VESICLES

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We have investigated by differential scanning calorimetry (DSC) and turbidity the effect of adding a micelle solution of sodium dodecyl sulfate (SDS) into a dispersion of the cationic vesicle-forming dioctadecyldimethylammonium chloride DODAC with Aliquots of concentrated (typically 40 mM) SDS solution was added to a 1.0 mM DODAC dispersion and the DSC thermogram and turbidity was monitored as function of the SDS/DODAC molar ratio (R). At this concentration DODAC dispersions exhibit a single peak at the gel to liquid crystalline transition temperature, $T_m = 49^\circ\text{C}$. Up to $R = 5.0$, we observed no vesicle-micelle transition, but instead a growth in turbidity and change in the DSC thermogram. The addition of small amount of SDS, up to ca $R = 0.4$, shifts T_m downward to 47.1°C . Above this ratio, the mixture exhibits a more complicated phase behavior and two or more broad peaks appear at temperatures higher than the T_m of DODAC/water. In spite of being oppositely charged, these surfactants take a rather long time to attain equilibrium, indicating that the mixture is kinetically driven.

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DNA INTERACTION WITH AMINO ACID-BASED CATANIONIC VESICLES

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Spontaneously formed stable vesicles, catanionic vesicles, can be prepared from aqueous mixtures of single chained cationic and anionic surfactants. In this paper we report the formation of novel amino acid-based catanionic vesicles. The used surfactants in this work were the anionic sodium octylsulfate (SOS) and the arginine-based cationic surfactant, ALA. The formation of vesicles was observed by cryo-TEM. The formation of amino acid-based catanionic vesicles is very interesting, since amino acid-based surfactants are more biocompatible than other cationic surfactants.

Catanionic liposomes complexed with DNA are promising as synthetically based nonviral carriers of DNA vectors for gene delivery. The addition of DNA to the formed amino acid-based catanionic vesicles, at different mixing ratios, has induced the disintegration of the vesicles and the formation of multilamellar structures. The structure of these multilamellar lipoplexes was studied by small-angle X-ray (SAXS) and cryogenic transmission electron microscopy (cryo-TEM), and a short-range lamellar structure composed of amphiphile bilayers with DNA molecules ordered and packed between these stacks was found. The structures were found to have similar structure to that found in the literature. [1]

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TRAPPING METAL NANOCLUSTERS IN 'SOAP AND WATER' SOFT CRYSTALS

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We report in this paper the elaboration of a lyotropic hexagonal phase doped with metal nano-clusters. This concept is general and may be applied to many metal clusters. The system is made from sodium dodecyl sulfate, water, pentanol and toluene. It displays a hexagonal phase of direct type, namely, nonpolar tubes in a polar medium swollen by the organic phase. We succeeded in trapping stable clusters of different metals, *viz.* palladium, ruthenium, silver, gold and copper inside the nonpolar tubes by using a suspension of metal clusters (2nm size) in toluene. The growth of the doped hexagonal phase was monitored using cross-polarized microscopy, and its structure studied by Small Angle X-ray Scattering. Evidence that clusters are inside the worm-like micelles is presented. By confining the nano-clusters in a well defined cylindrical micelle rods, we may direct their cold welding so they grow into wires.

We also present new results on the aging and temperature behavior of doped hexagonal phase obtained by SAXS and WAXS measurements.

*MICELLIZATION OF IONIC AMPHIPHILIC DIBLOCK COPOLYMERS IN
AQUEOUS MEDIA AND THEIR INTERPOLYELECTROLYTE COMPLEXES*

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The micellization of ionic amphiphilic diblock copolymers, polyisobutylene-*block*-poly(methacrylic acid), in aqueous media was examined. The molar values of the critical micellization concentration measured by means of fluorescence spectroscopy with a use of pyrene as a polarity probe were found to be around 10^{-6} M, these values being nearly independent of the degree of polymerization of the poly(methacrylic acid) block ($DP_n = 100 \div 425$) as well as of pH ($pH = 6 \div 9$) and ionic strength (≤ 0.5 M NaCl) in the system. The hydrodynamic characteristics of the copolymer micelles determined by means of analytical ultracentrifugation and dynamic light scattering were shown to be sensitive to the variations of pH and ionic strength of the solution: a decrease of pH or an increase of ionic strength resulted in a decrease of hydrodynamic radii of such macromolecular assemblies and an increase of their sedimentation coefficients.

It was demonstrated that the formed copolymer micelles mixed at $pH > 6.5$ with strong cationic polyelectrolytes, poly(N-ethyl-4-vinylpyridinium bromide) or 2,5-ionene bromide, at charge ratios $Z = [+]/[-]$ not exceeding a certain critical value Z_{max} , $Z_{max} < 1$, form water-soluble interpolyelectrolyte complexes. The results obtained by means of analytical ultracentrifugation, dynamic light scattering, and fluorescence spectroscopy allow us to consider their particles as peculiar onion-like micelles, each containing a two-component hydrophobic nucleus and a hydrophilic corona. The nucleus consists of a polyisobutylene core surrounded by a shell assembled from the fragments of the poly(methacrylic acid) blocks coupled with cationic macromolecules. The corona is formed by excess fragments of the poly(methacrylic acid) blocks not involved in the interpolyelectrolyte complexation. At relatively high ionic strengths in the system, the micellar complex species were found to dissociate to the individual copolymer micelles and cationic macromolecules because of the screening effect of small ions.

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PHOTOINDUCED VECTORIAL CHARGE TRANSFER ACROSS WALLS OF HOLLOW MICROCAPSULES

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Electron transfer (ET) reactions are enhanced in polar environment and strongly depend on the distance between donor (D) and acceptor (A) molecules. In this work a multilayer system is built up that enables vectorial electron transfer along an internal polarity gradient on a nm length scale.

Planar polyelectrolyte (PE) multilayer films prepared by sequential adsorption of poly(styrene sulfonate) (PSS) and different polycations showed a different polarity depending on the kind of polycation used for the multilayer build-up process. This result has been used to fabricate a material with an internal polarity gradient by successively adsorbing specific PEs onto charged colloidal templates.[1-2]

A high pyrene-labelled (1:30) poly(styrene sulfonate) (PSS-Py) was synthesized. High chromophore density is necessary for efficient electron transfer. PSS-Py was adsorbed with different polycations by the Layer by layer technique so that an internal nanoscale polarity gradient could be obtained and quantified together with the immobilization of electron donor molecules (PY) at defined positions.

Quantitative vectorial charge transfer across the walls was proven by means of fluorescence quenching studies.

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MORPHOLOGICAL AND STRUCTURAL INVESTIGATION OF MONOLAYERS OF POTENTIAL INHIBITORS OF PHOSPHOLIPASE A₂ (PLA₂)

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Sn-2 amide analogs of phospholipids are known as strong inhibitors of the secretory phospholipase A₂ when they have an ester, ether, thioether bond or an alkyl chain at the sn-1 position of the original glycerol backbone. Ether and ester amide phosphatidylcholines (PC) were prepared to investigate their interfacial properties and to prove their abilities to inhibit phospholipase A₂ at the air/subphase interface. Both potential inhibitors have been systematically investigated in two- and three-dimensional systems by pressure/area isotherms, Brewster angle microscopy (BAM), Differential Scanning Calorimeter (DSC), and X-ray diffraction (GIXD as well as SAXS/WAXS). Thermodynamic data obtained by π -A isotherm measurements at different temperatures are coupled with two dimensional (2D) texture and 2D structure information obtained by BAM and GIXD, respectively. Different typical domains with half-moon or star-shapes arise depending on the experimental conditions. In aqueous dispersions, phase transition temperatures and phase diagrams were measured and calculated by DSC and SAXS, respectively. As a potential inhibitor of phospholipase A₂, L-ether-amide-PC and L-ester-amide-PC exhibited good inhibitory activities. The π -t and A-t curves were measured at the air/subphase interface after injection of PLA₂ into the subphase, and the corresponding morphology changes with time were observed by BAM. Additionally, such inhibitors can provide valuable information about how phospholipids interact with phospholipase A₂.

POSTERS

2. Industrial Applications: Colloid Science in Action

INTERFACIAL CATALYSIS – ADSORPTION AND ACTIVITY OF ENZYMES PROBED AROUND THE ISO-ELECTRIC POINT

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We have investigated the effect of pH, salt, and surfactants on the adsorption and activity of hydrolytic enzymes around their iso-electric point. In the absence of surfactants, we find a direct correlation between affinity and interfacial activity of the enzymes. Depending on the surfactant-charge we observe different contributions from inhibition- and boosting-effects of the surfactants on the enzyme activity. These results are mainly gathered from surface plasmon resonance studies.

COLLOIDAL STRUCTURE OF HYDROCARBON LUBRICANTS AT HIGH TEMPERATURES: INFLUENCE ON OXIDATION MECHANISM

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It is well known that petroleum-based hydrocarbon lubricant compositions demonstrate properties of colloids [1]. This is due to 1) complex mixture of various hydrocarbon substances that compose base fluid, and to 2) a number of functional additives represented by various classes of organic compounds. However, little is known about behavior of reverse colloid systems in hydrocarbons under operation temperatures exceeding 150-200°C.

Liquid-phase oxidation of hexadecane at 150-170°C obeys classical radical chain mechanism only at low conversion rates. Utilization of aqueous-soluble dyes solubilization method for samples of oxidized hydrocarbon indicates that the oxidation process is accompanied with formation of second polar nano-phase at the very beginning of the process.

The wavelength value of methyl orange dye absorption band depends on oxidation degree, thus suggesting gradual changes in composition and structure of formed nano-phase. Possible formation mechanisms and micellar inhibition concept are discussed.

Rate of hydroperoxide formation (170°C) in hexadecane-AOT compositions indicates that oxidation mechanism changes at AOT concentration about 0.06 mol/l, which is relatively close to CMC of AOT at ambient temperatures [2].

Traditional antioxidant additives (AO) may be located predominantly either in hydrocarbon phase, in micellar core, or at the surfactant interface depending on their own hydrophilic-lipophilic properties, this determines their efficiency.

Thus, colloidal structure of hydrocarbons at high temperatures influences strongly on depletion mechanism of lubricants and this knowledge is important for development of novel efficient lubricant compositions. This is a fruitful area for cooperation of specialists in colloid chemistry and in chemistry of lubricant additives.

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BIOCATALYSIS USING LIPASE IMMOBILIZED IN MICROEMULSION-BASED ORGANOGELS IN SUPERCRITICAL CARBON DIOXIDE

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Increasing concerns regarding toxicity and environmental compatibility of industrial production have resulted in intensified efforts to find sustainable solvents and chemical processes since the last decade:

The employment of biocatalysts in organic synthesis has become an interesting alternative to conventional chemical methods [1]. One of the most intensively studied methods has been the technique of solubilising enzymes in hydrated reverse micelles or water-in-oil microemulsions [2]. In order to overcome problems in product isolation and enzyme reuse in these systems, the use of microemulsion-based organogels (MBGs) has been object of interest [3,4].

In parallel, liquid or supercritical carbon dioxide (scCO₂) has emerged as perhaps the most promising “green” solvent (apart from water): carbon dioxide is toxicologically harmless, not inflammable, readily available and inexpensive. Furthermore, it exhibits a moderate critical point and tunable solvent and solvation properties by simple control of pressure and temperature [5].

In the present project the two research directions in green chemistry are joined. Lipase from various sources was immobilized in AOT as well as lecithin water-in-oil MBGs formulated with hydroxypropylmethyl cellulose or gelatine. Model esterification reactions of fatty acids and alcohols were examined in both scCO₂ (35°C; 110 bar) as well as isooctane as reference system. In both solvents the gels proved to be reusable with a slight decrease of lipase activity. Kinetic studies showed that an inhibition by excess of alcohol occurs.

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RHEOLOGY OF FLUID GEL AND ITS APPLICATION

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Focusing on the particle size of fluid gel[1] dispersion using Gellan gum, we found that even with the same composition, the appearance and rheological characteristics of fluid gel dispersion were greatly different depending on the particle size. The smaller the particle size of fluid gel is, the smoother the liquid appearance of fluid gel dispersion seems to be. Comparison among rheological characteristics indicated that the larger the particle size of fluid gel was, the greater the yield stress and shear stress during flowage were and that there was an appropriate correlation ($r=0.97$) between the particle size of fluid gel and the yield stress of fluid gel dispersion. On the other hand, it was observed that among fluid gel dispersion samples having the same particle size, the less concentration of calcium ions added as crosslinking agent for double helix of the Gellan gum they had, the greater shear stress they showed. We considered it as an influence of interaction among fluid gel particles. From these results, it was found that the control of the particle size of fluid gel dispersion and the calcium ion concentration was effective as a method of controlling the solidity of fluid gel dispersion. It was also revealed that unsuitable balance between the calcium ion concentration and shearing force[2] might cause the fluid gel dispersion to be gelled again. We succeeded in preparing the fluid gel dispersion of fine fluid gel with the average particle size of $0.14 \mu\text{m}$ by controlling the concentration of calcium ions and the shearing force. Fluid gel particles with smaller size decrease the yield stress of fluid gel dispersion, deteriorating the dispersion stability of dispersoid. However, by encapsulating the dispersoid into fluid gel particles, we could prepare a pharmaceutical product providing an adequate compatibility between the product appearance and stability.

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THE THERMOLYSIS OF tert-BUTYL ESTER AT THE SURFACE OF SILICA FOR SILICA FUNCTIONALIZATION

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The generation of carboxylic acid groups grafted on the surface was achieved by the thermal deprotection of tert-butyl esters at 265 °C. This provides an easy way to prepare carboxylic acid grafted on silica, which are useful in various applications. Such a result was attained from a presently reported investigation of the thermolysis of various esters grafted on fumed silica. The thermogravimetric analysis showed that the thermal cleavage of esters took place at increasing temperatures in the order tert-butyl < isopropyl < methyl ester. The most labile t-butyl ester was cleaved well below the thermal decomposition of the remaining graft, allowing a selective deprotection. On the contrary, methyl and isopropyl esters cleavage did not reach completion keeping the remaining graft because of the overlap of the thermolysis domains. Several analyses showed that the thermal decomposition of t-butyl esters resulted in the elimination of isobutene. The kinetics of the thermal elimination of esters grafted on silica demonstrated the first order kinetics and the activation energy; it also allowed to optimize a process for its practical utilization. A thermal treatment at 265 °C during 45 min allowed 99.7 % deprotection into carboxylic acid groups, keeping the thermal degradation of the graft lower than 6 %.

The thermal cleavage provides an alternative to chemical deprotection (acid catalyzed elimination or hydrolysis) for the development of surface functionalization, because it is easy and clean (reagentless), it can easily be scaled up and implemented in microtechnology processes.

BLOCK COPOLYMERS AS FLUIDIZERS OF CONCENTRATED SLURRIES

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Concentrated colloidal suspensions of calcium carbonate in water are viscous gels because of the agglomeration of individual particles into large aggregates. Additives known as fluidizers or dispersants adsorb at the surface of the particles and provide an improved colloidal stability by means of either supplementary electrostatic or steric repulsions.

Block copolymers are quite efficient for that purpose. Thus, the block copolymers poly(ethylene oxide)-bloc-poly(acrylic acid) have a polyacrylate block that ensure a strong adsorption and a poly(ethylene oxide) block that brings about the steric stabilization. The rheological investigation of calcium carbonate slurries stabilized with such copolymers shows their fluidization action: the viscous paste (pseudo-plastic flow behaviour) turns progressively into a fluid suspension having a Newtonian flow behaviour as the copolymer is added to the slurry.

It is shown that the repulsions between CaCO_3 particles is steric because of the non-ionic nature of poly(ethylene oxide). Another advantage of the non-ionic character is a low sensitivity to the ionic strength that cannot be obtained with the usual polyacrylic acid homopolymer dispersants. Lastly, the phenomenon of depletion flocculation which mainly takes place at high volume fractions of CaCO_3 particles, is minimized with the di-block architecture as compared to homopolymers. The influence of the chemical structure (block lengths) on these properties have been studied.

CATALYTIC APPLICATIONS OF RESONANT DIFFUSION

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Diffusion of normal alkanes in one-dimensional zeolites is theoretically and experimentally studied on the basis of the stochastic equation formalism [1]. The calculated diffusion coefficient accounts for the vibrations of the diffusing molecule and zeolite framework, molecule-zeolite interaction, and specific structure of the zeolite. It is shown [2] that if the interaction potential is predominantly determined by the zeolite pore structure, the diffusion coefficient varies periodically with the number of carbon atoms of the alkane molecule, a phenomenon called resonant diffusion. A criterion for observable resonance is obtained from the balance between the interaction potentials of the molecule due to the atomic and pore structures of the zeolite. It shows that the diffusion is not resonant in zeolites without pore structure, such as ZSM-12. Moreover, even in zeolites with developed pore structure no resonant dependence of the diffusion constant can be detected if the pore structure energy barriers are not at least three times higher than the atomic structure energy barriers. The role of the alkane molecule vibrations is examined as well and a surprising effect of suppression of the diffusion in comparison with the case of a rigid molecule is observed. This effect is explained with the balance between the static and dynamic interaction of the molecule and zeolite. The role of the resonant diffusion on the rate of photo-catalytic oxidation over TiO₂ surface is also described [3].

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CATALYTIC AND SPECTROSCOPIC STUDIES OF LIPASES IN TERNARY HEXANE - ALCOHOL -WATER MIXTURES

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Ternary water-organic mixtures (also known as surfactantless microemulsions) consisting of a non polar organic solvent, a short chain-alcohol and water represent thermodynamically stable and optically transparent dispersions of aqueous microdroplets in the hydrocarbon solvent and have been already shown to serve as appropriate media for enzymic catalysis [1,2].

These ternary systems have the ability to dissolve both hydrophobic and hydrophilic reagents, possess enormous interface area and can be prepared from inexpensive non-toxic solvents. An important advantage of using surfactantless microemulsions as a reaction system is that the separation of the reaction products as well as the enzyme reuse are facilitated as compared to classic reverse micellar systems. In addition the solubility of relatively polar compounds is high due to the presence of large amount of polar alcohol.

In this work we investigated the catalytic behavior of lipases from *Mucor miehei* and *Candida antarctica* B in surfactantless microemulsions formed in ternary mixtures consisting of *n*-hexane, 1-propanol and water. Moreover, the localization of lipases as well as their interaction with the organic phase of the system was investigated by fluorescence quenching measurements and fluorescence energy transfer technique.

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PICKERING EMULSIONS: INTERFACIAL TENSION, COLLOIDAL LAYER MORPHOLOGY, AND TRAPPED-PARTICLE MOTION

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Emulsions are of enormous practical interest for their widespread occurrence in processes related to the food, cosmetics, and pharmaceutical industries. It is well known that stable emulsions can be readily obtained by adding surfactants to immiscible liquids. Yet, starting from seminal studies by Pickering [1], evidence has been gathered that emulsion stability does not necessarily require surface-active agents, but can also be efficiently promoted by dispersed particles in the colloidal size-range[2]. 'Pickering' emulsions play a crucial role in many industrial applications. For instance, stabilization of oil/brine emulsions encountered during oil recovery processes, which must be broken before crude oil refining, is brought about by clays, asphaltenes, and other dispersed particles. Presumably similar natural colloids cooperate in emulsifying oil spills, leading to serious environmental problems. We have explored basic features of Pickering emulsions using as the stabilizing agent 'model' silica particles containing a fluorescent core, which allow the interfacial adhesion processes to be detected and quantified by video-microscopy. We studied two colloidal systems, primarily differing in the particle-surface structure. The first one is composed of monodisperse, surface-smooth spherical colloids. Particles of the second batch, although still monodisperse, display noticeable surface 'roughness', mimicking therefore an important, and so far neglected, feature of natural colloids. In particular, we show that particle trapping at the water/oil interface does not lead to appreciable changes in O/W droplet interfacial tension, confirming therefore the steric origin of Pickering emulsion stabilization. We also found that surface roughness appreciably lowers particle emulsifying power, and that no straightforward relation exists between the degree of droplet surface-coverage and macroscopic emulsion stability. Finally, we have studied surface diffusion of the trapped particle, and we suggest that particle redistribution on droplets plays a role in stabilizing droplets with low or inhomogeneous particle coverage.

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SAMPLE PREPARATION FOR PHASE DIAGRAM APPLICATIONS BY MEANS OF A ROBOTIC LIQUID HANDLER

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A method, to facilitate preparation of large series of samples for phase diagram applications by using a robotic liquid handler, is presented. The concept has been used for preparation of samples containing lipid (monoolein (MO)), solvent (1-methyl-2-pyrrolidinone (NMP), dimethylsulphoxide (DMSO) or acetonitrile (AN)), and water (w). The amounts of all components have been varied between 0-100 % by weight. The phase behaviors of the three ternary MO/solvent/water systems are all presented. The concept has recently been validated [1].

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COMPETITIVE SORPTION FROM LIQUID PHASES ON POLYELECTROLYTE GELS – FROM THEORY TO APPLICATION

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In many industrial applications of water-soluble polymer, e.g. for the dressing of fabrics, in the paper-making equipment or for inking/deinking processes, it is important to understand the intermolecular and intramolecular interaction of these polymers both in solution and with the fibrous raw material.

Thus we investigated several polyelectrolyte solutions and latex dispersions either of negatively or positively charged polymer particles by viscometry, particle sizing in different alcohol water mixtures [1,2], and dye adsorption measurements [2,3] and determined the polarity parameter of the polymers by pyrene fluorescence[4]. We deduced from these measurements that the positively charged polymer starts to coil at a lower polymer concentration than the negatively charged one and induct differences in hydrophobicity between the positively and the negatively charged polymers [4,6].

In this work we extended our investigations to the competitive sorption from binary liquid mixtures and solutions of some polyelectrolyte microgels. Again differences in the behaviour of gels made from positively or negatively charged particles were detected like we had found for the water soluble polymer samples and for the latex dispersions. The difference in hydrophobicity between the positively and the negatively charged polymers is even reflected in the shape of the adsorption isotherms and the polarity parameter of the polyelectrolyte microgels determined hereof [5,6]. Future work on immobilised polyelectrolyte microgels will be suggested [7].

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OPTIMIZED PERFORMANCE OF COMPLETION AND WORKOVER BRINE BY USING WATER-BASED SURFACTANTS IN LOW-PRESSURE RESERVOIRS IN MARACAIBO LAKE

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Oil industry needs to optimize well drilling / workover costs to productivity ratio to maximize its earnings. To accomplish this issue, drilling, completion and workover fluids play a very important role. For this reason, an important effort in fluid formulation research has been devoted to the development of technological products based on physicochemical interfacial properties, that could improve hydrocarbon flow in near-wellbore reservoir region. These properties have a profound impact on oil productivity.

In addition, capillary effects and wettability are determined by parameters like chemical composition of liquid phases, rock mineralogy and morphology, among others.

This work presents the results of a guided study to identify the factors that affect the performance of surfactants used in water base completion and workover fluids formulation, in order to reach the maximum productivity in oil and/or gas wells[1]. A physicochemical evaluation of interfacial behavior was done, including measurements of surface tension, wettability and emulsion type and stability, as well as flow tests in porous media using commercial surfactants in the particular conditions of Bach-01 and UD-01 reservoirs in western Venezuela. Preliminary results indicate that chemical composition of the surfactant used in the workover fluid formulation has a remarkable effect on interfacial properties of the oil-rock-brine system and on the transport properties of oil inside the porous media. Appropriate selection of the surfactant leads to better oil productivity indexes. [2].

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COLLOID-MEMBRANE INTERACTION EFFECTS ON CONCENTRATION POLARISATION DURING CROSS-FLOW ULTRAFILTRATION

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Membrane filtration is a mild and energetically favourable separation and concentration technique, which has become increasingly important during the last decades. One of the main problems hampering its wide-spread use is the concentration-polarisation effect, which gives raise to flux decline. In order to minimise the effect of concentration polarisation, much attention has been paid to rather mechanical aspects, such as the cross-flow velocity and the promotion of turbulence, e.g. by gas sparging.

In this contribution, the colloid-chemical aspects of concentration polarisation will be investigated. For this purpose, colloidal silica suspensions of varying surface characteristics have been filtered on semi-ceramic Zirfon® ultrafiltration membranes. In order to investigate colloid-colloid, as well as colloid-membrane interactions, filtration tests were performed considering a range of electrolyte concentrations, as well as pH values. The surface properties of the colloidal silica particles were determined by electrophoretic light scattering, whereas the surface charge characteristics of the ultrafiltration membranes were derived from streaming potential measurements. From the flux versus transmembrane pressure curves, it was derived that both high and low salt concentrations were preferable to optimise the permeate flux provided that both particles and membrane had similar charge characteristics. At low salt concentration, this behaviour was due to large colloid-colloid as well as colloid-membrane repulsive interactions, which largely reduced concentration polarisation. At high salt concentrations, flocculation of the colloidal dispersions gave raise to large, porous flocs. As a consequence of the latter effect, the concentration-polarisation layer became highly permeable. On the other hand, a severe flux decline was observed at pH conditions where the colloidal particles and the ultrafiltration membrane were oppositely charged, giving raise to attractive electrostatic interactions.

The results indicate that the performance of ultrafiltration membranes is strongly affected by its interaction with the colloidal particles in the feed. Optimum conditions are obtained if repulsive interactions prevail, which may be accomplished by proper conditioning of the feed.

THE PERMEABILITY OF DIFFERENT GASES THROUGH THE FLUORINATED SURFACTANT THIN LIQUID MEMBRANES

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Membrane separation processes have been studied for years, but are just becoming of industrial importance. Present applications generally make use of a solid membrane through which the phase to be separated is preferentially passed. The work reported here involves the use of a liquid membrane, an aqueous surfactant film; to understand the permeability behaviour of different single gases through the fluorinated surfactant stabilized thin liquid membranes. A liquid surfactant membrane, or abbreviated as liquid membrane, is a film composed of surfactants and their solvent. When water-soluble surfactants are used, the film consists of water covered by two surfactant monolayers. This kind of film serves as gas separation membranes [1,2,3]. Liquid membranes have both advantages and disadvantages for gas separation when compared with solid membranes. Liquid membranes can be made extremely selective, can be made extremely thin resulting in large gas fluxes across the membrane, can be reused many times, and can be very inexpensive. The major disadvantage is that liquid membranes cannot support an appreciable pressure drop.

We have studied the permeability of Air, Oxygen, Argon and Nitrogen through the Fluorinated surfactant stabilized aqueous membranes as a function of surfactant concentration, electrolyte (KBr) concentration. In general, it is known that the solubility of oxygen in fluorinated chain is larger than on the carbohydrate chain. So, one would expect the higher order of permeability coefficient for oxygen through the fluorinated surfactant stabilized aqueous membranes compare to the carbohydrate surfactant stabilized one. But our results show that the absolute difference between the permeability of nitrogen and oxygen in Sodium Dodecyl Sulphate (SDS) stabilized membranes and this Fluorinated surfactant stabilized membranes or of the same order of magnitude though there is a difference in the absolute values.

All the permeability results are explained by using the existing theories for gas permeation through thin liquid membranes. Thickness and contact angles are measured on such membranes to discuss the obtained results.

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BRINGING INNOVATION IN APPAREL TEXTILES THROUGH CHEMISTRY

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A comprehensive approach to develop new chemical treatments for yarn and fabrics finishing to obtain innovative properties is presented. The employed chemicals belong to the class of organic (acrylic) polymers and inorganic compounds. The inorganic compounds are silicate, metal oxides and pure metals with the capacity to impart uv-protection, bacteriostatic effects, reduction of pilling, thermal comfort, antistatic effects, thermal insulation and flame retardant effect. Their dimensions range from micrometers to nanometers. The micrometric products are obtained by super milling while the nanoparticles by sol gel synthesis. The organic compounds are acrylics polymers and polyurethanes applied to fabrics or yarns to anchorage the inorganic particles and to impart wash resistance. All the products can be applied by impregnation (also on yarns), exhaustion or coating.

SYNTHESIS OF A SURFACTANT USED AS BIOCIDES AGAINST BACTERIAL CORROSION

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The ever increasing intensity of oil and gas reservoir exploitation requires the use of new methods and actions on the petroleum layers . However, a exploitation of certain reservoirs is complicated by the appearance of problems related to the presence of hydrogen sulphide (H₂S) induced by biological sulphate-reduction in the reservoir.

The H₂S thus formed attacks the materials and causes corrosion , resulting in a consequent loss of production.

This phenomenon does of course represent a real danger to the personnel working on drilling and production platforms. It also causes pollution of the environment, and in some cases, it may induce fire and explosion.

Sulphate-reduction corrosion is indeed dangerous as it is difficult to control and the material deterioration is rapid and unpredictable.

H₂S formation is due to sulphate-reducing bacterial activity (SRB). The best way to reduce its impact, is to use chemical treatment products known as biocides which eliminate micro-organisms.

Hexamethylenetetramine derivatives turned out to be compounds with a high inhibiting biological action on such micro-organisms. The main objective of our study is to elaborate a method for synthesis of an hexamethylenetetramine based biocide, and consider its application in the field of bacteria corrosion.

NON-IONIC SURFACTANTS SYNTHESIS AND THEIR APPLICATION IN THE ELIMINATION OF WATER IN CRUDE OIL

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At the time of the exploitation of an oil layer, the hydrocarbons are almost always associated to the salty water, what is a consequence of their genesis. While springing to the surface, these two phases are after bound intimately under shape of emulsion, water constitutes the dispersed phase, these emulsions can have a considerable stability because of the presence of some organic compounds or inorganic dissolved or in abeyance.

In order to get a most exempt oil possible of this salty water, it is necessary to separate water emulsified from the raw oil, its permits us to have a substantial reduction of the viscosity, the interesting advantages result from it on the operations of transportation as the reduction of the pumping pressures and the increase of the out-flow speeds, in more the evacuation of water avoids and decrease in a considerable manner the corrosion of the production facilities and permits to save the necessary energy to the transportation and to increase the heated load. The rupture of the emulsion takes place by a chemical heatment of the raw oil while using very small quantities of substances named desemulsifiers. These substances are tensio-active agent able to move to the interface of the phases dispersing/dispersed to facilitate the coalescence of the droplets of the phase dispersed and by there their decanting.

The objective of this survey consists therefore in the synthesis of a set of surfactants non ionic polyoxyethylened and to test them as desemulsifiers according to several parameters. The interest economic of this survey is the substitution of the products imported costly by synthesized locally products and to break the chain of interdependence vis-à-vis foreign societies.

EFFECT OF SURFACTANT AND EMULSIFICATION PROCEDURE ON THE DEPOSITION OF LIPIDIC OIL ABOVE LEAF SURFACE

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Water-in-oil (O/W) emulsions of lipids formulated together with a low proportion of agri-chemicals are usually employed to enhance the latter's foliar penetration. For example, herbicide phytotoxicity can be increased by emulsification together with a lipophilic carrier.

By selection of suitable surfactant and emulsification procedure, we show that the lipidic oil emulsion can be designed also for the opposite purposes, namely to retard foliar uptake (and phytotoxicity) of dissolved agrochemicals, such as insect repellents [1-3]. Thus, the agri-chemical is maintained over the leaf surface in the liquid state, available to the pest and protected from fast weathering.

The study is focused on the understanding of the relationship between the type of the surfactant (s) and the co-surfactant, the relative concentrations, emulsification temperature, the order of addition of components and the emulsion properties.

The solid-surface wettability of the emulsions was determined by contact angle methods and by measurement of spread factors of the emulsions both on leaves and on non-sorptive substrates of different polarity. The droplet size distribution of the resultant emulsions was determined by means of scattering methods as well as microscopy and was related to the emulsion stability.

Foliar compartmentalization of the dissolved agrochemical was analyzed by differential extraction. Foliar uptake was attributed mainly to the surfactants' type and concentration, as well to the droplet size distribution in the applied emulsion.

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PARTICLE SIZE AND VAPOR PRESSURE OF ORANGE OIL DROPLETS STABILIZED BY LIPOSOMES

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A liposome stabilized oil-in-water emulsion system was investigated for particle size, vapor pressure profile, and thermal stability. The oil used in this study is semi-volatile orange oil. A polymer stabilized liposome system was employed in this study.

The key objectives of this study include the elucidation of the location of the oil component and the key influential factors for the creation of a stable emulsion system with desirable particle size. The comparison was done between free liposome system and the polymer stabilized oil-in-water liposome.

The experimental results show that the particle size is increasing with oil concentration and decreasing with time due to the dynamic nature of the system that the oil is gradually diffused into the lipid bilayers. The vapor pressure of the liposome oil samples was less than the liposome free samples to a certain level. A sudden increase in the vapor pressure happens due to the present of two locations of the oil; between bilayers and around the hydrocarbons tails.

The stability of the oil into the emulsion reaches a certain concentration and for a limited time. The results suggested that more attention should be given to the stability of the oil emulsion, where the location of the oil can be in two places.

POSTERS

3. Colloids for Drug Delivery:

*drug delivery, encapsulation and host-guest systems for controlled
release in the colloidal domain*

CHARACTERISTIC TIME OF GLUCOSE DIFFUSION THROUGH MULTILAMELLAR VESICLES DETERMINED VIA AN ENZYMATIC REACTION

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Glucose sensors requires to immobilize the glucose-specific enzyme, glucose oxidase, on a solid substrate. This immobilization step that can be achieved e.g. by polymer trapping, usually results in a partial loss of enzyme activity. Encapsulation of the enzyme in vesicles[1] has been proposed to protect it from the surrounding medium during the immobilization process. However, this lipidic protection also confers a barrier to the diffusion of glucose towards glucose oxidase and thus, a delay in the biosensor signal response. Hence, it is worthwhile to estimate the characteristic time of diffusion of glucose through vesicles.

In this work, we encapsulate glucose into onion-type multilamellar vesicles[2,3] and estimate this kinetic parameter by modeling the glucose oxidase-catalyzed reaction rate as a function of time. The characteristic time for glucose diffusion is found to be 511 ± 11 s.

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PHASE BEHAVIOR OF LECITHIN/WATER/OIL TERNARY SYSTEMS

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The rich phase behaviour exhibited by surfactant systems is very promising in the field of drug delivery. The most significant problem associated with formulating microemulsions for pharmaceutical use is the difficulty associated with excipient acceptability. The largest part of our knowledge on surfactant self-assembly is related to systems made of surfactant, which do not have regulatory approval for use in pharmaceutical products. Lecithin is a notable exception. Notwithstanding the wide literature on lecithin-based systems[1,2], systematic investigations on their phase behaviour are still lacking. Here we report on the complete phase diagram of the soybean-lecithin/water/oil systems made of the following oils: cyclohexane (already published [3]), isoctane, decane, isopropylpalmitate, and ethyloleate. All the systems share the same tendency to form wormlike reverse micelles at low water loading. However such micelles can be disconnected or branched depending on the oil, leading to different *overall* phase behaviour. Systems that form disconnected reverse micelles are governed by the local curvature energy [4]. At variance, theories developed for self-assembled networks [5] accounts for the complex phase behaviour exploited by systems that form interconnected reverse micelles.

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CATIONIC LIPOSOMES AS CARRIERS FOR SUGAR-BASED CARBORANES: A SMALL ANGLE SCATTERING INVESTIGATION

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Sugar-based carboranes are considered promising boron delivery agents in Boron Neutron Capture Therapy (BNCT), an anti-cancer treatment based on neutron absorption by the ¹⁰B nuclei. Appropriate carriers to the inside of malignant cells can be represented by cationic liposomes, which are currently used in gene therapy for their well established ability to interact with the cell nucleus.

In the present study, we were seeking for the best way to insert carboranes inside the bilayer of cationic liposomes. Liposomes were made by the positively charged surfactant dioleoyltrimethylammonium propane (DOTAP) and by the zwitterionic phospholipid L- α -dioleoylphosphatidyl-ethanolamine (DOPE) in the 1/1 weight ratio. The boronated compounds used in this work contained the same 1,2-dicarba-closododecaboran icosahedral cage (C₂B₁₀H₁₁-) as the hydrophobic moiety to be anchored in the bilayer, while the polar heads were the lactosyl (LCOB) and glucosyl (GCOB) units, to be compared with the reference compound that did not contain any sugar ring (OCB).

The loading of these three different carboranes in the bilayer of cationic liposomes was investigated by X-ray and neutron small angle scattering. The combined use of X-ray and neutron scattering allowed to take advantage of the different contrast profile for these two techniques, thus providing a detailed description of the system structure by independent methods.

It was found that the glucosyl-carborane gave the highest rate of insertion into the liposome bilayer.

All the scattering curves were fitted as due to the form factor of monolamellar vesicles, whose thickness and overall size were determined as a function of carborane content.

In addition, specific volumes were calculated from density measurements and molecular constraints were taken into account to reproduce the scattering intensity in absolute units, while matching all requirements for internal consistency among different experimental data.

Nanoparticles of diblock amphiphilic polyaminoacid for long acting insulin delivery

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A long acting insulin maintaining the basal level during 24 hours is of major importance to avoid the severe long term side effects associated with type I diabetes. Flamel has developed a colloidal protein carrier, named Medusa I which, after parenteral injection, maintains the insulin concentration at a constant level over 24 hours. Medusa I are self assembled nanoparticles of block copolyaminoacids of -l-leucine and sodium-l-glutamate (bLE). Size, shape and mass of the nanoparticle can be varied depending upon the polymer composition and molecular weight. Characterization in diluted regime (TEM, AFM, DLS, SAXS, RMN, CD, IR, SFRT) reveals that the nanoparticles contain an hydrophobic leucine-rich core partially organized in alpha helices and surrounded by a polyelectrolyte brush of polyglutamate that stabilize the colloid both sterically and electrostatically. Proteins such as insulin adsorb spontaneously onto the surface of these Medusa I nanoparticles and more precisely onto polyleucine patches, via hydrophobic interactions. After the description of the particle structure, the presentation will focus on the description of the nanoparticle/insulin complexes. This topic will cover the adsorption/desorption kinetics of protein from the nanoparticles and will discuss the reasons of the slow in vivo release of insulin with this system. A clinical phase I trial demonstrating that this Medusa I/insulin complex can release insulin over more than 24 hours will be presented.

ASSOCIATION AND DISSOCIATION OF INTERFERON WITH Hydrophobically modified polyaminoacids

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Interferon- α 2b is a therapeutic protein used in the treatment of hepatitis C and cancer. The short half life in vivo of this protein necessitates frequent administrations. Moreover the high protein concentration after administration induces severe side effects. Flamel has developed a colloidal protein carrier, named Medusa II which overcomes these problems by increasing the duration of action of the protein and decreasing its concentration at peak. Medusa II is a colloidal water suspension of hydrophobically modified poly(L-sodium glutamate) (HMpGlu) that self associates via the lipophilic groups in side chain position. In water, interferon spontaneously associates with HMpGlu. This association mechanism, in part driven by hydrophobic interaction, has been studied using a vast array of techniques such as time resolved fluorescence spectroscopy, time resolved fluorescence quenching, NMR, isothermal titration calorimetry and chromatographic techniques. Associated interferon can be displaced by other proteins and by suitable surfactants. The kinetics of dissociation have been studied and compared with in-vivo release that extends over two weeks in dogs. A clinical phase I study is in progress using this Interferon/Medusa II complex.

OPTIMIZING MODELS FOR MEASURING DRUG PARTITIONING INTO MEMBRANES

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Drugs can be administered in various ways, although most drugs are taken orally. To be active and get into the blood circulation such drugs have to be absorbed through the epithelial cell layer of the small intestine. In most cases this translocation of the drug takes place via simple diffusion. Two physicochemical factors contribute to the permeability of the drug: the diffusion coefficient (D) in the lipid bilayer of the cell membrane and the partition coefficient (K).

When evaluating a new drug it is of importance to have knowledge about the ability of the drug to interact with membranes in the body. Methods for studying this have to be fast, easy and of course agree with the in vivo results. A simple way of measuring the permeability of the drug is the shake-flask method where the partitioning between octanol/water is determined. However this is a rough method and does not account for interactions taking place in the lipid head group region.

Due to their similarity to biomembranes liposomes are often used for studying permeability properties of membranes. One method that can be used to examine the partition coefficient is immobilized liposome chromatography (ILC). When the technique is employed the liposomes are immobilized in gel beads and the drug retention is analysed by use of liquid chromatography [1]. A problem with conventional ILC is that the use of immobilized multilamellar liposomes, may result in too low K values unless the drug equilibrates easily across the bilayer.

In our study liposomes have been prepared with the addition of DSPE-polyethylene glycol (PEG) 5000 to get unilamellar liposomes. The liposomes have been tested and compared with liposomes prepared without DSPE-PEG(5000) (multilamellar liposomes). The apparent partition coefficients of the drugs were higher for the unilamellar liposomes than for the multilamellar liposomes. Studies with isothermal calorimetry (ITC) were performed in order to verify the results. In addition, some novel lipid aggregates were investigated and compared to the liposomes.

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MIXED PHOSPHATIDYLCHOLINE: TWEEN VESICLES

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Phosphatidylcholine (PC) lipid vesicles have been widely used in pharmaceuticals and personal care products. Although PC is favoured because of its non-toxic nature, other lipids or surface-active agents are often added to provide improved stability as well as reducing production costs. Nonionic surfactants are often added to commercial products as they exhibit low toxicity.

The mixing of PC with other amphiphilic (non-bilayer forming) molecules to form vesicles frequently alters the physicochemical properties of the resulting vesicles (e.g. stability, phase transition, size and membrane leakage) due to the changes in the bilayer curvature and fluidity. The addition of too much non-bilayer forming lipid may ultimately destroy vesicle formation. For example the addition of a micelle forming surfactant to PC vesicles can ultimately lead to the solubilisation of lipid within surfactant micelles. The precise nature of the aggregates present is being dependent upon the composition of the mixture. In general at high PC lipid contents, the aggregates present will be predominately vesicles, at intermediate lipid/surfactant concentrations both vesicles and micelles may be present while at high surfactant concentrations mixed surfactant/lipid micelles will be present.

In this study the solubilisation of vesicles formed by various PC lipids (either dimyristoyl-, dipalmitoyl-, disteoyl- and dioleoylphosphatidylcholine - DMPC, DPPC, DSPC and DOPC respectively) with several Tweens (polyoxyethylene sorbitan monolaurate, mixtures of monopalmitate and monostearate, monooleate - 20, 40 and 80) has been studied. It was found that vesicles prepared from long diacyl chain lipids (dipalmitoyl- and disteoyl-) PC lipids were less susceptible to "dissolution" by polyoxyethylene sorbitan surfactants than vesicles formed by the shorter diacyl chain lipid (dimyristoyl-). Regarding however of the lipid used to prepare the vesicles, all preparations containing 20mol% Tween or less consisted of at least 95% vesicles. Interestingly mixtures of DOPC and Tween still formed vesicles at 50mol% Tween. In a number of instances the size of the vesicles increased in the presence of Tween due to the partitioning of Tween molecules into the bilayer membrane. Regardless of the Tween surfactant used, the degree to which the vesicles increased in size increased in the order DMPC < DOPC < DPPC < DSPC.

DRUG CONTROLLED RELEASE FROM MICROSPHERES

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Drug controlled-release formulations offer numerous advantages over free drug: greater efficacy because optimal concentration of active drug can be maintained on the environment of use thus decreasing the toxic side effects, greater convenience because fewer applications or treatments are needed and the possibility of a site specific delivery [1].

Microspheres, made of a biodegradable, biocompatible, nonantigenic polymer material, can contribute largely to drug delivery systems as they can be fabricated from a variety of polymeric materials and hold sufficient strength and durability which is a very important property for many modes of targeting. Microspheres offer enormous potential to be used as carriers for drugs especially anti-cancer agents as most tumour cells have been shown to phagocytose some spheres and anti-inflammatory drugs as they have shown a high adhesion to anti-inflammatory tissues when compared with the free drug [2,3]. This capacity of adhesion has been shown to increase when microspheres are coated with chitosan.

The drug release mechanism can be via drug diffusion through the microsphere or/and via microsphere degradation and may decide the kinetics of drug release from a zero to second order. These mechanisms depend on the type/properties of the carrier microsphere, on the structure and properties of the drug molecule and the type of interactions established between the drug and the polymeric matrix, which play a crucial role in the mechanism of release.

This work reports kinetic studies of drug release from two polymeric systems containing either ethylcellulose or polyphosphate. Drugs with different structures and sizes will be used.

The effect of different operating conditions - temperature, pH, salt concentration, hydrodynamic conditions (rotating speed) and the presence of chitosan - on the kinetic of drug release will be discussed.

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COLLOIDAL MICROGELS AS POTENTIAL TRANSDERMAL DELIVERY SYSTEMS

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Two decades of studies of protein delivery from polymeric systems has revealed great potential for gels that respond to environmental stimuli, such as changes in temperature and or pH, in fulfilling a delivery role. Thermally responsive colloidal microgels of poly(N-isopropylacrylamide) (polyNIPAM) have been reported to act as intelligent materials in controlled drug release [1], immobilization of enzymes and cells, and in separation of aqueous proteins [2]. This paper presents the synthesis of temperature-sensitive microgels based on a copolymer of butyl acrylate (5%) copolyNIPAM (95%), in the presence of and in the absence of ibuprofen (IBU) and methyl paraben (MP), by a surfactant-free emulsion polymerisation (SFEP) in water.

N', N'-methylenebisacrylamide was used as a cross-linking agent and potassium persulphate as an initiator. Physico-chemical properties of the microgels were determined using different techniques including dynamic light scattering, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC). Absorption of ibuprofen and methyl paraben into the gels, and their subsequent permeation across a model silicone membrane and human skin, were investigated. The transport rate of IBU from poly(NIPAM) microgel is significantly reduced by two orders of magnitude comparing with the transport rate of saturated solution of IBU. A huge reduction in the flux indicates that the microgel retards permeation of the drug across both membranes, and hence the microgel can be considered as a permeation retarder. However, fluxes of MP from poly(NIPAM) microgel are equivalents to fluxes of saturated solutions of MP. A relationship between the Log P value of the drugs and their subsequent release from poly(NIPAM) microgels will be reported.

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Modification of Alginate capsules by cationic derivatives of hydroxyethylcellulose

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Cationic derivatives of hydroxyethylcellulose (cat-HECs) were applied for modification of capsular shell made up of calcium alginate. To reach this aim, the effects of cat-HECs differed by charge density of their macromolecules and molecular weight were examined. Furthermore, alginates with various ratio of L-guluronic and D-mannuronic acid residues, which was elucidated by using $^1\text{H-NMR}$ spectroscopy, were taken for preparing the capsules. This allowed establishing an influence of their block composition on the formation and properties of capsular shells. To ascertain a dependence of the mechanical properties of shell on the molecular structure of polysaccharides, an experimental method was developed. It is based on a compression of a capsule and measurement of its radii. The deformation caused a shell extension that was described with the help of a developed mathematical model. This model enabled us to calculate a Young's modulus and thus characterize quantitatively the rigidity of capsular shell.

It was shown that cat-HEC influenced the mechanical properties of capsules. An increase of charge density of the macromolecule made the shell more rigid and less elastic. The same effect was observed with increasing the molecular weight of polysaccharide. The mechanical properties were also governed by the alginate, depending on its block composition. The rigidity of shell was increased when the amount of L-guluronic blocks were larger in the macromolecule in comparison with that of mannuronic ones.

The modified effect of cat-HECs on the mechanical properties of capsular shell was brought about by a formation of polyelectrolyte complexes by the oppositely charged polysaccharides. The correlation between the mechanical characteristics of shells and hydrogels prepared from alginates and cat-HECs was found. As followed from rheological measurements, the viscoelasticity of gelled solutions enhanced with increased the density of charged groups in the macromolecule and its molecular weight. An increase of the ratio of guluronic blocks to mannuronic ones favoured also the hydrogel formation by the oppositely charged polysaccharides.

SEGREGATIVE PHASE SEPARATION IN A COMPLEX ISOTROPIC SOLUTION

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A complex system has been used for investigation of a strong segregative phase separation. The segregative behavior originates from a repulsive interaction between a polymer and a polar lipid. By addition of a good common solvent, the repulsive interaction can be reduced [1]. A non-aqueous solvent that, in the concentrated regime, induces aggregation of the polar lipid has been used as common solvent. Therefore, the ternary polymer/polar lipid/solvent system can be regarded as a classical polymer1/polymer2 (or surfactant)/solvent system. In such systems, segregative phase behaviors are often observed [2].

The phase separation in the ternary polymer/polar lipid/solvent system has been investigated, by means of confocal laser scanning microscopy, in bulk liquid phases as well as in emulsions formed in the quaternary polymer/polar lipid/solvent/water system. Preliminary results indicate that the complex system offer possibilities for investigation of the phase separation process. The kinetics of the phase separation in the quaternary system can, to some extent, be controlled by an external parameter, *i.e.* evaporation velocity of the solvent, making it possible to study the mechanism of the phase separation.

We also present the phase behavior and some further applications of the same complex system. The phase separation in bulk phases will be further investigated by atomic force microscopy.

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CONTROLLED RELEASE OF 4-NITROANISOLE FROM POLY(LACTIC ACID) NANOPARTICLES

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The controlled release of 4-nitroanisole from polylactide nanoparticles with three different morphologies (I, II, III) is reported. Structure (I) has a liquid core [1], which contains the active ingredient (AI) surrounded by a continuous polymer sheath. This is the so-called "core/shell structure". In structure (II) the AI is contained in the continuous polymeric matrix, but mainly confined to the central region. Structure (III) is similar to (II), but the AI is more evenly distributed. Two theoretical equations have been used in an attempt to fit the experimental results. Good agreement between theory and experiment was found for short release time. The estimated values of the diffusion coefficient of 4-nitroanisole in these nanoparticles, at short times (up to 50 % release), were all $\sim 10^{-19} \text{ m}^2\text{s}^{-1}$. The very small diffusion coefficient values that have been obtained may be interpreted in terms of the very dense polymer matrix, which leads to a significant "hindrance" effect. At long release times, some small, but significant differences in release rate kinetic are observed depending on the exact particle morphology. In no case is 100 % release obtained; some of the "active ingredient" is always left, partitioned inside the nanoparticles.

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SOLUTION BEHAVIOR OF A SUGAR-BASED CARBORANE FOR BORON NEUTRON CAPTURE THERAPY: A NUCLEAR MAGNETIC RESONANCE INVESTIGATION

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The physico-chemical properties of β -lactosyl-closo-orthocarborane in water and ethanol solution were investigated by multinuclear NMR (^1H , ^{13}C and ^{11}B) and *ab-initio* calculations[1,2]. This molecule represents a very promising boron carrier in Boron Neutron Cancer Therapy and exhibits amphiphilic characteristics. Its structure and dynamical features were studied in both aggregating and non-aggregating conditions. Bidimensional NMR experiments were able to evidence a striking rigidity of the sugar moiety, with consequent loss of symmetry in the carborane cage. This feature was attributed to an intramolecular C-H \cdots O hydrogen bond and was found to persist after formation of aggregates in water solution[3].

^{13}C relaxation parameters and ^1H NOESY spectra were used to characterise the dynamical status of the investigated molecules as a function of temperature in water and ethanol solutions[4].

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IMMOBILIZATION OF CYCLODEXTRIN DERIVATIVES HAVING CHELATING GROUPS ONTO POLYMER SUPPORTS AND STUDYING THEIR COMPLEXATION PROPERTIES

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Cyclodextrins (CD) – are cyclic ‘torus shaped’ oligosaccharides that have found a large number of industrial applications. These are essentially polymers of glucose. Incorporation of functionalised CDs onto polymer supports leads to the production of materials which can find numerous analytical applications.

The aim of the present research is to modify polymer supports (silica gel, chito-san, etc) by cyclodextrin functionalised derivatives to obtain materials, which could be used as chelating agents for different metal cations (ions of heavy metals) and to study complex formation process on the solid-liquid interface.

The synthetic route for grafting the macrocycles onto the solid support consisted of three stages. In the first one, the cyclodextrins functionalised at their lower rim capable for adjusting onto different substrates were obtained. The second stage involved modifications of the upper rim of CDs with chelating amines and heterocycles. The last stage consists of immobilization of CDs derivatives having chelating groups onto polymer supports to give functionalised materials, which could be applied for water decontamination. The products obtained have been characterized by IR-spectroscopy, DTA, mass-spectrometry and potentiometry.

To determine of the complex formation ability of various CD derivatives the tracer technique method was used. As well known, the bulk cross sections of slow neutrons interaction with various atoms are highly diverge. Therefore, the neutron transmission (i.e. the ratio of the intensities of transmitted and incident neutron beams) of salt solution is greatly dependent on the quantity of ions diffused into the solid matrix. To observe the kinetic of ions concentration variation in the solution C with time t the neutron transmission perpendicular to the direction of the tracer flow through a chosen solution cross-section was measured. The corresponding functions of the ions concentration $C(t)$ were calculated from the transmission data using equation

$$C(t) = k \cdot \ln \frac{P(t)}{P_0}$$

where k is the constant, P_0 and P are the neutron transmissions of pure solvent and salt solutions at time t , respectively.

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STUDIES ON FORMATION OF O/W NANO-EMULSION SUITABLE FOR PARENTERAL ADMINISTRATION

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Nano-emulsions are a class of emulsions with uniform and extremely small droplet size (ranging from 20 to 500 nm), high stability against sedimentation or creaming and transparent or translucent appearance. Nano-emulsions of the oil-in-water type have experienced a growing interest in the last years due to their characteristic properties. They are used in the pharmaceutical field as drug delivery systems for parenteral, oral and topical administration. However, there is a need for the development of new formulations with biocompatible components, low amount of surfactant and high stability. The aims of this work have been to study the formation of oil-in-water nano-emulsions and the solubilization of drugs for parenteral administration. Nano-emulsion formation was determined by means of phase diagram studies in systems composed of water, biocompatible non-ionic surfactants and middle chain triglycerides. Droplet size and polydispersity were evaluated by dynamic light scattering and physical stability was assessed by measuring droplet size as a function of time. Maximum concentration of solubilized drugs (anti-inflammatory and analgesic agents) was also determined. Nano-emulsions with water content higher than 80wt% were identified and characterized. Droplet sizes of selected nano-emulsions ranged from 14 to 70nm, polydispersity indexes were lower than 0,2 and they were stable during the experimental time of six months. Their high kinetic stability and their small droplet size make these compositions suitable and interesting vehicles for the solubilization of drugs.

SYNTHESIS, PHASE BEHAVIOR AND APPLICATION OF MONOOLEOYL GLYCERYL ETHER

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The pharmaceutical applications of the aqueous dispersions of glycerol monooleate (GMO)/water and GMO/triglyceride/water reversed cubic and hexagonal phases as drug carriers have been considered [1]. Recently it was reported that a high intestinal absorption of insulin could be achieved by using a GMO-based Cubosome® delivery system [2]. It is noteworthy that liquid crystalline carriers can facilitate certain protection of peptide and protein drugs against degradation. Here we present an alternative of modification of such colloidal dispersions to further increase bioavailability of orally administered biomolecular drugs.

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The utilization includes the use of monooleoyl glyceryl ether (termed MGE below), which is an ether analogue of GMO. Non-polar glyceryl ether lipids of the 1-*O*-alkyl-2,3-diacyl-*sn*-glycerol type are major constituents in the liver oils of various species of elasmobranch fish such as dogfish and shark [3], where the most abundant glycerol ether is selachyl alcohol with C18:1 alkyl moiety. The ether lipids are non-toxic. However, surprisingly few studies of their physical chemical properties as well as metabolism in humans have been reported.

Here we present the aqueous phase behavior of synthetic MGE in the water content range of 0 – 40 % (w/w) and the temperature interval between 25 and 70°C. The temperature-composition phase diagram of the MGE/water system at low hydration and high temperatures is dominated by reversed micellar phase. A reversed hexagonal (H_{II}) phase is formed between 14 and 26 % (w/w) water and up to 60°C. A H_{II} phase coexisting with excess water is found at an even higher degree of hydration. Thus making MGE a suitable candidate for producing Cubosome® and Hexosome™ drug carriers.

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CHARACTERIZATION OF LIPOSOMES PREPARED BY GEL PERMEATION CHROMATOGRAPHY

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Liposomes are widespread used as drug delivery systems since they can easily entrap guest molecules of biological relevance. Among the several methods to prepare them, the use of detergent mixed micelles is preferred when the nature of the guest species requires mild condition of preparation.

Remove the detergent from lecithin/bile salts mixed micelles by gel permeation chromatography leads to the formation of small unilamellar vesicles (SUV)[1]. For the sake of reproducibility, this method is often preferred to dialysis, since equilibrium conditions are more easily attained[2].

The dialysis method for SUV preparation has been the subject of several papers, where the influence of the ratio bile salts/lecithin as well as of the dialysis conditions has been correlated to both SUV dimensions and polydispersity[3]. Such a systematic work lacks in the case of gel permeation method, where the only information available in the literature referred to a single preparation [4].

With the aim of offering a tool able to allow the direct correlation between the SUV dimensions and the mixed micelles composition, we will present the full characterization of liposomes prepared by detergent removal from cholate/lecithin mixed micelles by means of size exclusion chromatography, in terms of both vesicles dimensions and polydispersity (obtained by dynamic light scattering measurements), in a wide range of cholate/lecithin ratios and at increasing lecithin concentrations. We will also present data on the vesicles composition as well as on the efficiency of dextran columns to remove the detergent from the mixed micelles starting solution.

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ANTHRALIN SOLUBILIZATION IN COAGELS FROM 6-O-ASCORBIC ACID DERIVATIVES

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Ascorbyl 6-O-alkanoates (ASC_n) form aggregates that solubilize hydrophobic and degradable drugs. The aggregation properties of ASC_n have been studied in our laboratories [1-3], and depend on the surfactant's chemical structure, concentration and temperature.

The shorter surfactants (n = 8 and 10) form micellar dispersions or coagels, depending on temperature, while for n ≥ 11 they exhibit a coagl-to-gel phase transition. Strongly-bound and intermediate water molecules and the alkyl chain length seem to be the key factors that determine the phase diagrams and calorimetric behavior [4].

Anthralin is used in the treatment of psoriasis, but – due to its low water solubility and oxidation – it has several formulations problems such as irritation and staining of the perilesional health skin [5]. The solubilization of anthralin in ASC_n coagels can be advantageous, with an expected increase of apparent solubility, stabilization and formulation washability.

According to our studies, the anthralin solubilization capacity is higher for ASC_n derivatives with n ≥ 12. Addition of PEG 400 increases the solubilization. Compared to aqueous and ethanolic solutions of anthralin, the drug stability is dramatically increased in the ASC_n coagels. The semisolids from ASC_n showed a characteristic rheological behavior, which was not affected when anthralin was incorporated.

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PHASE BEHAVIOR IN THE BIOLOGICALLY IMPORTANT OLEIC ACID/SODIUM OLEATE/WATER SYSTEM

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The phase behavior in the oleic acid / sodium oleate / water (0.9 %wt NaCl) system was investigated and was found to be characterized by reversed phases. The micellar, hexagonal, and cubic phases, and a large region with a lamellar phase, were all found to exist in equilibrium with excess water. It was found that at a constant ratio of the oleic acid and the sodium oleate the pH is dependent on the water content. In combination with visual inspection of samples between crossed polarizers, X-ray diffraction was used to identify the various phases and their water uptake. Prediction of phase boundaries is accomplished on the basis of geometrical constraints and volume fractions of the components.

The knowledge gained from the present investigation is of relevance to an in vivo situation of systems that contain oleic acid and/or sodium oleate (i.e. oral drug formulations). Furthermore, the results have importance to the understanding of the behavior of digestion products from fat, and may be important in understanding their absorption, especially for persons suffering from low bile salt excretion.

MIXTURES OF BIOCOMPATIBLE LIPIDS: PHASE DIAGRAMS AND MICROSTRUCTURE FROM OPTICAL MICROSCOPY AND NMR SELF DIFFUSION

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Industrial products based on surfactants have great interest in international market. In particular, a great attention is addressed to products with minimum environmental impact and high biodegradability.

The aim of this work is the characterization of biocompatible systems for food, cosmetic and pharmaceutical formulations.

The work is based on the use of mixtures constituted of natural lipids and water. The utilized apolar lipid was triglycerol oleate (triolein, TRI), while glycerol monooleate (monoolein, GMO), diglycerol monooleate (DGMO) and technical lecithin (LCT) were used as surfactants.

For each studied system (GMO/TRI/W, GMO+LEC/TRI/W, GMO+DGMO/TRI/W), the ternary phase diagrams were investigated by visual inspection and optical microscopy in polarized light.

All the systems show a microemulsion region whose microstructure was characterized by NMR self diffusion measurements. Several emulsion regions were also identified.

POSTERS

4. New Methods of Investigation:

*3D imaging, scattering, diffusion and microscopy techniques for probing
colloids and interfaces*

DEVELOPMENT OF A FLOW CHAMBER AND A MICROFLUIDIC SYSTEM FOR STUDYING THE MECHANICAL PROPERTIES OF POLYELECTROLYTE MICROCAPSULES

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Recently much progress has been done in the fabrication of artificial microcapsules. These shells possess designed chemical and physical surface properties and enable the encapsulation of different materials. The production of such structures essentially involves the coating of a colloidal template that is later destroyed and removed via pH or solvent change. As different materials can be used as building block and as templates, the mechanical properties of these microcapsules can be tuned over a wide range. The knowledge of the mechanical properties as well as of the behavior of these shells under flow becomes important for delivery applications and for studying the transport phenomena through different filters and vessels. In order to analyze capsules morphological changes under flow and study their mechanical properties, two systems were designed and setup.

A parallel-plate flow chamber was projected in order to study the shear stress effect on the microcapsules when adsorbed on a modified surface under different flow conditions. The observations of the capsules under shear extend the understanding of their mechanical behavior and gives information about adhesion strength between the capsules and differently modified surfaces. Capsules constituting of PSS (poly (styrene sulfonate, sodium salt))/PAH (polyallylamine hydrochloride) were observed to suffer deformation under shear stresses of 12N/m^2 when adsorbed on a Polyethyleneimine (PEI) surface. The deformation shows to be non-reversible after stopping the flow.

A microfluidic system was build in order to study capsules deformation and squeeze trough when flowing in channels with dimensions and geometries simulating blood vessels. A silicon chip component was fabricated using lithography and bulk micromachining methods. The device allows the in-situ imaging of the capsules deformation under stimuli. Results on $20\mu\text{m}$ capsules constituting of PSS/PAH shows a plastic deformation of these shells when flowing trough $10\mu\text{m}$ constrictions.

Calibration Parameters in Pendant Drop and Bubble Tensiometry

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Drop and bubble shape analysis is the most frequently used methodology used presently in surface and interface tensiometry. It is a suitable method to investigate not only the dynamics of adsorption of surface active molecules at liquid interfaces but also to determine the two-dimensional dilational rheology of interfacial layers [1], i.e. to measure the elasticity and viscosity in a frequency range up to about 1 Hz of sinusoidal perturbations.

A method is reported for verifying and controlling the accuracy of the calibration parameters, operating in image acquisition, for drop and bubble shape-analysis tensiometry [2]. An error, impartially affecting the calibration parameters of both Cartesian axes, results in a squared error for the determined surface tension. Moreover, in the case when the calibration factors are affected by different errors, the determined value of surface tension is definitely unreliable, depending on the drop (or bubble) size and showing spurious in-phase or out-of-phase alterations. A procedure is illustrated for correcting the calibration parameters, on the basis of the observed results for a reference liquid. Method and procedure are validated by numerical examples.

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DETERMINATION OF MICELLAR SIZES AND SHAPES VIA ANISOTROPY DECAY MEASUREMENTS OF A NOVEL PORPHYRIN DYE

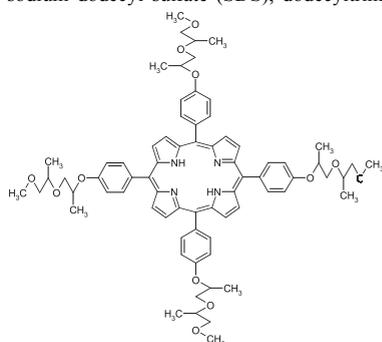
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The anisotropy decay of a novel porphyrin fluorophore in various micellar solutions was examined with a self-built frequency-domain fluorimeter. The fluorophore is a tetraphenylporphyrin derivative with four propylene glycol monomethylether chains, see Fig. It can be excited with a red 655 nm diode laser and it is water insoluble. The fluorophore has a diameter of ca. 35 Angstrom and is fixed rigidly in the core region of the micelles.

The examined solutions were aqueous solutions of sodium octyl sulfate, sodium decyl sulfate, sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide with or without 1-Hexanol and mixed solutions of SDS and tetradecyldimethylaminoxide.



Time-domain measurements have shown a monoexponential intensity decay of the porphyrin in all micellar solutions. The measured lifetime was ca. 10 ns in all cases. The sizes and shapes of all micelles, known from literature, were compared with the results of this examination. In the case of binary solutions with the exception of the tetradecylaminoxid solution the formed micelles are expected to be spherical. The FD anisotropy decay data could be fitted to a mono exponential decay in this case. The volumes of the rotating species were calculated with the Stokes-Einstein equation. In the case of ellipsoidal micelles the anisotropy decay data were fitted to a biexponential decay function. Theory predicts 3 rotational correlation times for a prolate rotator which are dependent on the volume and the axial ratio. Prolate micelles are modelled by variation of the volume and axial ratio until the short and the long correlation time are equal to both experimental rotational correlation times. In all cases good agreement between the published values and the fitted values of micellar shapes and sizes was found. Fluorescence decay measurements on this new fluorophore can thus be considered as an alternative or complement to scattering measurements.

MECHANICAL PROPERTIES OF HOLLOW CAPSULES

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In spite of the numerous applications of microcapsules in such diverse fields as drug delivery or textile coating, so far little quantitative studies on the mechanical properties of these structures have been carried out. This is in contrast to the great importance of these properties for capsule stability and performance.

We present here for the first time measurements combining AFM and Reflection Interference Contrast Microscopy (RICM) that allow us to probe the deformability of individual microcapsules in solvent environment. Using hollow polyelectrolyte shells as a model system, we demonstrate that we can obtain the elastical properties of the capsule wall material from the measured force-deformation relations in the regime of weak deformations. Due to the high force and distance resolution of the AFM, we are sensitive to changes of deformability due to nm changes in the capsule wall thickness. RICM allows us to monitor, simultaneously to applying external forces to the capsules, the extent of deformations induced by those forces and also the reversibility of those deformations upon release of the force. Thus we can ensure to stay in the regime of small deformations and we can distinguish plastic deformations from elastical deformations.

ASSIGNING MEMBRANE ORIENTATION OF PEPTIDES IN LIPID BILAYERS USING POLARIZED SPECTROSCOPY

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Studies of membrane protein function call for a thorough knowledge of conformations of polypeptide chains in the membrane. In order to develop a method that offers a simple approach to obtain information about the orientation and conformation of membrane proteins, we have investigated the location and orientation of a peptide bound to a liposomal membrane, using polarized-light spectroscopy (linear dichroism). The peptide penetratin is a cell penetrating peptide containing two tryptophan residues, derived from the homeodomain of the *Drosophila* transcription factor Antennapedia. Information about the binding of the peptide to the membrane is obtained by analyzing the linear dichroism signal from the tryptophan side chains as well as the $n \rightarrow \pi^*$ transitions of the amide chromophores within the polypeptide backbone. Tryptophan octyl ester was used as a reference compound for illustrating the use of indole transitions in assigning the orientation of membrane bound peptides. Our observations suggest that penetratin lies on the surface of the liposome membrane in a partly α -helical shape, with the ends of the peptide probably adopting a more planar structure. The observations also indicate that the tryptophan residues lie flat on the membrane surface.

RAMAN SPECTRUM AND RAMAN IMAGING OF POLYMER FILLED HOLLOW POLYELECTROLYTE CAPSULES

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Novel hollow polyelectrolyte microcapsules have recently been produced by stepwise adsorption of polyelectrolyte onto charged colloidal core via the Layer by layer (LBL) method, and then followed by core dissolution [1]. Many efforts have been devoted to altering the properties of the interior of the capsules, in particular through the encapsulation of biopolymers, drugs, minerals, dyes, protein and enzyme, etc. which can be applied in target drug delivery system and bio-engineering materials. In this poster, macromolecules, poly (styrene sulfonate) (PSS), have also been incorporated into the capsules by in situ polymerization of monomers inside the capsules by a “ship-in-bottle” synthesis [2]. Another approach, the “precipitation” method, has also been demonstrated as an effective way to encapsulated PSS inside capsule (PSS will release into the capsules interior after the extraction of multivalent ions, which constitute the inner layers of the capsules with PSS)[3]. However, no direct evidences prove that PSS are encapsulated inside capsules by two methods. On the other hand, there are many different behaviors between these two capsules, for example, the shape of capsules, chemical and physical properties, which is due to the properties of polymer inside capsules. Therefore, a new confocal Raman microscopy has been developed to evaluate the filled polymer inside and analysis the amount of loading material. By the results of their Raman spectrum and Raman imaging, the different behaviors of these two polymer-filled capsules can be understood and the mechanism of encapsulation inside capsule can be illuminated [4].

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PROBING EARLY-STAGE AGGREGATION PROCESSES BY MULTI-ANGLE STATIC AND DYNAMIC LIGHT SCATTERING

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Fast multi-angle static and dynamic light scattering is emerging as a novel, powerful tool for probing kinetic phenomena in colloidal systems. With modern instruments one can typically accumulate eight intensity correlation functions of the scattered light simultaneously with a time resolution of seconds to minutes. Such techniques permit to obtain detailed angle-resolved static and dynamic information of sample kinetics *in situ*.

The usefulness of the technique will be exemplified by discussing two novel applications for the measurement of the absolute aggregation rate constants of colloidal particles. First, we shall demonstrate the ability of this technique to measure the rate constant in the homoaggregation process without any reference to the optical and hydrodynamic properties of the particle dimers [1,2]. In fact, its hydrodynamic radius and the dimer form factor follows from the experiment as well. Second, it will be shown that in a binary mixture of colloidal particles A and B, one can discriminate between the formation of the different dimers AA, AB, and BB in a straightforward fashion. The absolute formation rate constants of all these dimers can be measured simultaneously.

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SELF ASSEMBLED MONODISPERSE STEROID NANOTUBES IN WATER

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Soft condensed matter is known to exhibit well-defined 1-D supramolecular assemblies such as thread-like micelles, fibres and tubules. Tubular architectures presenting the dual property of a cross-sectional monodispersity and a propensity to an easy orientation are promising candidates for numerous applications such as catalysis, selective separations, sensors, conducting devices in nanoelectronics, opto- or iono-electronics. We present here such an example of nanotubes obtained from a low-cost biological steroid, lithocholic acid in alkaline solutions [1]. As suggested by rheology measurements and evidenced by Small Angle X-ray Scattering (SAXS), the structure of the objects in the aqueous dispersion is not fixed in time but exhibits a clear evolution at different time scales. In a given period of time, roughly between a few hours and a few weeks after sample preparation, the structure remains stable and is well characterized by SAXS combined with cryo-TEM. It consists of highly monodisperse cylindrical nanotubes whose inner and outer diameters have been quantified. Before this period the shape and the size of the objects in the suspension change with time. When the concentration is increased, SAXS measurements show that the nanotubes order into well-defined phases. This spontaneous or easily induced orientation of the nanotubes is a promising property towards the design of bulk ordered and oriented materials.

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SIMULTANEOUS DYNAMIC LIGHT SCATTERING AND DYNAMIC RHEOMETRY

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We present a novel experimental set up for the study of non-linear phenomena such as shear thinning and yielding in soft matter systems by combined dynamic light scattering and rheological measurements. Light scattering equipment is adapted on a commercial control strain rheometer (ARES, Rheometrics) in order to perform simultaneously light scattering echo (LS echo) [1] and dynamic strain sweep measurements. The former provide microscopic information on particle rearrangements under oscillatory shear while the latter measures the macroscopic viscoelastic response of the sample. In addition, the two techniques are compensated by Fourier transform rheology [2] which monitors the increase of higher harmonics in the stress response of the sample under oscillatory shear. Such combination provides a powerful tool for the study of non-linear rheology in metastable soft matter systems such as concentrated colloidal suspensions, glasses and gels. Due to mechanical limitations the frequencies achieved in the rheometer are limited up to about 15Hz. For LS echo measurements at higher frequencies we used a home made parallel-plate shear cell which achieved frequencies up to 100Hz and strains up to 100%. Concentrated colloidal suspensions are used as standards to compare results from the two set-ups at various frequencies.

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EQUATION OF STATE OF SELF-ASSEMBLED DISC-LIKE AND ICOSAHEDRAL CRYSTALLITES IN THE DILUTE RANGE

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The investigation of the dilute range in the system myristic acid, cetyltrimethylammonium hydroxid and water shows that the formation of charged catanionic micro-crystallites induces measurable osmotic pressures [1]. These self-assembled disc-like and icosahedral crystallites are stabilized by long-range un-screened electrostatic forces in the absence of salt [2,3]. Even when the interparticle distances are in the range of 0.1 to 1 μm , strong electric repulsions occur and have been measured directly for the first time. In the coexistence region between $L\beta^+$ and disc phase an osmotic pressure drop was observed instead of an expected constant value, demonstrating that tie-lines and dilution lines are not equivalent in catanionic systems. From the osmotic pressure data and the Poisson-Boltzmann model, effective surface charge densities of $0.4 \mu\text{C cm}^{-2}$ and $0.32 \mu\text{C cm}^{-2}$ were determined for icosahedra and discs, respectively. These were slightly smaller than the structural charge densities deduced from known compositions of the aggregates: crystallization reduces dissociation, a probably general principle to be kept in mind while understanding phase diagrams of catanionic systems.

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STUDY OF COLLOIDAL SYSTEMS BY NEAR FIELD SCATTERING

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Near field scattering (NFS) is a novel optical technique recently proposed [1-3] as an alternative method for the measurement of the low-angle intensity distribution scattered by a particulate sample. Differently from the traditional static light scattering which works by collecting the scattered light in the far field, NFS operates in proximity of the sample and measures the two-point intensity correlation function in the near field of the scattered light. The technique requires a remarkably simple optical setup, in which a collimated laser beam is shined onto a square cell containing the sample, and the scattered light is collected by using a lens which makes an image of a plane in the near field of the sample onto a CCD sensor. Due to the stochastic interference between the scattered waves, the recorded images have a speckled appearance and contain information on the scattered electric field correlation function, ultimately related to the scattered intensity distribution $I(q)$.

The suitability of the techniques for the characterization of colloidal solutions was investigated by using calibrated mono- and poly-disperse latex spheres suspended in water, and the recovered $I(q)$ were compared with the ones obtained by using standard low-angle elastic light scattering instruments. A comparison with the theoretical expectations (Mie theory) was also carried out. Numerical simulations, in which synthetic speckle images generated under ideal conditions for samples with the desired particle mixture composition, were also utilized for establishing limits and approximations under which the technique works properly. They were also used for testing the stability and reliability of the method adopted for processing the data, based on a non-linear iterative algorithm [4] successfully used in the past for performing particle sizing from $I(q)$ data, and here optimized for NFS.

Applications of NFS to the sizing of aggregating colloids are finally presented.

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SANSPOL CHARACTERIZATION OF SURFACTANT FREE MAGNETIC FLUID CONSTITUTED BY SILICA-COATED COBALT- FERRITE NANOPARTICLES

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Magnetic fluids constituted by silica-coated and un-coated cobalt ferrite nanoparticles dispersed in water have been synthesized accordingly to the well-known Massart's method[1], introducing minor modifications. Magnetic nanoparticles are stabilized against aggregation through the charges present on their surface, without using any surfactant. Small angle neutron scattering of polarized neutrons (SANS POL) analysis has been used to characterize these ferrofluids prepared both in water and water/heavy water mixture. This technique takes advantage from the modification of the contrasts for the two polarization states, making possible to obtain the correct size distribution of the magnetic fluids constituted by the core-shell nanoparticles. Conventional SANS curves and TEM micrographs of the same samples have been collected, showing how the results obtained with these techniques can be in this case ambiguous and incomplete.

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LIQUID-NEMATIC TRANSITION UNDER A SHEAR FLOW

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The micellar system made up with the surfactant phosphatidylcholine (soybean lecithin), water and cyclohexane, forms a viscoelastic gel at room temperature and micellar volume fraction (lecithin plus water) of $\phi = 0.3$. The microstructure of the gel is constituted by a physical network of wormlike aggregates, whose long axis is of order of μm [1], which entangle each others to give rise a system very similar to conventional polymer solutions, though chains, here, are dynamics objects which can break and recombine. For $\phi > 0.35$ a phase transition occurs from liquid-isotropic (L) to liquid-crystalline (LC), in which micelles possess an orientational but positional order: such a phase has been characterized [2] as nematic calamitic (N). The L \rightarrow N transition can occur under the action of a mechanical shear flow as well, which induces the disentanglement of micellar chains and subsequent alignment along the direction of flow. The peculiar characteristic of the present system consists in the relaxation process of shear-aligned wormlike micelles back to the isotropic liquid state, which is unusually long. Indeed, this relaxation has been firstly investigated by performing time-resolved rheo-SANS measurements [3] and analyzed in terms of the second rank order parameter $P_2 = \langle 3\cos^2\theta - 1 \rangle / 2$, where θ is the local angle between the tangent of the micellar contour and the director of the phase, and calculated from the analysis of the anisotropic structure factor peak. Complementary to structural studies, deuterium NMR integrated with a miniature shear-stress controlled rheometer or rheo-NMR [4], is used, here, to correlate phase transitions to changes in the dynamic properties at a microscopic scale. The observed decrease as a function of time of the measured quadrupolar splitting of D_2O dispersed in the present system, provides information about the relaxation mechanism involved and which are qualitatively consistent with SANS experiments.

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SURFACE COMPOSITION OF TERPYRIDINE-CONTAINING MIXED MONOLAYERS ON GOLD

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Self assembled monolayers (SAM) of thiol functionalized molecules on metal surfaces have been the object of extensive studies in the last decade. In recent years there is a growing interest on fabrication of SAM by using molecules carrying functionalized tail-groups, suitable for mediating the subsequent binding at the surface of particular functional groups. Among the systems suitable for such applications, alkanethiols and substituted alkanethiols are probably the most studied. Monolayers based on aromatic molecules are less investigated, but their interest is raising [1]. In this respect, terpyridine-based ligands are quite attractive species to be incorporated in a monolayer because of their versatility in coordinating various metal cations, either with reversible behavior or for producing very stable complexes when the goal is a stable surface anchoring of a metal-containing system. One of the problems to be addressed in this context is the lateral spacing of the ligand groups, since they are intended to accommodate large, sterically hindering and intrinsically charged species. A possible way of overcoming this difficulty is that of preparing mixed monolayers where the component containing the active head is "diluted" by a shorter component which acts as a lateral spacer.

Here we report on a preliminary investigation on mixed aromatic self assembled systems on gold, prepared by using a terpyridine-substituted compound [4'(4-mercaptophenyl)-2,2':6'2"-terpyridine] mixed in various ratios with mercaptobenzene. Such mixed monolayers were investigated by means of X-ray photoelectron spectroscopy (XPS) and by time-of-flight secondary ion mass spectrometry (ToF-SIMS), one of the most powerful surface techniques, in terms of sensitivity and level of molecular information supplied. It is shown that for such kind of systems ToF-SIMS is able to provide quantitative information on the monolayer composition, useful for understanding the adsorption behavior of the mixed system.

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STUDY ON MICELLAR STRUCTURE AND INTERACTIONS IN IONIC MICELLE SOLUTIONS BY MEANS OF THE COMPARATIVE ANALYSIS OF COLLECTIVE AND SELF DIFFUSION COEFFICIENTS AND SCATTERING MEASUREMENTS

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Of the methods available to study systems containing colloidal particles, those based on scattering and on transport properties measurements have proved to be very useful. At the limit of infinite dilution the data of these techniques depend only on the geometry of the individual particles. On the other hand, for more concentrated systems, the data interpretation becomes complicated because of particle correlation. Normally information on size and shape of colloidal particles are extracted by extrapolating to infinite dilution the experimental data. However this extrapolation is impossible in ionic micelle solutions since these micelles grow by varying either amphiphile concentration or ionic strength. A comparative analysis of scattering and/or diffusion coefficient measurements offers a useful method to quantify the particle correlation effect on these techniques.

In this frame an approach based on the integrated study of Dynamic Light Scattering (DLS) and ¹H-Pulse-Gradient-Spin-Echo NMR (PGSE-NMR) measurements was tested on some bile salt micellar solutions. The particle correlation effects on collective and self diffusion coefficients were evaluated by comparing the two experimental data on the basis of simple interpretation models. In this way reliable micelle hydrodynamic radii and important information on particle interaction potential were obtained without extrapolating the data to infinite dilution. The almost spherical micelle of sodium taurocholate [1] and the cylindrical micelle of sodium taurodeoxycholate [2] were examined.

Results obtained by including Small Angle X-Ray Scattering (SAXS) data in this study are reported. Bile salt micelle dispersions at different ionic strength have been analyzed. Approximated models to estimate the particle correlation effect on scattering and diffusivity measurements have been used. To check the validity of these models, the agreement between the geometrical parameters obtained by the SAXS spectra fitting and the DLS and PGSE-NMR data interpretation is discussed.

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Topography dependence of adhesion forces as measured by AFM: a simple theoretical model

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In many of AFM imaging modes, forces acting of the surface on both the tip and the surface are about 1nN. Although this value could seem to be a very low force, and should so not to have disruptive effects over surfaces, the extremely small areas over which these forces are applied (usual values of tip apex radius are about 10 nm), lead to enormous values of exerted pressured, up to 100 Mpa [1,2]. In fact, this is the reason by which tips are made of materials and geometries mechanically robust enough for contact applications. A direct consequence of such a high pressures is that the AFM tip usually indents in some degree the sample, at least in contact mode.

Under the assumption that the tip indents the surface, the observed dependence on the adhesion forces values measured by AFM on the slope that the surface of the sample has at the point where force is measured (as for example in spherical cells) can be explained as a consequence of the decrease of the contact area (and then of the number of contact points) between the tip and the sample when the measurement is performed on a tilted region. A simple theoretical model, which assumes a perfect piramidal tip, has been used in order to compute the dependence of the contact area on the slope of the imaged sample. The resulting expression has been computed for an azimuthal angle of 0° (null slope) and for 45° . The theoretical decrease ratio depends on the sidewall angles of the tip, which is about 10° in our case (Ultralevers, ThermoMicroscopes). For this tip geometry, the ratio between adhesion force for 0° and 45° is about 1.6. A very similar value of the decrease ratio of adhesion force has been obtained experimentally, by collecting force curves over microspheres of three different materials, which seems to confirm the geometrical nature of this observed dependence of the adhesion force with the surface topography.

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CHARACTERIZATION OF NATURAL AQUATIC COLLOIDS: ARTIFACTS OF TRANSMISSION ELECTRONIC MICROSCOPE OBSERVATION

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Natural colloids (organic and inorganic) have important environmental functions, particularly the transport of heavy metals in surface waters. The understanding of colloid facilitated transport mechanisms will benefit from the characterization of colloids at the nanoscale. Transmission electronic microscope TEM allows the determination of colloids size, structure (crystalline or amorphous), conformation (spatial distribution) and morphology, on aggregated colloids as well as single colloids. However in addition to the artifacts generated during sampling, samples transportation and samples storage (e.g. aggregation), preparation artifacts that may hamper the relevance of TEM observations. In the last decade, many researches have investigated colloids by TEM, but no detailed study of these artifacts has been performed.

Two methods of sample preparation of natural colloid for TEM analyses have been investigated. The first is the simple mixing of natural colloids in suspension with a water compatible resin (Nanoplast FB101) [3]. The second is based on the transfer of colloids into a resin (Nanoplast FB101) on a TEM grid by ultra-centrifugation [2].

As organic colloids have a low contrast under TEM due to the low electron concentration, it is also important to raise their contrast using staining techniques. Several stains have been investigated in order to distinguish between different types of colloids.

Preliminary results suggest that, the observation of bulk natural aquatic colloids is very complicated. Instead of the "bulk fraction", further work will focus on colloids separation into fractions together with chemical analysis of these fractions, to render TEM observations more comprehensible and better interpretable.

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A SIMPLE BUT DESTRUCTIVE METHOD FOR THE DETERMINATION OF THE CONCENTRATION OF SODIUM CASEINATE IN MODEL EMULSIONS USING DENSITY AND SOUND VELOCITY

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This work shows a close correlation between density, SANS and USAXS measurements for industrial grade Sodium Caseinate (SC) solutions [1, see further for native caseinates 2,3]. USAXS as well as SANS is hardly applicable for every day use so we proof correlation between the structural data derived from two different scattering techniques with combined density and sound velocity measurements. This techniques require minimal sample preparation, has a short measuring cycle of just a few minutes, and yields very accurate, reproducible results.

In fact density measurements enable us to determine exact SC concentration in a continuous phase of an emulsion. For determination of concentration of SC at the interface, we use a droplet mean size measured by laser light diffraction coupled with polarization intensity differential scattering (PIDS). We separate dispersed and continuous phase using centrifugation at 2400g and confirm phase separation using DSC measurement of both phases.

In that way density measurements complement the determination of the surface coverage which is essential for emulsion studies [4]. Quantitative measurements permit the evaluation of the amount of caseinates in the hydrophilic phase. Pure sodium caseinate containing solution served as calibration for determination of excess caseinates (Figure1). Densimetry is proposed as a simple but destructive method to determine sodium caseinate concentration emulsion samples.

According to surface coverage of SC, lipid structures- inside emulsion droplets of $\varnothing \approx 0.5\mu$ -can be determined using Synchrotron X-ray diffraction as a function of the protein content. Up to recently, small droplet size leak concentration and complexity prevented any direct identification of the crystalline varieties formed by triacylglycerols within the emulsion droplets even in dispersed systems such as foams [5].

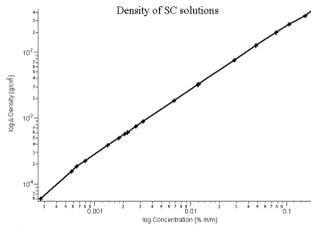


Figure 1. Density measurements of sodium caseinate solutions ranging from 0 to 100%. Showing a real linear behaviour endorsing the fact that changes between the different concentrations. The log of the variable is denoted in public as log concentration.

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NMR DIFFUSOMETRY AND THE SHORT GRADIENT PULSE LIMIT APPROXIMATION

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In NMR diffusometry, one uses the short gradient pulse (SGP) limit approximation in the interpretation of data from systems with restricted diffusion such as concentrated emulsions, but the validity of this approximation is sometimes questionable. The echo attenuation may be considered in the scattering wave vector approach, with q given by the gradient pulse area. A plot of the measured intensity versus q gives information about the porous morphology. The SGP limit approximation means that the gradient pulse length, δ , is so short that the spins do not diffuse during the gradient pulse, but often they actually do. Use of the SGP approximation results in a pore size smaller than the actual case. Many authors have discussed the problem, and the effects of this approximation have been investigated.

When the diffusion is not restricted to one pore, the problem is more complicated. This was treated in 1992 by Callaghan et al. within the framework of a pore hopping theory [1] and in a recent contribution, Ryland and Callaghan have calculated the echo attenuation for diffusion between pores under any gradient waveform [2].

The fact that the measured pore size is dependent on the pulse length can be proved by doing measurements with increasing δ and at the same time keeping q constant. This means that the pulse height, g , must be varied to keep the pulse area constant. The result will be that when the pulse length increases, the shape of the curve, in an intensity versus q plot, will change and the maximum will be displaced and finally disappear.

We work with highly concentrated water-in-oil emulsions based on 95% water solution (0.2M salt for stabilization) 3.5% heptane as oil phase and 1.5% Brij92 as surfactant. These emulsions, also known as gel-emulsions, are important in many technical applications such as food products and cosmetic and pharmaceutical formulations. They have a droplet size of 2.5-3 μ m and are stable for at least 15 hours, which is the time for the measurement. We will show how the NMR diffusometry approach yields important information about the diffusion of the various components in these soft matters.

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POSTERS

5. Inorganic Colloids:

*nanoparticles, organic-inorganic hybrids, hierarchical structures, new
templates*

AIR-STABLE MAGNETIC FLUIDS FROM MONODISPERSE $\text{Co}^{(0)}$ PARTICLES (10nm)

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Air-stable magnetic fluids (MF) i.e. magnetically stable colloidal systems of Co particles $\langle d \rangle = 10\text{nm}$ in carrier-liquids such as water, hydrocarbons, kerosene, mineral- and vacuum oils, silicones, and fluorocarbons were prepared using suitable surfactants which combine strong adsorption properties on the particle surface, good protecting abilities to prevent the particles from oxidation and a good solubility in carrier-liquids. The optimal quantity of the surfactants and the best conditions of stabilization were elaborated individually.

As the precursors air-stable 10nm Co-particles were used [1, 2]. The peptisation of these Co particles (10nm) in toluene, kerosene, vacuum and silicon oils was achieved using oleic- and lauric acid, AOT (Na-dioctylsulfosuccinate), LP-4 (fatty-acid-condensation-polymer), and Korantin SH. The resulting magnetic fluids show high magnetic properties at low Co concentrations (see Fig. 1), exhibit unusual magneto-viscous effects (Fig. 2), and interesting TMXR data (Fig. 3).

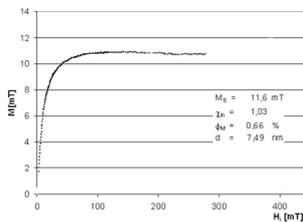


Fig.1

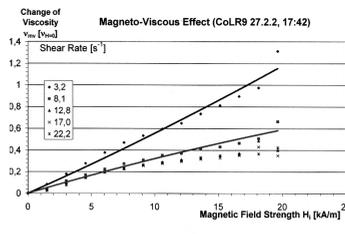


Fig.2

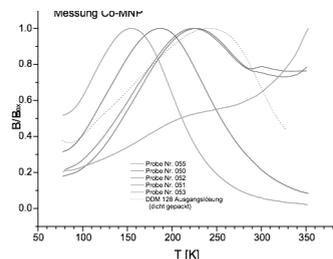


Fig. 3

Water based Co magnetic fluids were also prepared forming bi- or polylayers around the Co particles applying ionic, nonionic and double surfactants (e.g. oleic acid + Polyoxiethylen-nonyl-phenyl-ester). The long term air-stable Co magnetic fluids obtained in high concentration have a high potential of technical and biomedical applications.

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SILVER NANOPARTICLES AS PIGMENTS FOR INK-JET INKS

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Ink-jet printing is becoming a leading technology in the digital printing industry. The non-impact printing process is achieved by jetting low viscosity inks from a micron-size nozzle towards a support. The use of stable, concentrated aqueous dispersions of metallic nanoparticles with low resistivity as pigments in ink-jet inks offers new prospects in computer-defined direct-write noncontact technologies for deposition of metallic structures on various substrates.

We prepared stabilized concentrated dispersions of silver nanoparticles for the use as pigments in water-based ink-jet inks. Carboxymethyl cellulose (CMC) was found to be very effective stabilizer for the dispersions of silver nanoparticles, and also led to formation of small particles at silver concentrations higher than previously reported (average particle size at CMC concentrations from 0.025 to 0.2 wt% does not exceed 50 nm). X-Ray diffraction patterns, optical properties (UV-visible spectroscopy), size (TEM and Dynamic Light Scattering) and zeta potentials of the nanoparticles formed at various concentrations of the metal and stabilizer were studied. It was shown that the product is silver with cubic symmetry and absorption spectra characteristic of silver nanoparticles. TEM images of unstabilized and stabilized colloids indicate the formation of nanoparticles of different shapes (spheres, hexagons, cubes, rods) with rather wide size distribution in the range from several nanometers (spheres) up to several hundreds nanometers (length of rods). Both, unstabilized and stabilized silver nanoparticles display negative zeta potentials in the pH range from 2 to 9, the maximum negative values are observed at pH 6-8.

Concentrated dispersions of silver nanoparticles are characterized by the average particle size of 40-70 nm, this size increases only up to 90-120 nm after at least 7 months of storage at ambient temperature. Such dispersions were shown to be suitable as pigments in water-based ink-jet inks. Ink formulations containing silver as a pigment, surfactant and stabilizing agent, CMC, which also acts as a binder, were printed by an ink-jet printer on various substrates.

PHOTOREDUCTION MECHANISM OF SILVER IONS ONTO SILICA COLLOIDAL NANOPARTICLES

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THE FORMATION OF SILVER CLUSTERS ONTO SILICA NANOPARTICLES IN AQUEOUS SUSPENSION HAS BEEN OBTAINED BY LASER IRRADIATION. THE REDUCTION OF THE SILVER IONS ADDED TO THE SILICA COLLOIDAL DISPERSION HAS FIRST PERFORMED WITH THE HELP OF VISIBLE LASER LINES AT 457.9NM, 488.0NM AND 514.5NM, INSTEAD OF UV IRRADIATION [1] OR PULSE RADIOLYSIS TECHNIQUE [2]. THIS PROCESS HAS BEEN MONITORED BY MEANS OF UV-VISIBLE ABSORPTION SPECTROSCOPY, SURFACE-ENHANCED RAMAN SCATTERING (SERS) AND TRANSMISSION ELECTRON MICROSCOPY (TEM). THE PHOTOREDUCTION MECHANISM OF THE SILVER IONS PRESUPPOSES THE FORMATION OF AG-OH IN THE ALKALINE MEDIUM OF THE AQUEOUS COLLOIDAL SUSPENSION, FOLLOWED BY A SURFACE REACTION ON THE COLLOIDAL SILICA TO GIVE >SI-O-AG. THEN, THE LASER IRRADIATION OF THE COLLOIDAL DISPERSION PROVOKES THE FORMATION OF SILVER CLUSTERS, WHICH COVER THE SURFACE OF THE SILICA NANOPARTICLES. THE AG-COATED SILICA PARTICLES PRESENT SPHEROIDAL SHAPES AND SIZES OF 30NM AS AVERAGE DIAMETER. THEY ARE EFFICIENT SERS SUBSTRATES FOR THE DETECTION OF ADSORBED ORGANIC MOLECULES [3] AND CAN BE EMPLOYED IN THE INVESTIGATION OF THE ADSORPTION PHENOMENA OF DIFFERENT LIGANDS. THESE NOVEL SERS-ACTIVE COLLOIDAL SUBSTRATES PRESENT HIGH STABILITY WITH RESPECT TO THE USUAL METAL COLLOIDS CONSTITUTED BY PURE SILVER. MOREOVER, THE ABSENCE OF REDUCING AGENTS IN THE AQUEOUS SUSPENSION PREVENTS UNDESIRE REACTIONS AND SPECTRAL INTERFERENCE IN THE OBSERVATION OF THE SAMPLES, WHEN ADSORBED ON THE COLLOIDAL PARTICLES. FINALLY, THE SILICA COLLOIDAL NANOPARTICLES ARE ACTIVE SUBSTRATES FOR VARIOUS REACTIONS OF HETEROGENEOUS CATALYSIS. THE DOPING OF THESE PARTICLES WITH SILVER CLUSTERS COULD ALLOW STUDYING THESE REACTIONS, BY "IN SITU" IDENTIFYING THE PRODUCTS THROUGH THE SERS SPECTROSCOPY, WHICH REPRESENTS THE MOST SENSITIVE TECHNIQUE IN THE TRACE DETECTION.

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ALGINATE-BASED FERROGEL: CHEMICAL CONTROL OF THE GELATION PROCESS

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In this work we present the first results on the synthesis and the characterisation of a magnetic sensitive gel (ferrogel) with a chemical control of the gelation process. The gel is formed by ionic interactions between divalent ions (Ca^{2+} in this study) and an highly negatively charged polyelectrolyte in neutral and alkaline medium (namely sodium alginate). Alginate is a polysaccharide obtained from marine algae which has been widely used as gelling or thickening agent in the food, textile and pharmaceutical industry. The polymer chain is composed from guluronate and mannuronate motifs. The magnetic properties are due to the introduction of maghemite nanoparticles coated by citrate ions, dispersed in aqueous medium (called ferrofluid). In a previous work, gels were prepared by a direct addition of the required amount of calcium chloride to an alginate/ferrofluid stock solution [1]. Using this route, the gel formation is too quick to allow any study of the gelation process. Two other methods are then proposed on the basis of a kinetic control of the release of calcium ions in the medium. In the first one, the gels are obtained by the slow diffusion of the calcium ions from a dialysis bath of chloride calcium [2] into a stock solution of maghemite nanoparticles dispersed in an alginate solution. In the second one, calcium is introduced as a complex with EGTA [3]. The kinetics of calcium ions release, and consequently the gelation time of the ferrogel, is determined by the slow hydrolysis reaction of an acid agent (glucono-delta-lacton noted GDL). To characterise the obtained magnetic material, we have studied the rheological properties of the system alginate/maghemite particles without calcium chloride. The polymer/particle interaction has been also investigated at the nanoscopic scale by field induced dynamic birefringence measurements. In these experiments we measure the viscoelastic stress due to

SYNTHESIS OF FLUORINATED OLIGOMERS/SILICA GEL POLYMER HYBRIDS BY THE REACTIONS OF FLUOROALKYL END-CAPPED OLIGOMERS WITH TETRAETHOXYSIANE

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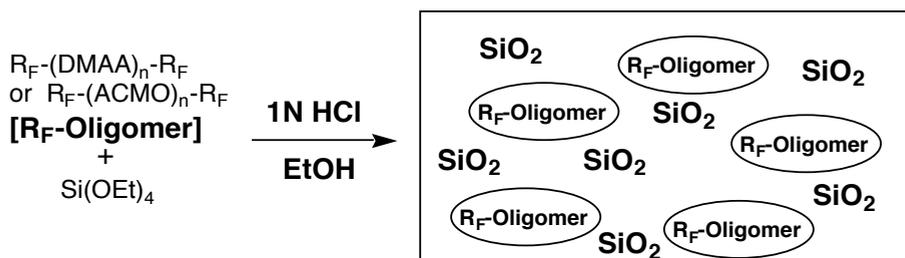
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Fluoroalkyl end-capped *N,N*-dimethylacrylamide oligomers [R_F-(DMAA)_n-R_F] and acryloylmorpholine oligomers [R_F-(ACMO)_n-R_F] were polymerized with hydrolysis and condensation of tetraethoxysilane to afford homogeneous fluoroalkyl end-capped oligomers and silica gel polymer hybrids as shown in the following schematic illustration.



The homogeneity of the fluorinated polymer hybrids thus obtained suggests that the organic polymer segments and the inorganic one should be blended at the molecular level through the intermolecular hydrogen bonding between amide and silanol groups. Interestingly, these novel fluorinated organic-inorganic polymer hybrids were applied to the surface modification of glass, and the modified glass surface treated with these fluorinated hybrids exhibited not only a good oil-repellency imparted by fluorine but also a good hydrophilicity.

METASTABLE NANOTUBES CONSTRUCTED FROM PbS NANOPARTICLES IN POLYMER-SURFACTANT SOLUTIONS

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In this work we examine the organization of PbS particles under SDS surfactant action in solutions containing hydrophilic polymers. Polymer and surfactant concentrations are such that the surfactant exists in the system mostly in the form of polymer bound micelles. PbS particles are formed by reacting Pb^{2+} salts with Na_2S in the presence of surfactants and polymers. The crystallization behavior of this system is rich and complex and has been examined in detail in the past [1-3]. Already from reaction onset, the PbS particles form layered structures and nanotubes, the walls of which are formed by alternating layers of ordered PbS nanoparticles and bilayers of surfactant molecules [4]. These nanotubes are not thermodynamically stable: they dissolve after some days leading to the formation of lamellar crystals of lead dodecyl sulfate ($\text{Pb}(\text{DS})_2$). We discuss the two possible mechanisms for formation of these interesting structures, which have been observed for the first time.

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STABILIZATION OF MAGNETIC Co⁽⁰⁾ PARTICLES (10 nm) BY “SMOOTH AIR OXIDATION”

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After thermolysis of the Co₂(CO)₈ synthetic air is slowly bubbled through a capillary into the a suspension of Co(0) particles (10nm) in toluene during approx. 6 h. The particles are then dried in vacuo giving a long term air stable magnetic Co-powder which can be handled under ambient conditions.

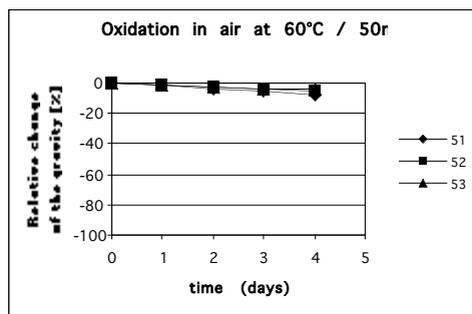


Fig. 1: Magnetic long term stability

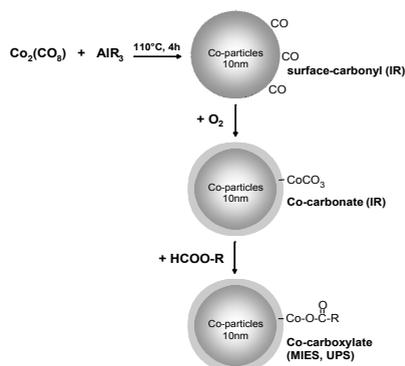


Fig. 2: Mechanism of the “Smooth Air Oxidation”

The test of the Co powder on a magnetic balance shows good magnetic long term stability under air both at room temperature and at 60°C. Whereas the powder appears to be completely stable at room temperature, first measurements show that at 60°C after 64 h the loss of magnetization is about 3-5% (see Fig. 1).

Infrared Spectroscopy (IR), Metastable Impact Electron Spectroscopy (MIES) and Photoelectron Spectroscopy (UPS) evidence have revealed that surface-carbonyl groups at the particles are oxidized to give dense CoCO₃ layer (see Fig. 2). This coat can be modified with carboxylic surfactants resulting in air stable magnetic fluids.

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A SIZE-SELECTIVE SYNTHESIS OF AIR STABLE COLLOIDAL MAGNETIC COBALT NANOPARTICLES

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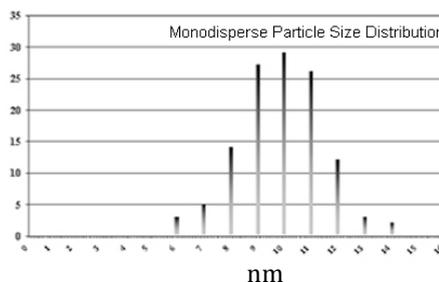
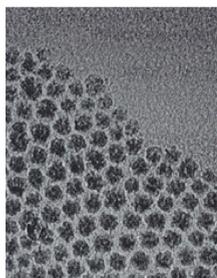
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A novel, size selective preparation route leads to air stable "monodisperse" colloidal cobalt nanoparticles via the thermolysis of $\text{Co}_2(\text{CO})_8$ in the presence of aluminum alkyls [1], [2]. Varying the al-alkyl chain length and the Co : Al ratio the particle size may be adjusted between 3 and 10 nm. The particle size distribution was examined by TEM and the structure was analysed by XANES.



1. Thermolysis
(110°C, 4h)

2. smooth
air oxidation
(20°C, 6h)



Subsequent smooth air oxidation according to X-ray Absorption Near Edge Structure (XANES) and other physical evidence leads to long term stable Cobalt(0) magnetic nanoparticles. The isolated particles may be peptised with the help of surfactants to give remarkably stable magnetic fluids applicable for a number of practical purposes.

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COLLOID SYNTHESIS AND CHARACTERISATION OF CdS, V₂O₅ AND WO₃ DOPED LAYERED HYDROGEN TITANATE NANOSHEET AS PHOTOCATALYSTS IN SELF-ASSEMBLED MULTILAYERS

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Hydrogen titanate/CdS and V₂O₅, WO₃ nanocomposites were synthesized by stepwise intercalation in aquatic colloidal dispersion with incorporation of semiconductor nanoparticles into the layer titanate. Hydrogen trititanate was prepared by heating a mixture of NaCO₃ and TiO₂ in a molar ratio of 1:3 and the sodium form was converted into their protonic form by being stirred in a HCl solution. Titanates do not swell readily in aqueous suspension because of their higher layer charge density. The titanate was pre-expanded by incorporation of n-butylammonium ions to facilitate the intercalation of semiconductor nanoparticles into the layers. Intercalation of n-butylammonium cations resulted in interlayer expansion from 0.78nm to 1.46nm. CdS nanoparticles were generated from their precursors in the interlayer space. V₂O₅, WO₃ nanoparticles were generated by sol-gel method from crystalline V₂O₅ and metallic tungsten in a solution of hydrogen peroxide.

Self-assembled nanofilms were also built-up from nanocomposites by over and over dipping of the glass substrate into the colloidal suspension of negatively charge semiconductor nanoparticles and positively charged PDDA solution. Incorporation of nanoparticles was monitored by X-ray diffraction, small angle X-ray scattering verified by transmission electron microscopy. The photocatalytic properties of these new materials was investigated on oxidation of phenol molecules. The effect of illumination time, photocatalyst content, and initial pH of a solution on the phenol decomposition degree was studied. The photochemical properties of nanocomposites were compared in bulk phase reaction mixture and on multilayer films.

SYNTHESIS AND PROPERTIES OF COLLOIDAL ZEOLITE-A

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We have recently shown that it is possible to synthesize colloidal monodispersed particles of crystalline zeolites by the mild hydrothermal treatment of aqueous solutions containing silicalite and aluminate oligomers [1]. Such zeolite colloids (see eg Fig.1.) are of particular interest because they can provide a route to membranes and thin films of zeolites when the particles are consolidated as a thin layer on a substrate (see eg Fig.2.), using sol-gel type processes[2].

An understanding of characteristics and mechanisms of formation of these zeolite colloids is required in order to optimize this preparation route. Here, we describe such investigations on zeolite-A colloids (light scattering, small angle X-ray and neutron scattering, SANS) to determine the mechanisms of nucleation and particle growth. In situ SANS measurements on colloids at progressively higher concentrations have also provided details of the inter-particle interactions which are important in the formation of consolidated particle layers. The application of SANS using contrast variation (H_2O/D_2O mixtures) to determine the role of organic structure directing cations (Tetramethylammonium) in the mixed alumino-silicate oligomers has also been employed as described here.

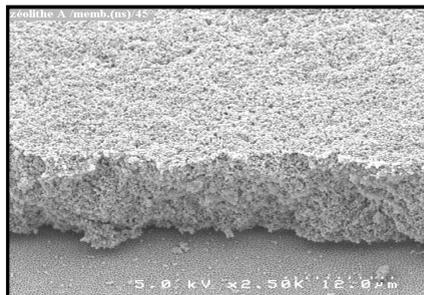
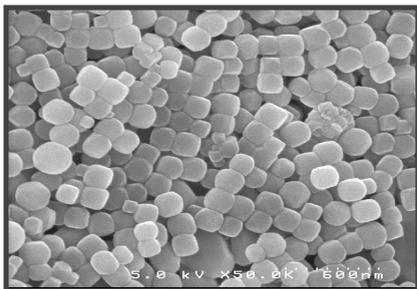


Fig.1. SEM Micrograph of colloids of zeolite A

Fig.2. SEM of a layer of zeolite A on an Anopore alumina membrane support

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STABILIZATION OF MAGNETORHEOLOGICAL SUSPENSIONS BY SURFACTANT AND THIXOTROPIC AGENTS

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Magnetic control of the flow of liquids is a challenging field for both basic research and applications. Two kinds of materials fulfilling these conditions are suspensions of ferromagnetic nanoparticles (ferrofluids) and micron-sized particles (metals or ferrites), commonly called magnetorheological fluids (MRF). The stability of these magnetic fluids constitutes one of the problems of larger interest from the point of view of the technological applications of these systems. Due to the high density of magnetic particles, the MRF suffer from excessive gravitational settling, the result of which can interfere with the magnetorheological response because of the non-uniform distribution of particles [1, 2]. To overcome these problems it is usual to add surfactants to avoid particle aggregation, and thixotropic agents to prevent sedimentation [3]. To sterically stabilize magnetic fluids in apolar solvents, oleic acid-grafted magnetic particles are frequently used [4].

The aim of this work is to check the possibility of stabilizing MRF, composed by iron particles in mineral oil, by adding oleic acid (OA) and investigate the anti-settling efficiency of silica nanoparticles. Adsorption isotherm of oleic acid on iron particles was obtained. The stability of these MRF has been investigated performing optical absorbance *vs.* time experiments, for different OA and silica concentrations, and in the presence or the absence of applied magnetic field ($B < 2$ mT). The optimum concentration of OA and silica that impart the desired stability, without hindering the magnetorheological effect, was obtained. In the case of iron-silica suspensions, the effect of the gel formation and the adhesion between iron and silica nanoparticles on sedimentation velocity has also been studied.

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NANOCRYSTALLINE TITANIUM OXIDE OBTAINED BY SOL-GEL TECHNIQUES AND SURFACTANT-BASED TEMPLATING

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Recently, an intense attention has been paid to the nanocrystalline materials, because of their spectacular physical and chemical properties. Typical compound, greatly studied in literature [1,2] is TiO₂, used as an adsorbent, a pigment, a catalyst support, a semiconductor for photovoltaic applications, etc.

The preparation of tailored TiO₂ is possible thanks to the sol-gel techniques and surfactant-based templating. Starting from molecular precursors such as alkoxides of Ti(IV), a macromolecular oxide network is obtained through hydrolysis-condensation reactions. The nucleation of solid phase supported by a controlled framework of tridimensional micellar aggregates leads to the formation of particles with tailored pre-fixed porosities. The peculiarity of these modern and innovative syntheses is the control of the phase-composition and of the morphological characteristics of the powders, such as shape, dimension, surface area and porosity, by changing several processing parameters, such as precipitation pH, temperature, time of reaction, kind of surfactant.

The aim of the present work was to study the effect of different procedures in sol-gel preparation of TiO₂ on the phase composition and morphology of the particles. The role of the solvent removal step for the precursors; the addition of alkyl pyridinium salts, as surfactants (added to the reactants or to the water for subsequent hydrothermal treatment); the effect of the concentration of the surfactants as well as the effect of the calcination temperatures were investigated. The powders were characterized by means of XRD, TGA, BET, SEM and doppler electrophoretic light scattering.

The outcomes of the different characterizations are discussed in relation to the different conditions adopted in the preparations.

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PREPARATION OF NANOCOMPOSITES THROUGH REACTIONS BETWEEN OXIRANE GROUPS AND NANOSIZED COLLOIDAL SILICA

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Generally, the sol-gel reaction of tetraethoxysilane (TEOS) or other organo-functionalized alkoxy silane compounds shows its great application in formation of polymer-silica nanocomposites [1-2]. However, the formation of volatile byproducts and the incomplete conversion of the silanol condensation reaction, certainly, bring some drawbacks and harms to the mass production and quality control of the nanocomposites [3-4]. Moreover, for promoting the interfacial compatibility between the organic polymer and the inorganic silica, some coupling agents, like silane compounds, are often added into the nanocomposite formulation [5-6]. The coupling agents are usually very expensive to increase the cost of the products. In this study, therefore, we are seeking for another approach of preparation of polymer-silica nanocomposites without employing sol-gel reactions and coupling agents. The reaction between the oxirane ring group and the silanol groups [7] of silica particles are utilized to functionalize the surface of nanosized silica particles, and the products are then used to prepare polymer-silica nanocomposites.

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SYNTHESIS AND CHARACTERIZATION OF NOVEL ORGANIC INORGANIC HYBRID BLOCK COPOLYMERS

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Poly(silsesquioxanes) (PSSQs) show very promising results as nanocomposite fillers and low-dielectric films [1]. In this study we developed a novel synthetic scheme to prepare organic-inorganic hybrid block copolymers based on atom transfer radical polymerization (ATRP) starting from functionalized PSSQ as initiating polymers. PSSQ [2] was modified with a useful initiator group (2-Bromo-isobutyroic acid 5-(chloro-dimethyl-silanyl)-pentyl ester). For initial demonstration, we chose PMMA as an organic block. Besides the chemical composition, we are able to control the block ratios and block length of the hybrid polymer.

Moreover, novel applications of PSSQ-PMMA hybrid block copolymer will be discussed. Nanocomposite formation in PMMA films and nanopore formation in PSSQ matrix were studied, and the relevant mechanical, electrical and thermal properties were characterized. The polymers showed a very interesting and promising thermal decomposition behavior, thus making these polymers potential candidates for pore generators in future nanoporous materials.

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POROUS SILICA GLASS OF NANOMETRIC PORE SIZE MANUFACTURED BY CONSOLIDATION OF SUSPENDED SILICA AND SOL-GEL SILICA

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To control pore size of separating media by permeation, acidic silica suspension having nearly homogeneous pore diameter and ethanol solution of tetraethoxysilane (TEOS) were mixed to cause hydrolysis of TEOS. Amount of ethanol was set for that the reacting solution should be kept homogeneous. After the reaction, the solvent of reacted solution was evaporated in vacuum to decrease shrinkage and cracking during drying of the succeeding gel. The silica sol-solution after evaporation was dried in plate-shaped casts in controlled atmosphere. Specific surface area and pore size distributions of the manufactured glass were observed by nitrogen adsorption method. Typical three sizes of pore are observed. One is the size of interparticle openings among the originally suspending sol-particles; this is the largest size of pore and observed mainly when silica from TEOS is poor. The second size is the pore size of originally suspending silica and mainly observed when silica produced from TEOS fills up the interparticle openings of suspended silica. The third is the pore size of silica from TEOS, and this is observed when silica from TEOS is sufficient to fill up all pores of suspended silica. So by varying the ratio of suspended silica and amount of TEOS, pore size of glass can be controlled. To get non-fragile glass, gel of glass was immersed in suspending materials. Glass filters are good for this purpose, but the pore size of thus manufactured filter was in order of hundred nanometers.

THE EFFECT OF SUPERPLASTICIZERS ON MICROSTRUCTURE AND HYDRATION KINETICS OF CURING CEMENT PASTES

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Cement is a widely used material in human construction activities. The main components are C_3S (50÷70%), C_2S (15÷30%), C_3A (5÷10%), and C_4AF (5÷15%), where: C=CaO, S=SiO₂, H=H₂O, A=Al₂O₃, and F=Fe₂O₃. Setting and hardening of the cement are due to the formation of calcium silicate hydrate (CSH). In order to improve workability and increase the cement' strength by decreasing its porosity, superplasticizers (SP) are usually added. Hydration kinetics, unreacted water relaxation and microstructure were studied in presence or not of different SP using several techniques in order to characterizing how SP affect cement hydration, where they distribute during the setting process and how they change the CSH globule size and interaction.

QENS and DSC techniques [1,2] permit both to distinguish between reacted and unreacted water probing mainly the hydration kinetics. Moreover, QENS provides deeper information on the state of water: a non-Debye relaxation for the mobile fraction with and without additives for all investigated phases, though they show very different hydration times ($C_4AF \approx C_3A > C_3S > C_2S$). SAXS/WAXD results prove that the additives have a selective binding to preferential crystal lattice directions of C_3S . The effect on the other phases (C_2S , C_3A and C_4AF) is weaker suggesting that additives mainly affect the C_3S growth.

Hence, a comprehensive DSC analysis of C_3S hydration has been performed to study its kinetics in the presence of SP. The main findings are that the induction time of the C_3S paste is increased and the activation energy of the nucleation and growth stage is about doubled. Moreover, a larger amount of water reacts with C_3S during the acceleration period in presence of additives, i.e. the water is more available and the paste is more fluid. SEM images show that acrylic additives produce a change in the morphology of the formed CSH gel, from a fiber-like structure to a sheets-like structure as we could expect from the DSC results.

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INFLUENCE OF CELLULOSIC ADDITIVES ON HYDRATION KINETICS AND PHYSICO-CHEMICAL PROPERTIES OF CEMENT PASTES

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In cement industry the extrusion technique is used to produce flat shapes with improved resistance to compression. The extrusion process requires the paste to be fluid enough to be mixed and to pass through the die and, on the other hand, the extruded specimen should be stiff enough in order to be handled without cracking. These characteristics are industrially obtained adding cellulosic polymers to the mixture [1]. The aim of this work is to understand the action mechanism of these additives on the pure phases constituting a typical Portland cement. A methyl-hydroxyethyl cellulose, MHEC, was selected among the best-performing polymers. The effect of this additive on the hydration kinetics was evaluated by means of differential scanning calorimetry [2], while the hydration products were studied using differential thermal analysis, x-ray diffraction and electronic microscopy. MHEC addition in calcium silicate pastes produces an increase in the induction time without affecting the nucleation and growth period. A less dense hydrated silicate (C-S-H gel) was deduced from the diffusional constants. C-S-H laminar features and less structured hydrates were noted during the first hours of hydration. In the case of the aluminous phases, the additive inhibits the stable cubic hydrated phases growth (C_3AH_6), with advantage of the meta-stable hexagonal phases in the earliest minutes of hydration. Nuclear magnetic resonance was used to observe the variation of the proton relaxation times during the hydration of tri-calcium silicate (C_3S): the immobilization of reacting water molecules into the hydrated phases is responsible for a consistent decrease in the T_1/T_2 values [3]. The “entrapping” action of MHEC on unreacted water is evident, causing a modulation in the C_3S /water interaction. A dramatic influence of MHEC on the time evolution of the pore size distribution was obtained from the longitudinal relaxation time [4].

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A NOVEL ROUTE TO CERIA-ZIRCONIA-ALUMINA MIXED OXIDES BY THE ORGANIC-FREE SOL-GEL TECHNIQUE

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Ceria-based materials are essential as components of promoters in the automotive three-way catalyst system. Their success is mainly due to the unique combination of elevated oxygen transport capacity coupled with $\text{Ce}^{3+}/\text{Ce}^{4+}$ exchange strongly dependent on the surface area and structural features. By combining CeO_2 - ZrO_2 mixed oxides with Al_2O_3 all the thermal stability, efficiency of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple, higher dispersion and lower cost of final material are greatly enhanced compared to the unsupported mixed oxides. Among different preparation methods, the sol-gel technique is found to be very beneficial since it yields products with high purity, homogeneity and well-controlled properties; it is a low temperature process as well. The $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ solid solution with high surface area derived by sol-gel route, released oxygen at much lower temperature than with low surface area prepared by the solid-state reaction. In the present work, we have developed the new organic-free version of sol-gel technique for synthesis the mixed metal oxides. Also we are studied the effect of ceria-zirconia-alumina preparation method upon the chemical state of cerium as well as crystallinity of final products. We examined films, powdered samples and glassy products derived from thermally treated xerogels (*X*) and precipitates (*P*) of Ce-Zr-Al hydroxides after the ammonia-promoted hydrolysis of aqueous Ce-Zr-Al nitrates. A series of samples with ceria-zirconia mixed oxide compound (with Ce/Zr ~ 1 molar ratio) dispersed in amorphous alumina was characterized with TEM, UV-Vis absorption, XRD, DTA, BET, IR, XPS, ESR, and photoluminescence. The crystallization temperature of the *X*-samples shifts up to 900°C instead of 500°C for the precipitated ones. Moreover, the ESR measurements of *X*-samples calcined at 600°C in air indicate the appearance of axial Ce^{3+} -centers ($g_{\perp}=1.962$ and $g_{\parallel}=1.940$) with concentration 10 times higher than that for the *P*-ones. IR-spectra of *X*-samples (calcined at 1100°C) possess the strong sharp signal assigned to the adsorbed CO_2 , while it is unnoticed for *P*-samples. Also, the *X*-samples showed $S_{\text{BET}}=163 \text{ m}^2\text{g}^{-1}$ instead of $S_{\text{BET}}=73 \text{ m}^2\text{g}^{-1}$ for *P*-ones. All above difference in the sample properties can be explained by conservation of amorphous structure through colloidal states followed by formation of new crystalline phases at the higher temperatures. By these points, we propose the simple and non-expensive method for preparation of nanostructured (20-40 nm) ceria-based materials very promising as a component of various catalysts. Catalytic properties of the *X*-samples are under study.

INCORPORATION OF SILVER NANOPARTICLES IN LAYER SILICATES AND GRAPHITES

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Silver nanoparticles were synthesized in two different layer structured supports. One of them was an aluminosilicate, kaolinite. Disaggregation of non-swelling kaolinite was achieved by intercalation of dimethyl sulfoxide. The surface of the negatively charged silicate lamellae is covered with charge compensating cations which may be easily exchanged for other metal cations for example Ag^+ . Reduction of the silver cations gives rise to nanoparticles because the interlamellar space limits particle growth.

The other support was graphite oxide (GO). GO was synthesized from graphite by oxidation with $\text{HNO}_3/\text{NaClO}_3$. GO has ionizable carboxyl groups, which have been used for complexing the silver cations and stabilizing the silver nanoparticles after the reduction.

The reduction agent was NaBH_4 in both cases. The NaBH_4 reduces the Ag^+ ions at room temperature to Ag^0 but it can't reduce the GO. Above 60 °C the complete reduction is carried out for GO and Ag^0 .

Changes in kaolinite structure brought about by disaggregation of the aluminosilicate layers, the reduction of GO to nanostructured graphite and Ag^0 nanoparticle incorporation are conveniently monitored by X-ray diffraction. It is proven by the change in basal spacing of supports that a fraction of the silver particles was formed in the interlamellar space. However, particle sizes obtained by transmission electron microscopy show that larger particles ($d=5.6$ - 10.5 nm) were also generated which are located on the external surfaces and on the edges.

Poly(diallyldimethylammonium chloride)/Ag/GO and Ag/kaolinite self-assembled nanofilms were prepared on glass surface. The absorbance of these nanofilms was measured as function of the layer number. X-ray diffraction experiments were also made for characterization of the ultra thin layer structure. The GO was reduced to graphite and the conductivity of nanofilms was investigated. It was found, that the silver nanoparticles in this size region didn't have conductive property, they were insulators.

ORGANIC-INORGANIC HYBRIDS FORMATION VIA INDUCED ASSEMBLIES OF DOUBLE HYDROPHILIC BLOCK COPOLYMERS AND MULTIVALENT IONS

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The interest for the interactions between metal ions and water soluble polymers has considerably increased in last years due to the various applications of the resulting objects (catalysis, pigments, biocolloids,...)[1]. Double hydrophilic block copolymers[2] (DHBC) represent a new class of functional polymers which present interesting properties when they are mixed with multivalent metal cations. They can be used to control the growth of inorganic particles prepared in water by hydroxylation of metal ions, and then directly prepare sterically stabilized colloids of metal hydroxides[3, 4].

We have studied the controlled formation of nanoparticle using DHBC which contain a metal-complexing polyelectrolyte block (such as sodium polyacrylate) and a neutral stabilizing block (such as poly(acrylamide) or poly(hydroxyethylacrylate)). The role of the first block, which is anionic, is to ensure a controlled growth of the inorganic phase ; the second block, neutral, ensures the steric stabilization of the colloids.

First, an induced micellization of the copolymers is observed by mixing the DHBC with oppositely charged ions. The aggregates formation, their size, shape and nanostructure were investigated. The DHBC- Al^{3+} , Al_{13}^{7+} , La^{3+} , Cu^{2+} systems were studied using Small Angle Neutron Scattering (SANS), Dynamic and Static Light Scattering, and TEM. Hydrodynamic diameters, radii of gyration, aggregation numbers and form factors have been determined. It was shown that the nanoaggregates present a well-defined architecture with a core-corona form. The nanostructure consists of a spherical and dense core composed of the inorganic-polyacrylate complex, presenting a sharp interface with the diffuse polymeric corona.

The last step consisting in mineralizing the aggregate core is achieved by completing metal hydrolysis and condensation processes. The use of DHBC allows to achieve a particle size control in a wide range (from a few nm to about 200 nm). Moreover, particle morphology may be varied and depend on the nature of the metal and on some synthesis parameters.

Finally, those hybrid micelles represent promising supramolecular precursors of tailored architecture for nanostructured materials.

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POSTERS

6. Interfacial Chemistry:

liquid-liquid, liquid-solid, liquid-gas interfaces, confined colloids near an interface, colloids in low dimension, adsorption, depletion, segregation, phase transitions

SURFACE PROPERTIES OF BINARY MIXED SURFACTANT SYSTEMS OF N-DODECYL- β -D-MALTOSE WITH ANIONIC, CATIONIC AND NONIONIC SURFACTANTS

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N-dodecyl- β -d-maltoside belongs to a new group of nonionic surfactants, so-called sugar surfactants. Such surfactants are very interesting class of surface active compounds owing to their less toxic, good dermatological compatibility and biodegradability [1-3].

In this study we have analyzed the surface properties of mixtures of n-dodecyl- β -maltoside with three different surfactants, namely: dodecyltrimethylammonium bromide (cationic surfactant), sodium dodecyl sulfate (anionic surfactant) and another sugar surfactant, n-dodecyl- β -d-glucoside (nonionic surfactant).

Mixed adsorbed films and micelles have been investigated by measuring surface tension of aqueous solutions as a function of the total concentration and mole fraction of surfactants. Experimental results have been analyzed thermodynamically applying the Motamura theory [4], which allows for calculation of the composition of mixed monolayers and micelles as well as the excess free energies of adsorption and micelles formation, corresponding to mutual interactions between surfactants in mixed adsorbed film and micelle. Phase diagrams of adsorption and micelle formation and values of the Gibbs free energy have been compared in these three systems.

The results of all the studied systems show that n-dodecyl- β -d-maltoside mix nonideally with other investigated surfactants in both adsorbed film and micelle.

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Lipid adsorption onto polystyrene particles

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The physical and chemical factors which determine the deposition of lipid bilayers from aqueous media onto solid spherical supports are still poorly understood despite the potential interests of this technology in numerous areas such as membrane mimetic chemistry, biotechnology and drug or gene delivery systems. The particle core acts like a cytoskeleton which confers to the liposomes a mechanical stability, a narrower size distribution and the capacity to easily purify the desired material. Concerning the lipid envelop, it has the great interest to be biocompatible and to allow the insertion of membrane proteins with retention of their native structures.

Among previous works achieved on the deposition of lipids onto particles (glass [1] and silica [2] beads, iron oxide core [3], polymer hydrogel [4]) we can note the very interesting studies of Carmona et al. [5, 6] on various supported spherical bilayers and the work of Biovector Therapeutics company [7] which has developed a system based on cross-linked polysaccharidic cationic particles surrounded by phospholipids.

The objective of our work is to develop a specific investigation on the adsorption process and on the type of interactions between lipids and particles in order to control accurately the elaboration of such assemblies. Models such as a DPPC / DPTAP lipid mixture and charged polystyrene particles were used. The electric charges of carrier and lipid formulation have a major role in determining the lipid supramolecular organization. We evidenced a drastic decrease of size of the obtained species with increasing of the opposite charge of the lipid mixture. The influences of operating conditions and lipids / particles ratio were also examined. These effects were evaluated by several measurements such as the mean particle size by QELS, the electrophoretic mobility in order to observe the charge inversion and by use of microscopy techniques.

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SMART SURFACTANT MESOPHASES

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Surfactants form liquid crystalline phases when mixed with water. The six main classes of these are the lamellar, hexagonal, cubic, nematic, gel and intermediate phases. By far the most common is the lamellar phase (L_{α}). It consists of surfactant molecules arranged in bilayers, which are separated by water layers and can be regarded as possessing one-dimensional long-range order. Gel phases (L_{β}) commonly occur in many surfactant systems. Like the lamellar phase, the gel phase is comprised of surfactant layers. However, in comparison to the lamellar phase, the alkyl chain packing has much more order. Usually L_{β} phases are treated as equilibrium structures on formation. However, when used in practical applications such as hair conditioners, the products often undergo changes in properties over a period of hours to days.

In this paper, a preliminary phase diagram for the mixed surfactant system LAS:C₁₆E₈,* as determined by optical microscopy, is reported. Interestingly this includes evidence for the formation of an L_{β} phase by a 50:50 mixture of LAS:C₁₆E₈ with no water present in the system. It is suspected that the phase is metastable and evidence for the non-ionic surfactant crystallising out of the phase indicated by DSC and XRD data is displayed. The very different phase behaviour of this mixture when mixed with water is also observed in comparison to the phase behaviour of the individual components. This can have important consequences for product use and manufacture as elimination of viscous phases can have beneficial consequences when considering properties such as dissolution.

An experiment has been designed to study diffusion processes in surfactant systems whereby a surfactant/ surfactant mixture is placed into a capillary cell and contacted with water to give a sharp interface. Emerging liquid crystal phases and their length in the capillary can then be monitored providing information about the diffusion processes occurring including diffusion rates through areas of known composition in the sample. Diffusion processes have been monitored using this technique for both individual components (C₁₆E₈ and LAS) and for the 50:50 C₁₆E₈:LAS mixture. The results indicate that diffusion of water into the mixture is twice as fast as the individual components and some hypotheses as to why this should be are made here.

PHASE BEHAVIOUR STUDY OF INOSITOL PHOSPHOLIPIDS AND THEIR MISCIBILITY WITH OTHER MEMBRANE LIPIDS

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Phosphatidylinositol (PI) and its phosphorylated derivatives i.e. phosphatidylinositol 4-phosphate (4-PIP) and phosphatidylinositol-4, 5 phosphate (4,5-PIP₂) are minor components of membrane lipids but play major role in cellular signaling [1]. The molecular mechanism of signal transduction is not properly understood. The phase behaviour of these lipids and their miscibility with other membrane lipids has been investigated in order to understand the mechanism of signaling.

The monolayer phase behaviour of these inositol lipids and their mixtures with distearoylphosphatidylcholine have previously been studied [2] and this work is now continued by examining their miscibility with another key membrane lipid, distearoylphosphatidylethanolamine (DSPE) in Langmuir monolayers. Their bulk phase properties have also been investigated with polarizing optical microscopy, differential scanning calorimetry (DSC) and x-ray diffraction (XRD) techniques.

Surface pressure-area isotherms of PI or 4-PIP and its mixtures with DSPE at the air-water interface have been obtained on substrate of HEPES buffer, pH=7 at room temperature. The preliminary results show that addition of PI or 4-PIP to DSPE expands the area per molecule of DSPE. Phase separation has also been observed for the mixed monolayers.

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EQUILIBRIUM STUDIES OF MESOPHASES IN AQUEOUS CATIONIC SURFACTANT SYSTEMS: HIGH SENSITIVITY, SURFACTANT SPECIFIC ELECTRODE

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For many surfactant systems mesophases occur far more often than micelles, but are mostly unrecognised. Whilst there are numerous detailed experimental phase diagrams for surfactant systems, few of these consider the detailed composition equilibria between mesophases and dilute surfactant solution. There are no studies in the way that surfactant monomer concentrations (activities) vary within mesophases because methods to obtain these data have not been available to date. The monomer activity is important for many applications, including the kinetics of dissolution, emulsification and adsorption because the monomer concentrations are related to the surfactant chemical potential.

In this study, we have constructed new coated-wire electrodes (CWE) for cetyltrimethylammonium and didodecyltrimethylammonium ions which show a response down to a surfactant concentration around $1 \times 10^{-7} \text{ mol dm}^{-3}$. The electromotive force (EMF) was measured as a function of total surfactant concentration at different temperatures. For our initial investigation of mesophases we have examined the onset of the solution (L_1)/gel (L_g) two-phase dispersion in the hexadecyltrimethylammonium bromide and hexadecanol systems. This system is similar to many used in commercial conditioner products. The results show that large non-equilibrium effects with very long relaxation times exist for the dilute gel systems. This is in agreement with the previous work. We are currently investigating the extent to which aggregate microstructure created by shear (vesicles, disordered bilayer leaflets) contributes to this. X-ray diffraction measurements on the dispersions confirm that the gel phase is stable in very dilute systems, where the CTAB resides mostly in water as monomers. In a CTAB lamellar phase with hexanol, a significant decrease in surfactant activity was observed above the CMC, much larger than expected. For DDAB using the coated-wire DDAB electrode, the measurements show that a lamellar phase exists to low temperatures, in conflict with literature data.

NON-EQUILIBRIUM PROPERTIES OF SURFACTANT GEL PHASES – DENSITY MEASUREMENTS AND BILAYER ORGANISATION

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A special group of surfactants, the phospholipids, is of particular interest because they are found throughout living systems and play a major role in the structure of the bilayer of cell membranes. The phospholipids group forms three major bilayer phases, the crystal phase (L_c), the gel phase (L_β) and the lamellar phase (L_α). Three different structures associated with the gel phase are believed to exist: the normal bilayer, the tilted bilayer, and the interdigitated bilayer, in some cases it is believed that some of these structures can exist in a partial form. This is a result of the type of molecules making up the bilayer. Individual lipids differ from each other by variation in functional groups in the head region, variation in chain length in the *sn*-1 and *sn*-2 positions as well as varying degrees of unsaturation and alkyl chain branches. These differences affect the lipids intrinsic properties such as, gel phase transition temperatures, internal energy and membrane permeability. Here we have studied two asymmetrical (pegleg) (C14:0/C16:0 and C16:0/C14:0) and two symmetrical lecithins (C14:0/C14:0 and C16:0/C16:0). Accurate density measurements have been made through the main gel/lamellar phase transition and the pretransition. There is considerable hysteresis and time dependence in the observations, which differ between symmetrical and pegleg derivatives. Equation (1), a form of the 1st law of thermodynamics, is used to estimate the internal energy changes involved with the phase transitions.

$$\Delta H = \Sigma \Delta U_i + p \Delta V \quad (1)$$

where ΔU_i and ΔV are the changes in the internal energy and volume, and p is the pressure at the transition temperature. For complex molecules such as phosphatidylcholine there are many different contributing internal energies. We have calculated the largest of these energies, the rotameric energy and the Van der Waals interaction energy. To further the knowledge of the molecular behaviour of the surfactant gel phase several complementary techniques have been used in this study including density measurements, Differential Scanning Calorimetry (DSC), X-ray Diffraction and Computer Simulation (Monte Carlo).

THE ROLE OF THE COSURFACTANT IN THE CTAB/WATER/*n*-PENTANOL/*n*-HEXANE SYSTEM: PENTANOL EFFECT ON THE PHASE EQUILIBRIA AND MESOPHASES STRUCTURE

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In series of papers we have previously investigated the microstructure of the CTAB/water/*n*-pentanol/*n*-hexane system in the oil rich region [1-3]. At these high hexane content the system forms water-in-oil microemulsions whose size is governed by the pentanol partition between the hexane bulk and the aggregates, as described in detail in another contribution from our group. Here we deals with more concentrated systems, where the influence of pentanol on the curvature of the interfacial film is reflected on phase behavior. Mixtures of fixed composition CTAB/water/hexane = 6/25/69 (wt) were loaded with different amounts of pentanol. As expected the cosurfactant induces changes in the interfacial film curvature. Therefore the system evolves from o/w (at pentanol/CTAB=1) to w/o structures (at pentanol/CTAB>5). In the the range of compositions investigated most of the phase equilibria reveals the coexistence of liquid crystals and hexane/pentanol solution. This permits the quantitative correlation between the film curvature (obtained from the mesophase structure) and the amount of cosurfactant present in the film (deduced from the composition of the oil phase and the overall sample composition).

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EMULSIFICATION BY TEMPERATURE CHANGE FOLLOWED BY TIME RESOLVED X-RAYS SCATTERING

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We have followed the process of spontaneous emulsification by temperature jump from isotropic solutions in the ternary system water/tetra ethylene glycol dodecyl ether/decane. During the temperature change the system suffers several structural transitions. Those structural changes can be observed by monitoring the corresponding x-rays diffraction patterns. The temperature jump is produced by the insertion of the sample, that was at the initial temperature, to the interior of a capillary that is heated to the final temperature. By following the evolution of the scattering patterns we detect the transformation from O/W microemulsion droplets to scattering profiles compatible with an L3 phase via a mixture of both patterns. At higher temperatures some indication of a lamellar phase (long range ordering) is present in the spectra mixed still with the scattering pattern of the L3 phase and finally the appearance of the signals of formation of a water-in-(water-in-oil) microemulsion emulsion. Those phase transitions occur at temperatures higher than the observed equilibrium phase transition temperatures, with differences as big as 6°C. The experimental velocity of heating seems to be fast enough to prevent the complete structuring of the liquid crystalline lamellar phase, even for the slowest rate of heating, or the complete disappearance of the signal of this phase at higher heating rates. From our results, the formation of the final emulsion is produced directly from the L3 phase structure. The structure of the emulsion continuous phase (W/O microemulsion droplet size) and emulsion droplet sizes slightly depends on the initial and final temperatures. In order to better understand the process the oil-to-surfactant ratio and total amount of water have been systematically investigated reaching compositions at which the emulsification procedure fails.

Interfacial behavior of two-component biodegradable polymer films suitable for drug encapsulation

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Biodegradable polymers used in designing novel drug delivery systems might decompose in the human body due to hydrolysis while releasing the encapsulated drug in the targeted area. Poly(lactic acid) PLA and poly(lactic/glycolic acid) PLGA are among the most studied polymeric drug carriers, because by varying their composition, the properties of these polymers can be adjusted to the specific needs. Their degradation products, both lactic and glycolic acids are metabolized in the human body. The morphological and physico-chemical characteristics of these biomaterials affect their function and effectiveness as drug carriers in pharmaceutical formulations. Hydrophobic as well as hydrophilic drugs, proteins, hormones can be encapsulated into the microspheres or implants, and both the encapsulation efficiency and drug release might be influenced, among other parameters, by the suitable matching of the surface properties of the encapsulated substance and that of the carrying polymer.

The surface hydrophobicity of polymeric drug carriers is unfavourable for keeping them circulating in the blood long enough to release the drug and take advantage of the "retard" effect [1, 2]. For that reason, reduction of the original hydrophobicity of the PLA or PLGA surfaces was performed by introduction of PEO-containing compound into the surface layer. The chemical composition of the outermost layer was determined by X-ray photoelectron spectroscopy. A considerable change of wettability indicated that increase in surface hydrophilicity was achieved by various triblock poly(ethylene oxide)/poly(propylene oxide) copolymer additives applied at a concentration of 1-9 w/w%. The degree of hydrophilization was found to be dependent both on the type of the additive and the composition of the original polymers (PLA or PLGA). Compatibility of the biopolymer with the additive in the surface layer and the solubility of the hydrophilic component were also considered.

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THE EFFECT OF THE ELECTROSTATIC SURFACE POTENTIAL ON THE RATE OF NICKEL ION EXTRACTION BY LIX 84 IN MICELLE SYSTEMS

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The rate of complexation between Ni(II) and 2-nonyl-5-hydroxyacetophenone oxime (LIX84) in a neutral micelle system, Teric G₁₂A₈, (octa-ethyleneglycol mono-n-dodecyl ether) was monitored using a stopped flow apparatus and UV-visible spectrophotometry. The effect of the electrostatic surface potential, Ψ , on the reaction rate was determined by adding SDS and DTAC to the neutral micelle system. Addition of SDS was found to enhance the rate of complexation while the presence of DTAC depressed the rate. These experimental results further the understanding of a reaction taking place at the free oil/water interface.

THERMODYNAMIC PROPERTIES OF DIBLOCK COPOLYMER E₄₅S₁₀ IN AQUEOUS SOLUTION

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Apparent molal volumes, V_ϕ , and adiabatic compressibilities, $K_{\phi(S)}$, of aqueous solutions of block copolymers E₄₅S₁₀, and the subscripts denote block lengths) have been determined by density and ultrasound velocity measurements. Copolymer E₄₅S₁₀ was studied in the temperature range 293.15-323.15 K and the critical micelle concentrations (cmc) were obtained. No appreciable change in cmc with temperature was noted, which is consistent with the high hydrophobicity of the oxyphenylethylene block [1]. Apparent molar volumes are dependent on concentration in the very dilute region; beyond that region V_ϕ tends to a constant value according to the transfer of the copolymer molecule from water to a hydrophobic environment. The aggregation process of copolymer E₄₅S₁₀ is characterized by an increase in $K_{\phi(S)}$ which reveals that monomers trapped in the micellar hydrophobic environment are more compressible than aqueous free monomer species, and characterizes the progressive dehydration in S blocks that accompanies the aggregation process. V_ϕ increases with the temperature reflecting the decrease of the hydration of hydrophobic blocks. The cmc and the enthalpy of demicellization have been also determined by isothermal titration calorimetry at 303.15 K. Enthalpy of demicellization was low (≈ -5 kJ mol⁻¹) as a consequence of the S blocks being tightly coiled in its dispersed unimer state so that its hydrophobic interaction with water is small [2]. Constancy of V_ϕ and $K_{\phi(S)}$ as the concentration increases is indicative that the micelle-only domain has been reached.

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TERNARY SURFACTANT SYSTEMS AS EMULSIFIERS

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When mixing two immiscible liquids, a third, surface active, component, is needed to form a one-phase solution, i.e. a microemulsion. If the molar ratios of the three components are chosen properly, a water-in-oil (w/o) microemulsion can form. The size of the aqueous droplets is determined by several factors: The surfactant head-group area, the bulkiness of the hydrophobic tail, and the interaction between surfactant and solvent. The stronger this interaction, the higher the curvature of the droplet, or, consequently, no interactions might lead to formation of a lamellar phase with zero curvature.

The surfactant didodecyldimethyl ammonium bromide (DDAB) is insoluble in aliphatic solvents as well as in water. This makes DDAB an excellent choice for the studies of solvent interaction, as **all** DDAB molecules are located at the interface between the aqueous droplet and the surrounding solvent. Furthermore, systems of water-DDAB-oil have been extensively studied [1-5]. It has been shown that DDAB has a strong interaction with hexane (leading to small water droplets), but much weaker with dodecane (with larger droplets). What is not clear, however, is the cause of the interaction between the surfactant tail group and the solvent molecules. One often-presented explanation is based on geometric reasons, i.e., the length of the solvent molecule and the tail. Evidently, this explanation is not satisfactory, and the reason should be sought in the thermodynamics of the system.

In this contribution, we will present new data on water-DDAB-oil w/o emulsions, where we have used mixtures of two oils in the bulk phase. The project aims at a thermodynamic understanding of the solvent-tail interactions in ternary systems.

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ADSORPTION PATTERN OF MIXTURES OF TRIMETHYLAMMONIUM-MODIFIED HYDROXYETHYLCELLULOSE AND SODIUM DODECYL SULFATE AT SOLID-LIQUID INTERFACES

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Previous studies of interactions between polymers and surfactants dealt mostly with mixtures in bulk solution. When studying adsorption at solid surfaces, the interest was focused on the separate or subsequent adsorption of components [1]. Relatively little work was done on the direct imaging of adsorption of polymers and surfactants, which were mixed prior to their interaction with the surfaces [2].

We studied mixtures of water solutions of polymer and surfactant bearing opposite charges (anionic surfactant: sodium dodecyl sulfate and cationic hydroxyethylcellulose JR400[®] polymer) using static light scattering and atomic force microscopy. A ternary phase diagramme was established. The phase diagramme exhibits three most interesting realms of the polymer-surfactant-water mixture: pre-precipitation area of modified viscosity (polymer excess), post-precipitation area (resolubilisation at surfactant excess), and highly diluted samples with stoichiometrical surfactant-polymer ratio close to that of maximum precipitation. Samples with various compositions representing these areas were imaged by atomic force microscopy on mica and on hydrophobically modified silica in contact mode. No pH adjustment was performed. A correlation between light scattering data concerning structuring and particle size, on the one hand, and AFM images, on the other hand, was observed. A resemblance between images of mixture samples of the same or similar composition, but acquired on different surfaces, was found. It turned out that the influence of surface properties is of less importance for adsorption, compared to the influence of the mixture composition in bulk. It should be remarked that this conclusion can only be drawn, when surfactant and polymer are mixed prior to adsorption. In contrast, the surface influence was predominant by subsequent adsorption of the mixtures of different composition.

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DYNAMIC SURFACE TENSION AND ADSORPTION KINETICS OF β -CASEIN AT THE SOLUTION/AIR INTERFACE

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The dynamic properties of protein layers have been studied quite frequently, however, there are only very few attempts to describe the measured behaviour by theoretical models. Typically, dynamic surface tensions were interpreted by a square root of time dependence, failing completely at low concentrations due to the appearance of the so-called induction time [1].

A diffusion model is proposed to describe the adsorption kinetics of proteins at the water-air interface. The model is based on the simultaneous solution of the Ward-Tordai equation and a set of recently developed equations describing the equilibrium state of the adsorption layer: adsorption isotherm, surface layer equation of state, function of adsorptions distribution over the states with different molar areas [2]. The new kinetics model is compared with dynamic surface tensions of β -casein solutions measured with the drop/bubble profile and maximum bubble pressure methods. The adsorption process for low concentrations is governed by the diffusion mechanism, while at large protein concentrations it is only the case in the initial stage. The effective diffusion coefficients agree fairly well with literature data. The adsorption values calculated from the dynamic surface tension data agree very well with the used equilibrium adsorption model.

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Dilational rheology of surfactant layers studied by oscillating bubble experiments

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For studies of the dilational rheology of interfacial layers only few methods exist. The methodology based on oscillating drops and bubbles provides the broadest frequency interval, reaching from 0.001 Hz or less up to about 100 Hz [1]. Under certain conditions even higher frequencies can be reached, as it was achieved by the experimental module FAST flown on Shuttle Columbia during the STS-107 space research mission [2]. Experiments have been performed during this mission for the model surfactant dodecyl dimethyl phosphine oxide in a broad concentration interval and a frequency range reaching up to 800 Hz.

The data have been analysed on the basis existing theories as well as a new model developed recently [3]. This new model considers a limited compressibility of a packed adsorption layer upon compression. The compressibility as additional parameter has a large impact on the dynamic viscoelasticity, however, almost no effect on the equation of state. The experiments performed during the space mission yield a particularly complete set of dynamic data for a model surfactant adsorbed at the solution-air interface.

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THE STRUCTURE OF LATEX DEPOSITS FORMED DURING FRONTAL FILTRATION

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Monodisperse latex microspheres can be produced and packed in several controlled conditions. Those arrangements have been extensively used as template of new materials [1]. Here we have considered the structure of latex (Poly[styrene+hydrophylic monomers]) deposits obtained by frontal dead-ended microfiltration at low pressure gradients. The deposits are formed onto the porous membrane, since the permeation flux is high relative to the back-transport mechanisms of colloidal particles. For these particles, in the size range of 300 nm, the osmotic pressure is negligible as compared with the transmembrane pressure. We have measured the mass transfer across the membrane, and observed as the concentration polarization of the membrane drastically reduced the permeation flux. Small portions of the deposits are observed by electron microscopy for structural characterization.

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SOLUBILIZATION OF CARBON NANOTUBE INTO WATER AND ORGANIC MEDIA WITH A VARIETY OF FLUOROALKYL END-CAPPED OLIGOMERS

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We have studied on the solubilization of single-wall carbon nanotube (CNT) into water and organic media with fluoroalkyl end-capped acrylic acid oligomers [R_F-(ACA)_n-R_F], *N,N*-dimethylacrylamide oligomers [R_F-(DMAA)_n-R_F] and acryloylmorpholine oligomers [R_F-(ACMO)_n-R_F]. Among these fluorinated oligomers, it was demonstrated that R_F-(ACMO)_n-R_F [R_F = CF(CF₃)OCF₂CF(CF₃)OC₃F₇] oligomer is more effective for the solubilization of CNT into water. Additionally, solubilization of CNT into organic media such as xylene, toluene and chloroform was studied by the use of R_F-(DMAA)_n-R_F oligomers, R_F-(ACMO)_n-R_F oligomers, and fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers [R_F-(DOBAA)_n-R_F] under similar conditions. R_F-(DOBAA)_n-R_F [R_F = CF(CF₃)OC₆F₁₃] oligomer was found to be useful for the solubilization of CNT into organic media. Interestingly, it was clarified that R_F-(DOBAA)_n-R_F oligomer is a convenient tool for the arrangement of CNT on the PMMA surface.

SURFACE RHEOLOGY OF VISCOELASTIC FLUIDS

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The surface rheology of viscoelastic fluids plays an important role in the energy dissipation of lubricants due to the energy transfer between the bulk and the interfaces. The first theoretical description for the surface waves of this type of fluids was given by Harden et al. [1]. These authors assumed that the bulk had a Maxwell-like relaxation, and that there was no excess surface adsorption of any component. The theory described the coexistence of elastic and capillary surface modes. This coexistence has been experimentally proved in a recent work. [2] Huang et al. [3] have considered a model for which surface adsorption, and the existence of a viscoelastic monolayer were allowed.

In the present work we have measured the spectra of the light scattered by the air-liquid interface of Pluronic F68 + water. At high concentrations (c) of F68, the bulk system is viscoelastic, and beyond a critical c^* (~ 35 mM at 22°C), the system presents a reversible sol-gel transition. This transition can also be reached at a given c by increasing the temperature T .

We have measured the spectra at 22°C in a broad range of concentrations ($10^{-6} < c/\text{mM} < 35$), and as a function of T ($10 < T/^\circ\text{C} < 40$) for $c = 30$ mM. We have also measured the bulk rheology and the surface tension for the same systems. Below $c = 0.1$ the results can be fitted by using the dispersion equation of a viscoelastic monolayer, and using the experimental viscosity. However, for concentrations close to and above c^* , the spectra show features that cannot be accounted for by such dispersion equation. In effect, for $c = 25$ mM the spectra show a shoulder in the low-frequency range. Increasing further c lead to spectra with a sharp peak centered at zero frequency, and a second broad band whose peak goes to zero frequency at c^* .

The theory of Huang et al. [3] has been found to describe qualitatively the change of shape of the spectra as c or T are increased using the experimental surface tension data. However, we have found that a quantitative description of the spectra above 30 mM can be only obtained using a viscoelastic modulus for the bulk that is not in agreement with the experimental results.

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INTERFACIAL PROPERTIES OF SILICONE COPOLYMER INDUCING CRUDE OIL/WATER PHASE SEPARATION

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Crude oil/water emulsion stability is one of the major obstacles to efficient offshore separation of undesired aqueous phase. Chemical demulsifiers based on polysiloxanes have been successfully tested as accelerators of phase separation at concentrations of 50-100 ppm and moderate temperatures, but their mechanism of action is not fully understood [1].

Comprehensive study of the interfacial properties of water-soluble PEO-(polydimethylsiloxane)-PEO block copolymer ($M_w \approx 2000$) has been undertaken. The influence of polymer concentration on the surface tension of aqueous solutions was investigated in the range 0.0001 to 5 g/L. The behaviour was found similar to classical surface-active molecules regarding lowering of surface tension and then reaching a plateau at approximately 25 mN/m for concentrations higher than 0.1g/L. From the $\gamma = f(\ln C)$ curve, the critical micellar concentration was estimated to lay between 0.03 and 0.1 g/L. The absence of a clear-cut break in the mentioned curve suggests the possibility of two-dimensional phase transitions in the adsorbed monolayer of polymer molecules, as it was already reported for PEO-PPO-PEO copolymers [2]. Nevertheless, the two-dimensional compression isotherms of the polymer monolayer at the air/water interface are typical of liquid-expanded phase with no clear phase transition, although very stable and reproducible. No sign of polymer loss into the aqueous sub-phase was observed even at high degree of compression. Just before collapse of the monolayer, the area per molecule can be estimated to 100 Å². Further studies of compression isotherms at crude oil/water interface with a Langmuir interfacial trough are underway.

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INFLUENCE OF NON-IONIC SURFACTANT TRITON X-100 IN THE FREE ENERGY OF AQUEOUS SOLUTION-CALCIUM FLUORIDE INTERFACE STUDIED BY CAPILLARY RISE AND ADSORPTION EXPERIMENTS

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A study about the influence non-ionic surfactant Triton X-100 has on the wettability of Calcium Fluoride has been carried out in order to know the modification produced in the free energy of the solid-liquid interface. With this aim, capillary rise experiments, consisting of the measurement of the increase in the weight of porous columns made of powdered Calcium Fluoride as a result of the imbibition, have been made by employing aqueous solutions of Triton X-100. The analysis of the experimental results associated to these experiments has been carried out by means of a analytic procedure developed by us [1-2], which is based on the well-known Washburn's equation. From such analysis, it is deduced that the surfactant concentration does not modified the imbibition rate of the aqueous solutions into the porous columns of Calcium Fluoride, and that this velocity is similar to that one observed in capillary rise experiments with water. According to Washburn's equation, from this fact it is deduced that the free energy of the calcium fluoride-aqueous surfactant is not affected by the presence of the surfactant, surprising result if it is taken into account that the surface tension of the solution decreases with the increase of surfactant concentration. In an attempt of going deeply in the knowledge of the physical interactions between the surfactant molecules and the surface of Calcium Fluoride, adsorption experiments employing aqueous solutions of Triton X-100 has been carried out. From their analysis, it is deduced that preferential adsorption of the molecules of this surfactant against water molecules does not take place on the surface of the solid, which reveals that, according to Gibbs's equation of adsorption, the free energy of the interface Calcium Fluoride-Triton X-100 remains unaffected despite the presence of the surfactant molecules in the solutions. Also, this study states that the value of the free energy of the solid-aqueous solution interface is identical to the interfacial free energy of the solid-water system, similar result to the one deduced from the imbibition results.

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SURFACTANT ADSORPTION AT A LIQUID-SOLID INTERFACE: VIOLATION OF THE NO-SLIP CONDITION

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Standard textbooks assume stick boundary conditions when calculating fluid flows through cylindrical pipes even though it is usually noted that there is no solid physical basis for this assumption [1]. Systematic experiments showed that in both cases of hydrophobic fluid flow through hydrophilic capillaries and water flow through hydrophobic capillaries slippage did occur [2]. These experiments were interpreted in terms of an apparent increase of the capillary radius called the "slip length". Recent surface force experiments indicate that also on the molecular level slippage along surfaces does occur [3]. Such violations of the no-slip condition have important consequences on the lubrication models, where one typically deals with thin layer of molecules, and, in general, on mass transport as is the case for chemical reaction at an interface.

We experimentally observed such behavior when surfactant solutions are flushed through a laser-etched membrane. Adsorption takes place at the solid-liquid interface and a bilayer is formed. When increasing the flow rate, and hence, the shear rate, a break is observed in the flow-pressure curve whereas a straight line is observed with regular liquid such as water. We attribute this effect to a stick-slip transition. The system is described by means of irreversible thermodynamics where electroviscous effects and concentration gradients are taken into consideration.

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EMULSION POLYMERIZATION OF STYRENE WITH IN SITU FORMATION OF POLYMERIC STABILIZERS

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In recent years, voluminous research has been carried out in nanoengineering and design of nanometric materials with tailored properties. In particular, polymeric nanoparticles with controlled surface properties have been increasingly used as tools in studies of colloidal models and in a variety of applications: adhesive technology and coating, drug delivery systems, medical diagnostic tests, separation media, etc... This work deals with the synthesis of polystyrene nanoparticles covered with a polysaccharidic shell via emulsion polymerization of styrene.

In spite of the lack of surface active properties of native dextran, a neutral natural polysaccharide, stable particles with a permanently adsorbed dextran layer at their surface were obtained simply by performing emulsion polymerization of styrene in the presence of dextran dissolved in the aqueous phase. Starting from an aqueous solution of dextran and potassium persulfate topped by a styrene layer, stable latexes with very low amount of coagulate were obtained despite of the quite high solid content (10 wt %). During the process, chemical modification of dextran leading to in situ formation of surface active species occurred in the aqueous phase, allowing the emulsion radical polymerization of styrene. Such chemical modification was assumed without evidence in former works. [1-2]

The formation of a graft copolymer combining dextran and polystyrene branches was studied by means of NMR spectroscopy and size exclusion chromatography measurements. Furthermore, the influence of initiator solubility, dextran concentration, and solid content, on particle size and dextran layer thickness was evidenced essentially by means of light scattering and zeta potential measurements.

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SPECIFIC REACTIVITY OF PROTONATED SURFACE SITES ON GIBBSITE PARTICLES (γ -Al(OH)₃)

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Most of the physical-chemical processes involved in soils and natural water (sorption, complexation or dissolution) are mainly controlled by solid-water interfaces. In the case of inorganic oxide colloids, the structural heterogeneity of these particles is often characterised by different crystallographic faces and surface sites speciation. If we assume that the reactivity of surface sites depends essentially on its structure, the surface charge of such particles is expected to vary according to its morphological anisotropy.

The aim of this study is to understand the macroscopic behaviours (such as global charge or sorption processes) resulting from mechanisms at surface sites which are specific of the crystallographic faces. Gibbsite γ -Al(OH)₃ is a good experimental sample to check this hypothesis: it crystallises in a hexagonal plate-like shape which presents basal and lateral faces, with different surface groups distribution.

Growth of gibbsite particles has been controlled to vary the aspect ratio, i.e. the ratio between lateral and basal faces areas. The 3D-morphology is characterised using both gas (Kr) adsorption local isotherms [1] and Atomic Force Microscopy (statistical analysis of 3D-images), defining specific faces area and size distribution (length, height). Acid-base properties have been investigated using potentiometric titrations and simultaneous *in situ* infrared spectroscopy. Indeed the absorption at 3460 cm⁻¹ on IR spectra depends on lateral surface sites [1] and seems to be modify by physical-chemical parameters in the solution (pH, ionic strength) [2]. These results show a good correlation between the distribution of crystalline faces and proton adsorption properties determined both by IR spectroscopy and potentiometric titrations.

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MIXED SURFACTANTS FOR BETTER UNDERSTANDING CONDUCTIVITY IN WATER-IN-OIL MICROEMULSIONS

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The electrical conductivity of D2O-in-n-heptane microemulsions stabilized by cationic/non-ionic surfactant mixture was studied as a function of D2O content, surfactant concentration and surfactant mixture composition. The surfactant mixtures employed were cationic didodecyldimethylammonium bromide, DDAB, with either a non-ionic poly(oxyethylene) monododecyl ether, C₁₂E_J, with J = 3 - 8, 10 and 23, or with a non-ionic polymeric surfactant of the type PEO-PPO-PEO (Pluronic) or the reverse structure (Pluronic®). Qualitative structural information was drawn from a comparison between measured conductivities and predictions based on a charge fluctuation model (CFM) for spherical droplets. The conductivity versus water content curves were found to be typical for water-in-oil systems composed of spherical droplets. For these blends it was concluded that microemulsion conductivity is independent of cationic surfactant (DDAB) concentration. This finding agrees well with theoretical microemulsion conductivity models.

MONOLAYERS OF A ZWITTERIONIC SURFACTANT. EFFECT OF pH ON THE STATIC AND RHEOLOGICAL PROPERTIES

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In general terms, surfactants derived from amino acids are of interest due to their biodegradation characteristics. From the practical point of view, tryptophan-derivatives have been used for improving the hydrophobic behavior of wool [1]. From the point of view of fundamental research, Hexadecyl 1-N-L-tryptophan-glycerol-ether (C₁₆-TGE) offers the opportunity of studying the effect of pH on the behavior of insoluble monolayers of a zwitterionic surfactant.

We have measured the surface pressure (Π) vs. area (A) curves of C₁₆-TGE at 25 °C using a Wilhelmy balance. The monolayers were spread on aqueous subphases which pH ranged from 6 to 1. The Π vs. A shape of curves changed with the pH. More specifically, a surface phase transition appeared at low values of Π as the pH decreased from 6 to 2, and then disappeared as the pH was further decreased. The existence of the phase transition was also confirmed by surface potential measurements and by fluorescence microscopy. The area at which the phase transition appears presents a sharp peak at pH = 2. We have estimated that at this pH, 70% of the surfactant is in the cationic form. The analysis of the surface potential and the infrared reflection-absorption spectroscopy data indicates that the phase transition is associated to a change of orientation of both the C₁₆ hydrocarbon chain and of the aromatic group of the surfactant with respect to the air-water surface. This change of orientation may be related to the change of interaction between the charged groups of the molecule. When an inert salt is added to the subphase these interactions are screened, and the effect of pH on Π vs. A curves is almost suppressed.

We have studied the surface rheology of the monolayers by measuring the spectra of the light scattered by thermal capillary waves. The results indicate that there must be at least one surface relaxation process in the monolayer.

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MIXED LANGMUIR MONOLAYER PROPERTIES OF PERFLUOROCARBOXYLIC ACIDS WITH DIPALMITOYLPHOSPHATIDYLCHOLINE (DPPC)

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Surface pressure (π)-area (A), surface potential (ΔV)-area (A), and dipole moment (μ_s)-area (A) isotherms were obtained for Langmuir monolayers made from four different perfluorocarboxylic acids (FCs) [perfluorododecanoic acid (FC12), perfluoro-tetradecanoic acid (FC14), perfluorohexadecanoic acid (FC16), and perfluoro-octadecanoic acid (FC18)], and dipalmitoylphosphatidylcholine (DPPC), mixed combinations. Monolayers were spread on a substrate solution of 0.15 M NaCl (pH 2.0, 298.2K) at the air/water interface by the Wilhelmy method, ionizing electrode method, and by fluorescence microscopy. The new finding was that collapse pressures of FCs decrease with the chain length increasing though those of hydrogenated fatty acids increase. The variation of the phase transition pressure as a function of FC12, FC14, and FC16 molar fraction and DPPC are miscible in the monolayer state. While, the constant transition pressure as a function of FC18 molar fraction (X_{FC18}) showed that FC18 and DPPC are immiscible in the monolayer state. This result was confirmed by deviations from the additivity rule when plotting against the variation of the molecular areas and surface potentials as a function of X_{FCs} over the whole range of surface pressures investigated. Assuming a regular surface mixture, the Joos equation, which was used to describe the collapse pressure of mixed monolayers with miscible components, allowed calculation of the interaction parameter (ξ) and the interaction energy ($\Delta\epsilon$) between FCs (except for FC18) and DPPC. We also observed the surface morphology of FCs, DPPC, and their mixed monolayer systems by using fluorescence microscopy in order to examine the miscibility of their mixed monolayer systems. As a result, fluorescence images of FC12/DPPC, FC14/DPPC, and FC16/DPPC ($0 < X_{FC16} < 0.3$) mixed systems showed miscible patterns, however, those of FC16/DPPC ($0.3 < X_{FC16} < 1$) and FC18/DPPC mixed systems showed immiscible patterns.[1,2]

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SELECTIVE FLUORIDE SORPTION ON ACTIVATED ALUMINA

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Fluoride is found in natural waters due to geological reasons. For humans it normally does not count as an essential trace element, however a daily uptake up to 4 mg is needed, especially for children. Higher concentrations may lead to fluorosis of teeth or skeleton. To avoid health problems from long-term consumption drinking water standards of 1.0 to 1.5 mg/L have been established by WHO and many countries. Ground waters with elevated concentrations and, therefore, the respective drinking water problems are encountered in about 25 countries throughout the world. Selective fluoride elimination is possible with aluminium or zirconium-based materials among which the semi-crystalline and highly porous activated alumina is the most widely tested sorbent material.

Activated alumina has also been used for the investigations presented. In the first part the sorbents were characterised with respect to surface, porosity and dissociation/protonation. The second part comprised investigations of sorption equilibria in pure systems and in the presence of competing ions like phosphate and sulphate. To cover sorption and regeneration the range of pH was 3 to 13.

Initially, commercially available products have been investigated. Because of the pH dependent sorption and the necessity to decrease the feed water pH for an effective sorption modified activated alumina products were used for the further experiments. Results demonstrate that the Fluoride sorption properties could be improved substantially. Furthermore, magnetic activated alumina with a particle size below 0.2 mm has been investigated to improve the sorption kinetics.

Data were evaluated by means of a theoretical approach to allow the prediction for natural raw waters.

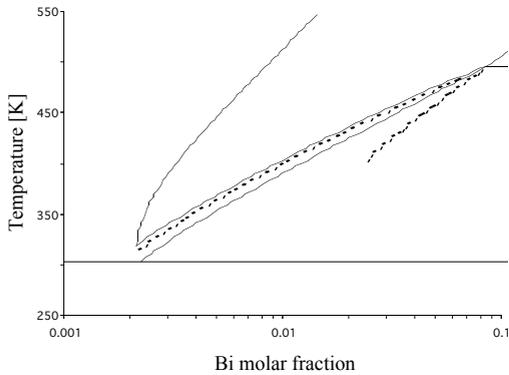
WETTING AND SURFACE FREEZING IN Ga-Bi ALLOYS

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Thermodynamic model calculations of the surface phase transitions in Ga-Bi alloys are performed, which accounts in particular for the finite thickness of the adsorption films. The excess chemical potential of bismuth in the films is calculated by employing a screened Coulomb potential. The calculated dependence of the liquid film thickness predicts prewetting and complete wetting transitions, which are in qualitative agreement with the experimental data [1]. On the base of surface tension calculations the surface freezing-melting transition is modeled and the results coincide with the experimental observations via second harmonic generation [2] and surface light scattering [3]. Using an appropriate description of the nucleation mechanism in liquid films the line tension between the liquid and solid films is determined by a fit of the experimental data. A complete diagram of the surface liquid-solid phase transitions on the vapor/liquid Ga-Bi interface is derived:



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PHASE SEPARATION OF PROTEINS AT INTERFACES. A BROWNIAN DYNAMICS STUDY

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Recent microscopy experiments have investigated the structure of mixed adsorbed protein films [1, 2]. These studies have provided contradictory results about the extent of miscibility of different proteins at fluid interfaces. We address this problem here using a Brownian dynamics simulation approach [3]. We find that formation of bonds between model protein molecules can lead to either phase-separated or effectively mixed film structures, depending on the attributes of the bonds. The effect of the adsorption rate on the miscibility of the systems is also investigated. We discuss the conditions under which genuine thermodynamic interfacial phase separation can arise in relation to the bulk–interface coupling.

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POLYSTYRENE SULFATE LATEX PARTICLES IN PRESENCE OF POLY(VINYLAMINE): AGGREGATION KINETICS AND CHARGING BEHAVIOR

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Dispersions of solid nanoparticles represent an important class of chemical products. In particular, the applications of these materials are formulation of pigments and paints. Most of these applications require colloidal particles in the form of stable aqueous dispersions. When suitably chosen, polyelectrolytes provide excellent dispersion agents. An important situation arises when the polyelectrolyte carries a charge opposite to the charge of the particles. In that case, the polyelectrolyte adsorbs strongly to the particles and one typically observes charge reversal at moderate polymer dose.

The present study focuses on the early aggregation stage of the negatively charged polystyrene latex particles in the presence of a linear cationic polyelectrolyte: the poly(vinylamine). By using dynamic light scattering, we have systematically studied the effects of polymer dose and ionic strength on the aggregation phenomenon. The colloidal stability is controlled by the particle charge, which results from the particles surface charge and the opposite charge of the adsorbed polyelectrolyte. The aggregation rate depends sensitively on ionic strength and can be well correlated with electrophoretic mobility.

CHANGE OF INTERMEMBRANE SPACING AS A FUNCTION OF STRESS IN A LAMELLAR PHASE WITH CLAY PARTICLES DISPERSED

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We report on the change of the interlamellar spacing as a function of stress in a nonionic lamellar phase ($C_{12}E_4$ in D_2O) containing clay particles (Laponite RD). The system was studied by means of small angle light and small angle neutron scattering under shear. Grillo et al. studied the phase behavior of these samples at rest. [1] The neutron scattering experiments were conducted using two samples with the same surfactant volume fraction ($\Phi=0.365$) but different H_2O/D_2O ratio. Two H_2O/D_2O ratios were chosen to match the scattering length densities of the laponite and the lamellae, respectively, thus being able to examine the influence of shear on lamellae and clay platelets separately. The rheological properties show the familiar shear thickening regime associated with MLV-formation, and a shear thinning regime at higher stresses. Here the variation of viscosity is less pronounced as commonly observed. [2-5] Depolarized SALS reveals an unexpectedly strong variation of the MLV size in this region. SANS reveals a change of the interlamellar spacing of up to 30% for the highest stress. These findings are explained by a microphase separation with water rich areas, where the clay resides in order to avoid the highly curved regions of the MLVs' interior. This phase separation leads to a change in the lamellar spacing which is much more pronounced than the change observed when shear suppresses thermal bilayer undulations. [6] The SANS experiments using the samples with laponite contrast suggest an isotropic orientation distribution of the clay platelets.

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INTERPRETATION OF NOVEL RESULTS ON MOLECULAR EXCHANGE PROCESSES AT FLUID INTERFACES

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Interfacial rheological properties have a decisive influence on the stability of foams and colloid systems. For example, the stabilizing effect of dissipative processes at interfaces was demonstrated by improved experimental methods like a new oscillating bubble device using the frequency range $1 \text{ Hz} < f < 500 \text{ Hz}$ [1,2]. The interpretation of the related interfacial rheological properties requires models which describe the dynamics at the interface in detail. In particular, the influence of molecular exchanges on these properties should be investigated. This is possible by monitoring of the instantaneous adsorption state on an oscillating bubble by SHG light. The comparison of the change in surface concentration (amplitude and phase are detected by SHG signals) with the surface dilational modulus determined by independent pressure registrations within an oscillating bubble, exhibits details of the molecular exchanges at the interface, e. g., the exchange rates and the thermodynamic states (equilibrium or nonequilibrium state) between monolayer, sublayer, and bulk phase. In addition, it allows the estimation of the of dissipative losses per molecular exchange in nonequilibrium states. With the first SHG measurements the discrepancy between experimental and theoretical values of rheological and adsorption parameters could be explained [3]. Besides, the results allow to verify or reject known dynamic models of fluid interfaces.

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CHARACTERIZATION OF RAMSDEN EMULSIONS STABILIZED BY SURFACTANT-FREE MONODISPERSE POLYSTYRENE LATEX PARTICLES

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Ramsden emulsions prepared with monodisperse polystyrene (PS)-sulphate latex particles alone have been characterized at various particle concentrations, electrolyte levels and dispersed phase volume fractions. The particles were synthesised by a surfactant-free method [1]. Both lyophilic and hydrophilic initiators were used to prepare latexes of between 180 and 375 nm in diameter. Irrespective of particle size, the latexes all had a ζ -potential in water in the range -50 to -57 mV. Equal volume water + hexadecane emulsions prepared from the aqueous particle dispersions were all water-in-oil (W/O). Upon increasing the particle concentration, at a constant electrolyte level, emulsions had a smaller median drop diameter and were more stable to coalescence. For example, particles of diameter 235 nm at a concentration of 2.0 wt. % gave a coarse emulsion of median diameter = 50 μm , whereas at 3.0 wt. % the diameter was 6 μm . Emulsions remained W/O at all oil:water ratios, i.e. such particles are sufficiently hydrophobic.

The concentration of electrolyte was found to be most important with respect to emulsion stability. Emulsions, stable to both sedimentation and coalescence, could only be prepared at or above the critical coagulation concentration (c.c.c.) of electrolyte in the aqueous particle dispersion. We observed that W/O emulsion drops changed in appearance from white and opaque to clear and transparent as the [electrolyte] was increased above the c.c.c., implying particle transfer from water to oil and/or the oil-water interface. Finally we show that the addition of the oil-soluble electrolytes, sodium tetraphenylborate and Aerosol OT, causes an enhanced rate of flocculation and ultimately sedimentation of the water drops in these emulsions. We argue that this is evidence of the ability of electrolytes to screen repulsive long-range electrostatic charges acting through the continuous oil phase, in agreement with previous work for particles spread at planar oil-water interfaces [2].

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DENSE PACKING OF COLLOIDS

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The ordering of homogeneous colloidal particles like rods or platelets can be characterized by the numbers of nearest, next-nearest and third neighbors T_1 , T_2 , T_3 from the center of gravity. Usually the minimum self-coordination numbers 1 1 1 of particles with low symmetry like proteins are increased to maximum numbers 6 6 6 (2D hexagonal packing), 12 6 24 or 12 6 2 (3D cubic or hexagonal close-packing) for spherical particles like colloidal SiO_2 . The density $\rho = 0.91$ of the 2D 6 6 6 circle packing is decreased at decreased T_1 contact numbers to 0.84 (5 2 2 or 5 2 1 packing), 0.79 (4 4 4 square net packing), 0.71 (3 2 1 packing of distorted hexagons), 0.45 (2 4 2 structure of hexagonal net containing vacant positions) and 0.26 (1 1 1 structure of hexagonal net). The density of other circle packings with the same T_1 contact numbers like the 5 5 5 packing ($\rho = 0.78$), 4 4 6 kagomé ($\rho = 0.68$) or 3 6 3 honeycomb net ($\rho = 0.61$) is decreased. The packings can be approximated by a set of different tiles **a** - **o** as was outlined in the Coimbra conference. The corresponding 3D packings can be constructed by the 3D combinations of these tiles. The cubic close-packing for example is obtained from a combination of tetrahedra and octahedra, which are assembled from the triangular tiles **a**. Non-periodic packings are either clusters with finite cluster size and an aperiodic center or infinite crystal packings containing Fibonacci sequences of tiles. The shape of the clusters depends on the polyhedron (3D) or tile (2D) in the center of the cluster. An approximately 2D circular cluster is obtained for $c = 1$ colloidal particle in the center, a triangular cluster for the triangular central unit **a** with $c = 3$ particles. The total number x of particles in a cluster increases with the numbers j of shells around the center by $x = 3j^2 + 3j + 1$ ($c = 1$) or $x = 3j^2 + (3 + c)j + c$ ($c = 2 - 12$). The combination **b**₂***d** of distorted squares **b*** (containing one vacant position) and distorted hexagons **d** with T_i values 2 2 0.7 containing particles with $T_1 = 1, 2$ and 3 contacts has a higher density $\rho = 0.56$ than a homogeneous packing with $T_1 = 2$ of all particles. The same applies to the combination **b**₅***d*** (1 2 1) with three vacant positions in the unit cell and $T_1 = 0$ or 2 contacts ($\rho = 0.44$).

DYNAMICS OF PROTEIN ADSORPTION AT THE OIL-WATER INTERFACE

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Adsorption of proteins at liquid-fluid interfaces and their behaviour in the adsorbed state play an important role in the formulation and stabilization of different foam-based (air-water interface) and emulsion-based (oil-water interface) products in the food industry [1]. Therefore, an understanding of the kinetics of protein adsorption and the properties of adsorbed films is essential in comprehending the important physico-chemical factors that determine the formation and stability of food colloids. In the present study, we present a characterization of adsorption kinetics by dynamic interfacial tension measurements. Adsorption of several food proteins is compared for air-water and oil-water interfaces under identical experimental conditions in a Langmuir type pendant drop film balance [2]. Rates of adsorption and equilibrium concentrations values are analyzed for both interfaces and differences are discussed in terms of interaction of molecular forces of the proteins with these interfaces [3].

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ANION EFFECT ON MONOLAYERS OF CALIXARENES

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Calix[*n*]arenes are cavity shaped molecules made up of *n* phenolic units linked via alkylidene groups and differently substituted in the 'para' positions. Their characteristic shape makes them able to complex metallic ions and so to be used for analytical chemistry and in the decontamination of nuclear wastewater. Moreover, because of their structure, calixarenes can adsorb at air/water interface and can be characterized through Langmuir spreading isotherms. Their complexation properties toward cations have been deeply investigated, however the effect of anions if the monolayers' parameters has received only superficial attention. In this paper we want to check the effect of some anions on the calix[6]- and calix[8]-arene's spreading isotherms at air/water interface. We selected a wide range of different potassium salts to be used as subphase: KCl, KI, KBr, KSCN, KNO₃, CH₃COOK, K₂SO₄, K₃PO₄. Since potassium ions are complexed by the investigated calixarenes, the differences in Langmuir isotherms can be ascribed to the different anion in the subphase.

Our results show a significant specific anion effect and indicate the formation of supra-molecular species positively charged that interact via electrostatic repulsion, and their interactions are modulated by the particular anion dissolved in the subphase. In particular, the anions, with the exception of Br⁻, follow the so-called Hofmeister series. This exception can be due to the complexity of the system under exam; in fact three different interfaces are present: aqueous solution/calixarene's film, aqueous solution/air and calixarene's film/air, so in the case of Br⁻ the effects can mix in such a way that it results the more effective anion. To understand this phenomenon, we analyze the variation of some parameters from spreading isotherms as a function of some physicochemical parameters: the lyotropic number (*N*), the molar surface tension increment (σ), the Gibbs' free energy of hydration (ΔG_{hydr}), partial molar volume (v_s) and molar refractivity (R_2').

FORMATION OF MULTILAMELLAR VESICLES BY OSCILLATORY SHEAR

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The formation of multilamellar vesicles (MLVs) in the sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/brine system can be controlled by oscillatory shearing. The formation kinetics can be scaled onto constant controlled stress measurements and the scaling parameter can be deduced from the measured loss tangent. A minimum strain amplitude for onion formation is deduced and shown to be frequency independent. This also holds for the final size of the MLVs, depending only on the stress amplitude. The final MLV radii agree with those found at constant stress.

SATELLITE HOLE FORMATION DURING DEWETTING: EXPERIMENT AND SIMULATION

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The dewetting of thin polymer films on solid substrates has been studied extensively in recent years [1-2]. These films can decay either by nucleation events or by spinodal dewetting, essentially only depending on the interface potential describing the short-range and long-range intermolecular interactions between the interfaces, and the initial film thickness. Here, we describe experiments and simulations concerned with the decay of thin polystyrene films, which occurs by the formation of a correlated pattern of holes (“satellite holes”). The development of this complex film rupture process can be mimicked precisely by making use of novel simulation code based on a rigorous mathematical treatment of the thin film equation (performed by J. Becker and G. Grün, University of Bonn) and on the knowledge of the effective interface potential of the system [3]. The conditions that determine the appearance and the position of the satellite holes around pre-existing holes are discussed [4].

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NANO-FOAMING IN HARD SOLID SILICA

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Nano-scaled cellular foams were found to be formed in hard silica matrix by water molecules vaporized by instantaneous heating of sol-gel derived silica. The chemical and physical formation mechanism of the nano-foamed structure were clarified. Water molecules released from silanol group in silica condensation cause the spherical “ballooned” structure in the scale of 10⁰nm. Acidic condition for hydrolysis of tetraorthoethyl silicate (TEOS) is necessary for the released water molecules to be enclosed in the silica matrix and to induce the “ballooning” behavior. Sol-gel derived silica obtained in basic condition is constituted of aggregated nano-particulate structures and offers those water molecules way out of the silica without causing the ballooning. The finally obtained foamed structure greatly depends on the temperature of the instantaneous heating process triggering the ballooning. The volume fraction of the closed pores formed as the cells went up to 65% at the maximum where the foamed silica floats even on the surface of ethanol. A remarkable feature of the cellular nano-foamed structure is that the nanopores are mostly closed-type pores, being contrastive to those obtained by the templating method adopted in normal preparation of nanoporous materials. Considering the simplicity of the whole process of this method, the nano-foaming is expected to be practically useful in various applications requiring nanoporous inorganic materials.

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FORMATION OF LANGMUIR MONOLAYERS WITH NEW 5-METHYLENE-UREIDO-5'-METHYL-2, 2'-BIPYRIDINYL UPPER-RIM FULLY TETHERED CYCLODEXTRINS

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Several amphiphilic cyclodextrins bearing at the upper rim bipyridyl or bithiazolyl [1] moieties and free hydroxyl or methoxyl groups at the lower rim, were synthesized using a one step "phosphine imide" approach. These metal complexing molecules have fluorescence [2] properties potentially interesting for optical applications. Here, the cyclodextrin derivatives were used as probes for evaluating the role of different moieties in the self-assembly process expected to be crucial for elaborating functional devices. The behavior of these molecules and of Eu(III) complexes of some of them in Langmuir films was studied using surface pressure (Π) and surface potential (ΔV) measurements performed as a function of film compression (compression isotherms). For chosen cyclodextrins, Brewster Angle Microscopy in monolayers was used. Chosen cyclodextrin films were transferred on mica using Langmuir-Blodgett technique, and the properties of the film were analyzed using Fringe of Equal Chromatic Order technique (F.E.C.O), and fluorimetry.

The monolayer structure and the fluorescence properties of the Langmuir-Blodgett film indicate that the derivatives studied can be used for preparing cyclodextrin-based optical devices.

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SOLUBILISATION OF PENTACHLOROPHENOL IN MICELLES OR CONFINED MICELLES

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The solubilisation of pentachlorophenol (PCP) in cationic surfactant micelles or in surfactant/silica mesostructures is studied. The micelle/water partition coefficient is derived from both theoretical models and experiments. The sorption isotherm in the mesostructure is determined by the solution depletion method and compared to that of phenol, mono-, di- and tri-chlorophenol. The interaction energy between the PCP and the various surfactant phases are obtained by microcalorimetry. The interaction between the anionic form of the PCP molecule and the cationic surfactant is so high that the precipitation of a phenolate form of the surfactant is observed. This phenolate form can be considered as a surfactant that replaces the bromide form of the cationic surfactant. The water/micelle partition coefficients, the solubilisation enthalpies in micelles and the sorption enthalpies in the mesostructure increase with increasing hydrophobicity as defined by the octanol/water partition coefficient that increases itself with the number of chloride molecules in the phenol derivative. On the other side the affinity for the mesostructure follow a non-monotonous evolution with the same parameters. This could be due to steric effects with increasing molecular size.

ADSORPTION OF POLAR ORGANIC COMPONENTS ON SILICA

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Adsorption of polar organic components onto rock surface is one of the mechanisms that is believed to cause wetting alteration of a reservoir rock. Polar components in crude oil that are believed to be responsible for surface interactions and wetting properties include carboxylic and phenolic acids, and organic bases. Known compounds, representative of these naturally occurring compounds in crude oil, have been chosen for adsorption studies.

Adsorption isotherms in solid-oil-brine model systems have been examined as a function of component concentration in either water or oil. The systems investigated consist of isooctane as model oil phase and water solutions of NaCl as aqueous phase. Silica was used as the solid phase. The organic polar compounds chosen as adsorbates were 1-naphtic acid, 5-indanol and quinoline, i.e., a strong and a weak organic acid and an organic base. The polar compounds were adsorbed from the oil phase as well as from the aqueous phase in adsorption isotherm experiments. The results are compared to adsorption isotherms for the same compounds on α -alumina as earlier studied [1] and demonstrate the difference in adsorption behavior between compounds with different functional groups of varying polarity and acidity.

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SYNTHETIC APPROACH TO FEW-ATOM CLUSTERS ON AN ORGANIC MONOLAYER

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Nanoparticles, in contrast to bulk materials, have unique properties, e.g. quantum size effects, which can be utilized to design various intriguing nanodevices [1]. Usually these nanoparticles are pre-made and thereafter transferred onto appropriate substrates to fabricate nanostructures. Their sizes range from 100 nm down to 1 nm. Even 1 nm particles already comprise tens of atoms. Much effort is currently dedicated to further reduce the size of the nanoparticles and finally develop single atom devices. Individual adatoms on single crystal surfaces in ultrahigh vacuum, which have been extensively studied [2], cannot be directly developed into single atom devices because of the high adatom mobility at room temperature. However, those single atoms tightly immobilized via chemical bonds might meet that need. Thus this work intends to show a tentative approach to fabricate well-separated and stable “sub-nano” metal particles consisting of few atoms or even of a single atom in the extreme case.

In this contribution we report on the fabrication of few-atom gold clusters on functionalized silicon oxide surfaces. Gold nanoparticles are studied because of their high inertness and biocompatibility. Single crystal silicon wafers with flat and well-defined oxide layers are selected as substrates. The silicon surface is modified by a PPh₂-terminated silane as coupling agent. We show that the silane self-assembles into a flat and continuous monolayer. Thereafter, the PPh₂ groups immobilize Au(I) ions by a coordination complex, when the wafer is treated with an Au(I) containing solution. According to the need of electroneutrality and stoichiometry, one PPh₂ group chemically binds only one Au(I) ion. Other unwanted physisorbed Au(I) ions can be rinsed off. Thus it is envisaged that in the ideal case gold ions are individually distributed only on phosphorus atoms. Consecutively, Au(I) ions are reduced by NaBH₄. We can obtain discrete few-atom clusters and single-atoms, providing the affinity between phosphorus and gold atoms overrules the mobility of gold atoms. Ellipsometer, AFM, contact angle goniometer and TOF-SIMS are employed to characterize the samples. The surfaces are suitable for further functionalizations, such as grafting biomolecules or magnetic particles.

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THIN FILM FABRICATION OF IRON OXIDE-SILICA NANOCOMPOSITES AND THEIR RESPONSES TO HUMIDITY

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It has been reported that the films fabricated by conventional solid state reaction of iron oxide particles coated with silica are more stable and more sensitive to humidity than those without silica coating [1]. This is because the silica film isolates the sensing material from the condensate at high humidity and thus inhibits the degradation of the response [1-3]. In this work, the films of iron oxide-silica nanocomposites have been prepared using the sol-gel process and spin coating technique. The sol-gel process allows homogeneous distribution of uniform nanoparticles that yield a high surface-to-volume ratio. The effect of the spin rate, the additive, the aging duration of the gel and the molar ratios between iron (Fe) and silicon (Si) in the gel, on the film properties are determined. After being calcined at 400, 600 and 800°C, hematite is formed in the film containing Fe:Si ratio of 100:0 and glasses are synthesized in those having Fe:Si ratios of 90:10, 50:50, 10:90 and 0:100. Each set has a uniform particle size and the particle size decreases as the silicon content in the film increases. This is probably because silica inhibits crystallisation and particle growth. The films having high iron content shows more cracks than those having high silicon content. Hydroxypropylcellulose (HPC) is found to reduce cracks successfully. It increases the gel strength and makes the film porous. The humidity sensing property of the films is being tested.

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GEOMETRIC CHARACTERIZATION OF POROUS COLUMNS OF CALCIUM FLUORIDE BY IMBIBITION OF HYDROCARBONS

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Surface characterization of solids usually requires contact angle estimation. In the case of porous solids, this is achieved by means of experiments based on the flow of liquids in porous beds of the solid. This methodology needs of the previous evaluation of some geometrical features of the porous system, as its porosity and the equivalent radius of the interstices of the medium. This is usually carried out by means of imbibition experiments with saturated hydrocarbons into porous columns made from powdered solids. However, physical interpretation of the experimental data is not actually clear, since there are some misunderstood points such as the effect that the imbibition rate has on the proper capillary rise experiments [1], or the influence of the length of the tail of the hydrocarbons on the values of the effective radius deduced from the experimental results [2]. An attempt of going deeply in the former questions, in this work we are carried out capillary rise experiences into porous columns made of calcium fluoride employing as penetrating liquids some n-alkanes. This has been made by studying the increase in the weight of the porous solids as a results of the imbibition. The preparation of the columns has been made by a new procedure developed by us that ensures both the homogeneity and the reproducibility of the porous systems, generally a difficult task for this kind of system. In relation to the analysis of the experimental data, it has been also carried out by an new method based on the Washburn's equation, which gives the relationships between the increase in the weight of the solid and the time, and the Savitzky-Golay's algorithm, which allows to deduce the rate of the liquid inside the pores as a function of the time. From our results, we have found that the kinetics of the capillary rise does not influence appreciably on the values of the radius deduced from experiments, since the experimental data correlated very accurately Washburn's equation, which is founded on the independence between contact angle and the imbibition rate. Also, we have found that the deduced value of the effective radius deduced from our experiments are in a good agreement with that one deduced from White's equation.

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LOW-FREQUENCY DIELECTRIC DISPERSION OF SUSPENSIONS OF SPHEROIDAL HEMATITE PARTICLES

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The determination of the Low-Frequency Dielectric Dispersion (LFDD) of colloidal systems can provide rich information on the dynamics of electrical double layers. Most theories and experiments have been performed on spherical colloidal systems, but it may be of interest to extend the methodology (and also the theory) to systems that are not so ideal. In particular, the theoretical study of the dielectric constant of spheroidal particles has been undertaken by Grosse et al. [1]. These authors give an expression for the dielectric increment ($\Delta\epsilon'$) of a suspension of spheroidal particles randomly oriented. The main conclusions of the model are: i) $\Delta\epsilon'$ is generally larger than that of dispersed spheres, the more so the further we are from sphericity, and ii) $\Delta\epsilon'$ increases with surface conductivity, although the rate of growth can be slower than in the case of spheres. The model also permits us the knowledge of the critical frequency. Thus, it can be possible, in principle, to determine when the relaxations corresponding to the two particle orientations can be well separated.

In order to experimentally check this model we have measured the permittivity of monodispersed prolate spheroidal hematite particles with two different axial ratios. We use a two electrodes conductivity cell to measure the impedance of the suspensions, varying the pH to change the surface charge of the particles. In order to eliminate the contribution of the electrode polarization we use the logarithmic derivative method [2]. The results show that: i) with the logarithmic derivative method we can actually separate two relaxations for the most elongated particles and near the zero point charge, and ii) the zeta potential predicted by electrophoretic mobility and dielectric dispersion qualitatively agree, but those obtained by LFDD method are always higher.

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ELECTRIC PERMITTIVITY OF SUSPENSIONS OF COLLOIDAL SPHEROIDS AT HIGH FREQUENCY

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The determination of the High-Frequency Dielectric Dispersion (HFDD) of colloidal systems can provide useful information about the surface conductivity of the particles in suspension. Previous works have mostly dealt with spherical particles. Extension of the technique to spheroids may be of interest, because this is a more realistic situation from a practical point of view. Since at this frequency range (MHz to GHz) only electromigration fluxes and displacement currents have time to polarize the interface, the dynamics is in this case quite simple and only related to the difference between the surface, particle and solution conductivities and permittivities. Hence, the total surface conductivity and the zeta potential can be deduced more easily than at low frequencies.

We measured the dielectric response, at the 300 kHz-3 GHz frequency range, of suspensions of two kinds of hematite particles, with low and large axial ratio. We used a reflection cut-off cell working as a waveguide below cut-off [1] and obtained the dielectric spectra at different pH's in order to analyze the effect of surface charge modification. Like at low frequencies, two relaxation phenomena are expected, related to both orientations of the particles. A single broad peak was however observed which did not behave as a Debye function. It was analyzed using the logarithmic derivative method [2] to obtain the imaginary part of the dielectric constant. We conclude that both relaxations are present, but they are close in frequency to each other.

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DYNAMIC MOBILITY OF CONCENTRATED SUSPENSIONS. EXPERIMENTS AND THEORETICAL PREDICTIONS

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Electroacoustic techniques, including Colloid Vibration Current or Potential, and ESA (Electrokinetic Sonic Amplitude) are gaining interest in the characterization of colloidal dispersions mainly because they are in principle suitable for a large variety of colloidal dispersions and have achieved a considerable degree of automation in commercial devices. One of the fields where these techniques are expectedly most useful is concentrated suspensions, since they are free of the problems involved in direct observation or light scattering of the individual particles. In spite of this, the problem of electroacoustics of concentrated suspensions is far from being fully resolved. In this work, the method used is ESA. The quantity of interest is the complex mobility (or dynamic mobility) of the particles. Calculations based on cell models, already used for the evaluation of the permittivity of suspensions [1], are compared to formulae where hydrodynamic interactions between particles are directly taken into account [2]. Both types of results will in turn be compared to experimental dynamic mobility data obtained with concentrated suspensions of alumina, and latex particles.

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ENTHALPY OF MICELLISATION OF DIBLOCK COPOLY(OXYETHYLENE/OXYPROPYLENE) BY ISOTHERMAL TITRATION CALORIMETRY. COMPARISON WITH THE VAN'T HOFF VALUE

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Block copolymer P₉₄E₃₁₆ (P = oxypropylene and E = oxyethylene, the subscripts denote number-average block lengths and the order of appearance in the formula the sequence of polymerization in the preparation) has been studied by isothermal titration calorimetry using a VP-ITC titration calorimeter from MicroCal Inc., Northampton, MA to determine critical micelle concentrations (cmc) and enthalpies of micellisation at temperatures in the range 20-35° C. Comparison with values of the cmc determined previously by other methods [1-2] shows good agreement. Comparison of the enthalpies of micellisation, ranging between 145-155 kJ mol⁻¹ being the preferred value depending on the method of analysis, with standard values determined using the van't Hoff equation (350 kJ mol⁻¹) indicates a marked difference in values derived from the two methods. We speculate that the effect is caused by the P-Block length distribution in the copolymer, including the small proportion of short chains generated during its polymerisation as a consequence of the transfer reaction [3]. The cmc, and hence the van't Hoff enthalpy of micellisation, relates to the most readily species (that is to those copolymers with lengthy P block), whereas the enthalpy of micellisation determined by ITC relates to the whole sample.

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MICELLIZATION OF ANIONIC/CATIONIC SURFACTANT MIXTURES AS STUDIED BY DYNAMIC SURFACE TENSOMETRY AND

¹H-NMR-SPECTROSCOPY

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Recently it was found that SDS/DTAB surfactant mixtures with SDS being in excess show an interesting dynamic surface tension behaviour. For long adsorption times the adsorption of the highly surface active anionic/cationic complex leads to a decrease of dynamic surface tension in comparison to the single SDS system. However, the situation is vice-versa for short adsorption times where the dynamic surface tension is increased by addition of DTAB although the overall concentration is increased. With increasing concentration of both SDS and DTAB these unexpected effects disappear [1].

It is known that highly surface active compounds like anionic/cationic complexes are solubilized by surfactant micelles present in the bulk [2]. However, in this case we have to assume that a partial solubilization of free SDS molecules into micelles formed by SDS/DTAB complexes takes place. With increasing overall concentration when eventually the CMC of the pure SDS is reached the anionic/cationic complex itself is solubilized by SDS micelles. Finally, no complex micelles are present which for their part can solubilize an excess of SDS molecules and the mixture starts to behave like pure SDS. This model was further investigated by means of ¹H-NMR-spectroscopy which supports the finding of dynamic surface tensiometry.

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SURFACE PROPERTIES OF MIXED PROTEIN-POLYELECTROLYTE LAYERS ADSORBED AT THE WATER/AIR INTERFACE AND AT THIN LIQUID FILMS

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Although polyelectrolytes are often only slightly surface active, in mixtures with proteins they have a strong influence on the adsorption layer formation. In the bulk solution proteins and polyelectrolytes interact to form aggregates. The strength of interaction depends on parameters such as pH, ionic strength, total concentration and mixing ratio. Thus the properties of adsorption layers formed at the surface of solutions are determined not only by the surface active protein but also directly and indirectly by the presence of the polyelectrolyte, i.e. the complexes.

The present contribution focus on the effect of acacia gum on the adsorption behaviour of β -lactoglobulin at the surface of aqueous solutions. The studies are performed using various experimental techniques, such as dynamic surface tensiometry, dilational and shear rheometry, surface ellipsometry, X-ray reflectivity. The tensiometry data give insight into the formation mechanism of the mixed adsorption layers, complemented by the measurements of the dilational and shear rheology, i.e. dilational and shear elasticity and viscosity. The ellipsometry shows the change in the adsorbed amount and adsorption layer thickness. The results are correlated with measurements on the stability and thickness of freestanding films drawn from the same solutions.

Limits of oscillation frequencies in drop and bubble shape tensiometry

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Dilational rheology has much impact on quite a number of technological processes, such as foaming or emulsification. The formation process and the mechanisms of stabilisation or destabilisation are linked to the dynamic interfacial properties, such as the interfacial dilational viscoelasticity. Only recently, commercial instruments became available for measuring the viscoelasticity of adsorption layers. This made the topic quite interesting to many research groups.

The methodology accessible via commercial instruments to measure the elasticity and viscosity of adsorption layers is the drop or bubble shape analysis as described in detail recently [1]. The technical parameters allow to perform oscillations of a drop or bubble at various frequencies, from very slow oscillations of about 10^{-3} Hz to frequencies of even 10 Hz and above. High frequency oscillations, however, do not provide drops and bubbles with a Laplacian shape due to hydrodynamic effects.

The poster to be presented deals with experiments of oscillating drops and bubbles performed in order to find the physical limits for this methodology. The experiments are performed with drops in air, air bubbles in water, and also water drops in oil. The results obtained show first of all the capacity of this type of experiments, suitable as interfacial rheological studies. The physical limits of oscillations for the various systems depend on the liquids' parameters, such as density, viscosity and surface (interfacial) tension.

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SURFACE ACIDITY OF ALUMINIUM AND GALLIUM SUBSTITUTED M41S MESOPOROUS SILICAS: AN INFRARED SPECTROSCOPIC STUDY OF ADSORBED PROBE MOLECULES

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Ordered mesoporous silicas belonging to the M41S group are a class of molecular sieves characterized by large surface area and uniform pore shape and layout. In contrast to zeolites, which have pore openings usually smaller than 1 nm, the pore diameter in M41S silicas spans the 15 to 80 nm range. This large pore size endows M41S silicas with a potential to act as molecular sieves and catalysts for conversion of large organic molecules which cannot enter the pores of conventional zeolites. However, as compared to protonic zeolites, pure M41S-type silica has a very low acidity. This is a severe setback for catalytic applications since, in general, the catalytic activity for reactions involving hydrocarbons is largely related to the number, nature and strength of surface acid sites. An efficient way to generate acidity in M41S mesoporous silica is through isomorphous substitution of silicon atoms by trivalent elements (M) in the silica framework. Bridging Si(OH)M hydroxy groups can thus be generated, and these species are expected to show Brønsted acidity; similar to that of Si(OH)Al groups in protonic zeolites. We report on the synthesis of Al and Ga substituted MCM-41 and MCM-48 silica, both of which belong to the M41S class, and of the study of their acidity by FTIR spectroscopy of adsorbed CO (at 77 K), pyridine and lutidine (DMP). Brønsted acidity was shown most distinctively by the characteristic IR absorption bands of both the pyridium ion and DMPH⁺ (1637, 1550 and 1650, 1630 cm⁻¹, respectively). The synthesized materials also showed Lewis-type acidity, which is very relevant for Ga-M41S; since catalytic activity of gallium-containing porous solids for some important industrial processes (e.g. dehydrocyclization of alkanes) is known [1,2] to require both Brønsted and Lewis acid sites.

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WETTING IN A PHASE SEPARATING COLLOID-POLYMER MIXTURE: THEORY AND EXPERIMENT

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Mixtures of colloids and polymers display a rich phase behavior, involving colloidal gas (rich in polymer, poor in colloid), colloidal liquid (poor in polymer, rich in colloid) and colloidal crystal phases (poor in polymer, highly ordered colloids). Using confocal light microscopy we studied the interface between the coexisting gas-liquid phases and their wetting properties in a system consisting of fluorescent polymethylmethacrylate (PMMA) spheres and polystyrene polymer in decaline. Due to the colloidal length scale the interfacial tension is much lower than in the atomic or molecular analog ($\mu\text{N/m}$ instead of mN/m). This low interfacial tension has clear effects on the kinetics of phase separation and on the colloidal gas-liquid profile near a single wall. The liquid phase wets the wall and the resulting profile is accurately described by theory. Precise measurements of the contact angle are more difficult and focussing on the wetting transition both experiment and theory will be presented. Colloid-polymer mixtures slightly off coexistence and hence in the one phase region show the formation of a liquid condensate when confined between two walls.

CRITICAL PARAMETERS FOR CONDENSATION OF ORGANIC ADSORBATES AT ELECTROCHEMICAL INTERFACES: A MEAN FIELD ANALYSIS

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A variety of organic compounds undergoing two-dimensional (2D) condensation at electrochemical interfaces is well known [1]. In the 2D condensation, lateral interactions between the adsorbed species play a crucial role [2]. The phase transitions may be inferred by constant values of differential capacity in capacitance-potential (C-E) plots. These transitions can be analyzed using exact and mean field analysis of 2D nearest neighbor Ising model formalism [3,4]. The two-state lattice gas model employed in the present analysis to simulate differential capacitance – potential plot using molecular parameters obtained from non-linear regression analysis. The required interfacial parameters viz. Permanent dipole moment of the adsorbate (p_A), number of molecules per unit area (N_T) and the inner layer dielectric constant (ϵ) are subsequently derived. The potential pit-width values are obtained from the simulated differential capacitance–potential plots for various adsorbates. The critical parameters such as critical temperature and critical concentration of the adsorbate are obtained by plotting potential pit-width (ΔE_{tr}) vs temperature (T) and potential pit-width (ΔE_{tr}) vs $\log(C_A)$ (where C_A is the adsorbate concentration). The obtained critical parameters are in good agreement with the experimental value.

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INFLUENCE OF DIFFERENT SOLUTES ON THE HYDRATION OF LIPID LAYERS

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PHOSPHOLIPID BILAYERS ARE THE SMALLEST BUILDING ELEMENTS OF THE LIVING MATER. THE LATERAL ORGANIZATION OF THE LIPID MOLECULES IN THE BILAYER AND THEIR INTERACTIONS NORMAL TO THE LAMELLA PLANE AFFECT THE STABILITY AND THE TRANSPORT PROCESSES THROUGH MEMBRANES. THE PRESENCE OF SOLUTES IN THE MEMBRANE SURROUNDING INFLUENCES THE SHORT-RANGE INTERACTIONS BETWEEN THE PHOSPHOLIPID BILAYERS IN DIRECTION NORMAL TO THE MOLECULAR ARRAYS. THIS WORK PRESENTS A STUDY ON THE INFLUENCE OF LOW MOLECULAR WEIGHT SUGARS, DIMETHYL SULFOXIDE (DMSO), AND ETHANOL (ETOH) ON THE INTERACTIONS BETWEEN PHOSPHOLIPID MOLECULES. SUGARS AND DMSO ARE PROTECTANTS WHICH STABILISE THE MEMBRANES AGAINST DESICCATION AND FUSION DURING FREEZING OR FREEZE-DRYING. ETOH IS WELL KNOW DEHYDRATION AGENT [1]. THE STUDIES ARE CARRIED OUT WITH DIMIRISTOYL PHOSPHATIDYLCHOLINE (DMPC) AND DIMIRISTOYL PHOSPHATIDILGLICEROL (DMPG).

Free-standing liquid films were used to model the interactions between bilayer membranes. The short-range interactions were altered by adding the solutes in the film forming dispersions. The film thickness increases in presence of sugars and decreases in presence of EtOH and DMSO. The thickness changes correspond to inclusion or removal of several water layers in the film aqueous core. The observed variation in the film thickness is attributed to a modified lipid hydration.

Neutron reflectometry was used to study the influence of the solutes on the formation of lipid bilayers on polymer cushions prepared from polyelectrolyte multilayers. It is observed that addition of solutes changes the structure of the formed lipid bilayers.

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MICELLIZATION PROPERTIES OF *n*-OCTYL- β -D-GLUCOPYRANOSIDE IN PRESENCE OF HYDROXYPROPYL CYCLODEXTRINS

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Isothermal titration microcalorimetry was employed to determine, in a direct way, the critical micelle concentration (cmc) and the heat of demicellization (ΔH_{demic}) of the nonionic surfactant *n*-octyl- β -D-glucopyranoside (OGP) at 298.15 K in aqueous solution. Gibbs energies and entropies of the demicellization process were calculated by using the classical thermodynamics relationships. The cmc obtained, 25.8 mM, is consistent with the values previously reported in the literature. Similar experiments were performed in presence of α , β and γ cyclodextrins at different concentrations, between 0 and 30 mM. Addition of cyclodextrins to the surfactant solution increases linearly the cmc and decreases in a similar way the estimated ΔH_{demic} . Changes in the micellization properties are interpreted in terms of inclusion complex formation.

PHOTOCONTROLLED PHASE SEPARATION IN SPIROBENZOPYRAN-COATED MICROCHANNELS

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We have developed various microchemical systems according to a concept of “continuous chemical flow processing” [1]. To make further progress, integration of fluid control units such as pumps and valves is required. Although micromachining technologies can provide such micro-fluid control units, the fabrication requires complex and many processes. On the other hand, fluidic characteristics in microchannels are strongly affected by surface properties of the channel wall due to the large surface area. Here, we will demonstrate a novel method to control fluid flows utilizing wettability changes by spirobenzopyran (SP)-coated surface in microchannels.

SP derivative having *N*-alkyl carboxylic acid was synthesized according to the previous paper [2]. Microchannels were fabricated on pyrex-glass substrates by a photolithography/wet-etching method (Y-shaped pattern, width 200 μm , depth 100 μm). The inner surface of the channels was treated with by (3-aminopropyl)triethoxysilane, and then, modified by the SP derivatives.

Before fluid introduction, VIS- and UV-irradiation of one branch in the Y-shaped channel and another, respectively, were performed. This process made the VIS-irradiated channel more hydrophobic than the UV-irradiated channel. Then, two-phase flow (water/air or water/*n*-hexane) was introduced to the channel by a syringe pump. In the case of water/air, water flows through the UV-irradiated channel and air flows through another one. When the irradiation lights were switched, the water/air flow was switched reversibly. In the case of water/*n*-hexane, moreover, separated flow was observed similarly with water/air flow. These results clearly show that the SP-coated microchannels can work as a photocontrolled phase separation device. Further quantitative discussion for the separation behaviors, such as size or flow rate dependence, is now in progress.

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BINARY COLLOIDAL SYSTEMS IN TWO-DIMENSIONAL CIRCULAR CAVITIES: STRUCTURE AND DYNAMICS

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We study the melting behavior of a binary system ($R = 4.5\mu\text{m}$, $r = 2.8\mu\text{m}$) of paramagnetic colloidal spheres in two-dimensional circular cavities. A repulsive interaction between the particles is caused by a perpendicular external magnetic field B which induces magnetic dipole moments perpendicular to the plane of the particles. By means of video microscopy we investigate the positions of the particles and their trajectories. For small interaction strengths we observe a completely liquid phase where large and small particles diffuse across the entire system. With increasing B the larger particles become – due to their larger magnetic moment - localized and form a stable structure while the smaller particles behave still as a liquid. For even higher magnetic fields the small particles also become increasingly localized and preferentially arrange as interstitial sites between the structure formed by the large particles. We present a systematic study of this rather complex multi-stage melting process which strongly depends on the particle numbers of large and small particles.

W/O ISOOTTANE/LECITHIN/WATER MACROEMULSIONS ARE A USEFUL TOOLS FOR BIO-REACTIONS WITH LIPOPHILICS COMPOUNDS

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The advantages of the bioconversions are manifold in comparison with the chemical synthesis and they do not only concern their great catalytic efficiency but surely the fact they work under less drastic conditions, for instance at room temperature [1]. The bioconversions can be achieved by enzymes or by microorganisms. To prefer of the microorganisms rather than the enzyme is due, on the one hand, to the possibility to exploit the many-sided metabolic reactions of the cells and, on the other hand, to their lower cost in comparison with the specific enzymes. Furthermore its use has been limited by the screening or engineering steps necessary to obtain the desired microbial cells; besides the microorganisms own the great advantage to reproduce themselves. Nevertheless since the most of the bioconversions needs aqueous environment, it is difficult to use them when lipophilic molecules are involved. These unsuitable drawbacks are overcome using two-phase or microemulsion systems. Elsewhere we proposed another interesting alternative [2-3]: the emulsion systems, where the disperse phase has the dimensions of micrometers and an higher surface/volume ratio than the biphasic systems, with an enormously increased ability of transfer between the phases and a greater facility of demixing, at the end of the bioreaction, in comparison with the more stable microemulsions. Our studies were focused, mainly, on the *Rhodotorula minuta* var *texensis*' growth analysis in the ternary systems of isooctane/lecithin/water [4]. Some authors used these microorganisms to make biotransformations entrapping the cells in gels [5]. Conversely the isooctane/lecithin/water emulsions allow the cell growth of the same yeast using a more simple medium and might be an interesting alternative for the bioconversions.

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INFLUENCE OF CELL MODEL ELECTRICAL BOUNDARY CONDITIONS ON THE ELECTRICAL CONDUCTIVITY OF A CONCENTRATED COLLOIDAL SUSPENSION

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In the last few years, different models and approximations [1-3] have been developed facing the problem of the electrical conductivity of a concentrated colloidal suspension, according to the cell model concept. Most of them are based on the Kuwabara cell model [4] to allow for the hydrodynamics particle-particle interactions. On the other hand, these models differ when it comes to the electrical considerations at the outer surface of the cell. Many analytical and numerical studies have been developed using mainly two different kinds of electrical boundary conditions. We will call them as Levine-Neale's (L-N) and Shilov-Zharkikh's (S-Z), respectively, according to the authors who first proposed them. In this contribution, we will study the conductivity predictions of different analytical results, and compare them with full numerical calculations according to the theory developed by the authors [2]. In this way, the conductivity will be analyzed as a function of particle volume fraction, zeta potential and reduced particle radius κa (κ^{-1} is the double layer thickness, and a is the radius of the particle). Likewise, we will demonstrate that whatever the electrical boundary conditions may choose (L-N or S-Z), the full numerical solution for the conductivity yields to the same values in both cases. It is worth mentioning that for the electrophoretic mobility, as it has been previously reported, the use of the above-mentioned different boundary conditions yields to very different results, and to decide which one better describes the electrophoresis problem in concentrated suspensions, it is still a subject of controversy. Unlike the electrophoretic mobility result, this unexpected unique electrical conductivity prediction has to be with the definition of the macroscopic electric field in the suspension, the different definitions of the electrophoretic mobility for the concentrated case, and the particular consideration of the perturbations in ionic concentrations at the outer surface of the cell.

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VESICLE-MICELLE TRANSITION IN LIPID-DETERGENT-WATER MIXTURES STUDIED BY ISOTHERMAL TITRATION CALORIMETRY AND FT-IR SPECTROSCOPY

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The temperature-induced solubilization of lipid vesicles describes the vesicle-to-micelle transformation, which can be caused by the incorporation of a surfactant into phospholipid vesicles [1]. This approach may in principle be used for the investigation of the solubilization of membrane proteins by cooling a membrane saturated with surfactant, or the reconstitution of the membrane proteins into lipid vesicles by heating of mixed micelles. Therefore, the prediction of transition temperatures as well as the explanation of transition pathways for these biomembrane model systems is indispensable and demands the construction of the respective phase diagram.

According to the three-stage model of Lichtenberg [2] we describe the construction of the lipid-surfactant-water phase diagram of dimyristoylphosphatidylcholine (DMPC) and sodium dodecyl sulfate (SDS) applying isothermal titration calorimetry (ITC) and Fourier transform infrared spectroscopy (FT-IR). Both methods allow us to investigate the incorporation of SDS in the DMPC bilayer, the destruction of the DMPC vesicles and the formation of mixed DMPC/SDS micelles. The ITC method is applied to understand the endothermic effects observed upon heating and crossing the coexistence region of mixed vesicles and mixed micelles. These effects can be assigned to the endothermic heats of transfer of surfactant and lipid into the lipid vesicles [3]. For the first time we followed the vesicle-micelle transition by FT-IR spectroscopy. Here the change in the wavenumber of the CD₂-stretching and CO-stretching vibrations for DMPC with perdeuterated chains as well as of the CH₂-stretching vibrations for SDS allows the observation of the vesicle-to-micelle transformation.

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PERMEABILITY OF DEXTRAN INTO POLYELECTROLYTE MULTILAYER CAPSULES MEASURED USING PFG-NMR TECHNIQUE

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We present here a study of the diffusion dextran macromolecules in a dispersion of polyelectrolyte multilayer nano-capsules using pulsed field gradient NMR spectroscopy (PFG-NMR). This study is the first of its kind, using polyelectrolyte capsules, and demonstrates the power of the PFG-NMR technique in characterization of these complex systems. A number of publications have dealt with the permeation of macromolecules into hollow capsules. These studies have primarily used fluorescent probes to monitor the permeation into individual capsules. We use here a method that is not dependent on fluorescence, or a selection of individual capsules, but monitors the average diffusion behavior in the entire sample.

The amount of dextran inside the capsules can be measured directly here since the apparent diffusion coefficient of those molecules is orders of magnitude slower than the diffusion rate of free dextrans in solution. By following the time evolution of the encased dextrans we gain insight into the real average permeability of the molecules through the capsule walls. We study three different sizes of dextrans, varying in length from 25 to 2700 monomers. The measurements reveal a striking difference in the fraction of dextran molecules trapped inside the capsules depending on the dextran size.

This study opens up a new field for capsule characterization using PFG-NMR diffusion measurements.

EFFECT OF FOAM BOOSTER ON THE SURFACE PROPERTIES OF AQUEOUS SURFACTANT SOLUTIONS

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Effect of a new type of foam booster, alkanoyl N-methyl ethanolamide (NMEA-8; octanoyl, NMEA-12; dodecanoyl, NMEA-16; hexadecanoyl), on the cmc and surface tension of SDS aqueous solution was investigated. The cmc of SDS solution is considerably reduced upon addition of a small amount of NMEA and the reduction is dependent on the hydrophobic chain length. However, the cmc curves are not smoothly connected from 100%SDS to 100%NMEA. The hydrophilicity of NMEA is not strong and they don't form aqueous micelles, since liquid-liquid phase separation takes place in the NMEA-8 system, NMEA-12 forms a vesicle or lamellar liquid crystal, and NMEA-16 is in a solid state at each saturation concentration. Hence, the saturation concentration of monomeric NMEA is much lower than the cmc of SDS. Judging from dynamic surface tension data, the reduction of surface tension is much faster in the SDS solution than that in the NMEA systems due to the high cmc. Among NMEAs, the reduction rate of surface tension is in order of NMEA-8>NMEA12>NMEA16. If the reduction rate is compared at the concentrations of 0.5 cmc, cmc, and cmc+2mM, the SDS alone decreases surface tension faster than the SDS-NMEA mixture. Moreover, when a mixing fraction NMEA or the hydrocarbon chain length of NMEA increases, the surface tension reduces slowly most probably due to the low cmc.

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MICRO COUNTER-CURRENT FLOW ON A MICROCHIP

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Micro space in microchannels is noted as novel methods of analytical chemistry, synthetic chemistry, etc. A liquid micro space is characterized by large specific liquid/liquid interface area and short diffusion distance. We have demonstrated various applications utilizing these characteristics and the liquid/liquid interface formed in microchannels under the flow condition [1-4]. The more stable liquid/liquid interface in microchannels is necessary for realizing complicated microfluidic chemical systems. Since surface tension is dominant rather than gravity in microfluid, the interface is expected to be more stable by controlling surface tension. In order to control hydrophilic/hydrophobic character of the microchannel walls, a surface modification patterning method has been applied [1]. Namely, the upper and lower walls of the microchannel were modified with hydrophilic and hydrophobic groups, respectively.

We successfully realized for the first time a counter-current flow in microchannels utilizing surface modification. In order to visualize flow of solution, fluorescent microparticle dispersion solution was used. In the micro counter-current flow, reflux of the microparticles near the interface was observed. When the micro counter-current flow was unstable, vortex was observed at the junction of aqueous and organic solution. Since this micro counter-current flow is stable even at slow flow rate as 0.5 mm/s, the system can be applied to solvent extraction with high recovery efficiency. Then, we have demonstrated a counter-current extraction in microchannels by utilizing this micro counter-current flow. This system was applied to the extraction of Co-chelating complex in the aqueous solution by toluene. The number of theoretical plates was observed as 10.

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POLYANILINE AT THE AIR/WATER INTERFACE STUDIED BY INFRARED REFLECTION-ABSORPTION SPECTROSCOPY (IRRAS)

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We used infrared reflection-absorption spectroscopy (IRRAS) to study polyaniline films at the air/water interface. In particular, we wanted to test the possibility to get information on the orientation of the polyaniline molecules from angular dependent IRRAS measurements with polarized light.

The pH dependent IRRAS spectra (pH 2 and pH 6) showed large differences in their baseline behavior. This can be seen for measurements with s- as well as p-polarized light and with different angles of incidence. The IRRAS spectra at pH 6 are similar compared to other film forming substances at the air/water interface, whereas the spectra at pH 2 showed huge deviations of the baselines. The spectra at different angles of incidence with s- or p-polarized light showed a large derivative-like band of the OH stretching vibration between 3000 and 3800 cm^{-1} and large vertical baseline shifts.

Measurements of spin-coated polyaniline films with the Internal Reflection Waveguide Coupling Technique in the near IR region (1550 nm) showed a complex refractive index over a range from transparent (pH 7) to highly absorbing films (pH 2), depending on the pH of the respective film [1].

It was possible for the first time to simulate IRRAS baselines for weakly and highly absorbing films taking into account the ordinary and the extraordinary complex refractive indices of the film over the entire infrared region for different angles of incidence and s- or p-polarized light, respectively. Additionally, the tilt angle of the optical axis of the film and the film thickness could be determined. The assignment of the aromatic vibrational bands of the polyaniline in the IRRAS spectra showed a shift of about 10 cm^{-1} to lower frequencies on the acidic subphase compared to pH 6. All spectral information indicate, that the polyaniline molecules lie almost flat on the water surface.

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INFLUENCE OF ANTI-INFLAMMATORY DRUGS IN MEMBRANE FLUIDITY STUDIED BY FLUORESCENCE ANISOTROPY MEASUREMENTS

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Non-steroidal anti-inflammatory drugs (NSAIDs) are the principal drug treatment for inflammation, pain and fever. As for other drugs, the therapeutic and toxic effects of NSAIDs are strongly influenced by their lipid affinity. In fact, depending on their hydrophilic characteristics, drugs can interact either with the hydrophilic headgroups, the hydrophobic aliphatic tails or both parts of the membrane. These interactions can have several consequences, including modification of membrane fluidity which is also of considerable interest to elucidate about the mechanism of action of the drugs. Moreover, a relation has been suggested between the ability of drugs to change membrane fluidity and their membrane antioxidant action which has, in turn, been associated with possible anticancer and cardioprotective actions. In this study we used fluorescence anisotropy measurements in order to assess the influence of different NSAIDs (nimesulide, tolmetin, acetaminophen, indomethacin, ibuprofen, meloxicam and lornoxicam) in the membrane fluidity. Liposomes, prepared by the thin film hydration method, were used as models of the biological membranes, since they can mimic the chemical and structural anisotropic environment of cell membranes. The anisotropy measurements reveal the rate and extent of rotational diffusion of a fluorophore (probe) during the lifetime of the excited state. Quite subtle changes in rigidity of the matrix which forms the environment of the probe, will produce changes in the rotational motion of the probe and, as a result, will produce changes in the fluorescence anisotropy [1]. To estimate the effects of the NSAIDs upon the internal viscosity of the membrane, the so called *fluidity gradient* was investigated using the n-(9-anthroyloxy) fatty acids where the carboxyl terminal group is located at the interfacial region of the membrane and the fluorescent anthracene group is attached by an ester linkage at different positions along the fatty acid chain. This permits labelling at a graded series of depths in the bilayer so that determination of anisotropy provides a relatively easy means of establishing the depth-dependence of fluidity.

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LANGMUIR MONOLAYERS OF PERFLUOROPOLYETHER ACIDS AT AIR/WATER INTERFACE

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Monolayers of perfluoropolyether carboxylic acids (PFPE-H, $\text{Cl}(\text{C}_3\text{F}_6\text{O})_n\text{CF}_2\text{COOH}$ with 3 to 5 perfluoro-isopropoxy units n) have been studied by the Langmuir and the ionizing electrode methods. Surface pressure (π)–area (A) and surface potential (ΔV)–area (A) isotherms have been measured at 20°C on pure water subphase. Surface potentials have been interpreted in terms of the Helmholtz equation, thus obtaining the vertical component of the dipole moment (μ_{\perp}). The area per molecule of each surfactant, obtained by extrapolating the high-pressure portion of the π - A isotherms to zero pressure, is in the range 75-80 Å², slightly decreasing with surfactant chain length. Also the stability of the monolayer increases, as well as the collapse pressure decreases, with surfactant chain length. Compressibility modulus values in the high-pressure zone range from 20 to 80 mN/m, confirming the more expanded features of the fluorinated surfactants isotherms.

ELECTROCHEMICAL CHARACTERIZATION OF AGGREGATED SYSTEM: ALGINATE SOLUTIONS AND GEL PARTICLES DISPERSION

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Formation of alginate gel microparticles induced by calcium in aqueous electrolyte solution was characterized by chronoamperometry at the dropping mercury electrode, DME [1], circular dichroism, CD [2] and spectrophotometry. The sol-gel transition of alginate solutions in presence of divalent cations leads to a physical hydrogel (non-covalently crosslinked network) which is accompanied by a sharp change in CD spectra and a decreasing solution transparency.

The transformation of alginate free polymers in a solution to microscopic gel particles, induced by the addition of calcium, was followed with DME through distinct differentiation of adsorption/adhesion electrochemical responses. The gel-like particles show a characteristic dip-shaped signal whose amplitude reflects the gel particle size while the dip signal frequency depends on gel particle concentration. In this study we present for the first time the electrical signals of alginate microgel particles that appear owing to their collision at the DME/aqueous electrolyte interface. The appearance of electrochemical signal in alginate gel dispersion is identical to electrochemical response of native microgel particles in seawater [3].

Alginate gels can be used as a model system for the characterisation of natural microparticles observed in the Northern Adriatic seawater and of their role in the aggregation processes and mucilage formation [4].

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PHOTOINDUCED PROCESSES IN BINARY SYSTEMS OF C₆₀ WITH VISIBLE CHROMOPHORES

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Binary systems of fullerenes with visible chromophores, such as metal porphyrins and phthalocyanines, are of current interest for their potential applications in molecular electronic devices, such as photovoltaic cells. In the present work results are presented of optical absorption, photoluminescence excitation and emission spectra of the fullerene C₆₀, and zinc derivatives of porphyrins and a phthalocyanine in solutions and in multiple-layers. In solution, the absorption spectra of the mixtures were identical to the superposition of the absorption of components, suggesting no interaction in the ground state within the dilute concentration range used in this study. Photoluminescence emission spectra of ZnPc solution and mixture of C₆₀ and ZnPc in nonpolar solvent gave tendency of ZnPc aggregation [1]. Films and multilayer structures have been prepared using various methods and have been analyzed with respect to the preparation method. Binary films of the components were prepared by casting alternate layers from appropriate solvents. The film thickness dependence of photoluminescence and absorption, in binary systems of C₆₀ with visible chromophore were studied. A series of the structures were characterized. These exhibited absorption and photoluminescence bands associated with the interaction between C₆₀ and the ZnPc within the bilayer structure that can be analyzed in a context of the symmetry reduction of C₆₀ at the C₆₀/ZnPc interface [1,2]. This will be discussed in terms of energy and electron transfer between C₆₀ and the chromophore. Possible applications in molecular devices will be considered.

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SURFACES TREATED WITH HIGHLY FLUORINATED MOLECULES AND THE ANCHORING OF NEMATIC LIQUID CRYSTALS

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The strong homeotropic anchoring (perpendicular orientation) of nematic liquid crystals (NLCs) at the surface of solid or liquid particles allows the self-alignment of micrometric particles in the NLCs [1]. The NLC orientation at the nematic/substrate interface is fixed by the interaction forces arising partially from the interaction among the LC molecules with those of the substrate, and partially from the interaction among the molecules of the liquid crystal itself. A convenient method to control the NLC orientation induced by the surfaces is to treat them with surfactants or grafted molecules. The substrates treated with hydrogenated aliphatic chains are known to favor perpendicular anchoring principally when the LC and monolayer hydrogenated chains can be interdigitated.

The fluorinated chains present specific surface properties compared with the hydrogenated ones: very low surface tension, strong incompatibility with H-chains... consequently, there is a fundamental difference between the molecular mechanisms responsible for numerous properties as friction, adhesion... [2]. Despite this specific behaviour, to our knowledge, only a few works concerning the influence of the fluorinated chains on the anchoring of NLCs were published. So we are interested in the ability of the fluorinated surface, in the framework of these new colloidal interactions, to promote the alignment of liquid or solid particles.

In a first time, we study the NLC orientation induced by the iron plates or water surface treated with highly fluorinated molecules. We show a high tendency of the fluorinated chains in loose or dense packing to orient the LC perpendicular to the surface. In a second time, for dense or loose packing of fluorinated chains at the surface of particles, we show that the anchoring conditions are strong enough to obtain linear chains of particles using dipolar topological defect properties. These results will be discussed in relation with the surface properties of the *F*-molecules.

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ADSORPTION OF A HYDROPHOBICALLY MODIFIED POLYELECTROLYTE AND ITS UNMODIFIED ANALOGUE IN THE PRESENCE OF SALT

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The adsorption of a pair of polyelectrolytes onto colloidal particles has been investigated by dynamic light scattering. The polyelectrolytes are one hydrophobically modified poly(vinyl alcohol) with a moderate charge density. The other polyelectrolyte is the unmodified analogue. The adsorption onto colloidal particles is measured in terms of thickness of the adsorbed layer at different levels of salt addition. When the polymer concentration is kept constant and the salt concentration increased the thickness of the adsorbed layer decreases and then increases again, for the hydrophobic polyelectrolyte. For the unmodified polyelectrolyte the thickness of the adsorbed layer decreases continuously as the salt concentration is increased. This variation in adsorbed layer thickness is thought to arise from a balance between the electrostatic and hydrophobic interactions. The interplay between electrostatics and hydrophobic interactions are changing as salt is added to the solutions and this is believed to be reflected in the variation in the adsorbed layer thickness.

INFLUENCE OF SUBSTRATE ON CHARGE CARRIERS MOBILITY IN P3HT THIN FILMS

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The properties of thin polymer films are important for many technological applications: protective coatings, optical coatings, displays, storage systems and polyLEDs. Since films will become thinner with the miniaturization of devices, it is of increasing interest to know how bulk polymer properties are modified in thin film geometry. Surface modification of a substrate can be used to control the charge carrier mobility in devices. However, the contribution of any resulting organization in the polymeric layer, or of the thickness of the polymeric film on its physical properties is not well understood. We have observed a difference in charge carrier mobility measured in a field effect transistor device based on a conductive polymer (poly-3 hexylthiophene) depending of the type of substrate used. This can be an indication for a difference in conformation. A higher mobility is reflected in a better order in polymer layer [2].

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GOLD/PALLADIUM AND SILVER/PALLADIUM COLLOIDAL NANOPARTICLES AS NOVEL ACTIVE SUBSTRATES FOR SURFACE ENHANCED RAMAN SCATTERING

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During the last years, an increasing interest in the preparation of colloidal metal nanoparticles has developed, due to their peculiar physical and chemical properties. For “coinage” metal colloids, constituted by Au, Ag or Cu nanoparticles dispersed in aqueous medium, a huge enhancement (up to $10^6 - 10^7$ times) of the Raman signal of the adsorbed molecules is usually observed with the SERS (Surface Enhanced Raman Scattering) technique. Noble metal colloidal substrates are also used in catalytic applications, because of their reactivity, stability and selectivity. The colloidal character ensures large specific areas to a catalyst for chemical and photochemical reactions. Hence, the SERS spectroscopy allows investigating “in situ” on the catalytic processes by irradiating the reagent with the same laser light used in the Raman measurements and detecting the products of reaction, when adsorbed on the colloidal metal nanoparticles. Recently, bimetallic nanoparticles are widely employed in catalytic research, because their properties are different from those of the monometallic nanoparticles [1,2]. In particular, palladium clusters can find a large application in several classes of reactions [3,4]. Here, new metal colloids, constituted by gold or silver nanoparticles coated with palladium clusters, are prepared and their optical properties are studied by UV-visible absorption spectroscopy and Surface Enhanced Raman Scattering. By doping the gold or silver colloids with a small amount of palladium (1 – 5 %), the plasmon resonance bands, due to the excitation of the surface electrons of the gold or silver particles, are strongly damped. The SERS spectra of adsorbed organic ligands are, however, detected, albeit their intensities undergo a significant decrease with respect to those observed in pure metal hydrosols.

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METAL LIGAND COMPLEXATION IN WATER IN OIL MICROEMULSION

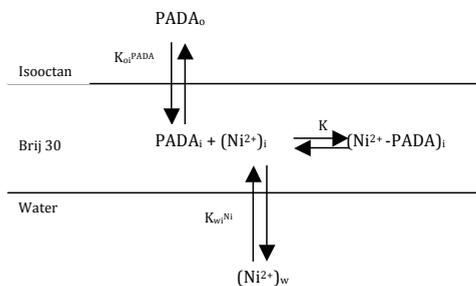
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The complexation constant of Ni^{2+} by pyridine-2-azo-p-dimethylaniline (PADA) in microemulsions of tetraethylene glycol monododecyl ether (Brij 30)/ isooctane / water at 25°C was determined. The macroscopic results show that the complexation constant depends on the composition of the microemulsion. To carry out a quantitative interpretation of the experimental results we propose a complexation scheme which takes into account the microheterogeneous character of the microemulsion.

The PADA is found to be distributed between the continuous medium and the interphase of the latter, whereas the Ni^{2+} are distributed between the aqueous microdroplet and the interphase.



SOLID PHASE TRANSITIONS OF N-ALKYLAMMONIUM CHOLATES

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Novel series of cationic surfactants *n*-alkylammonium cholates (the number of carbon atoms per chain being $n = 10, 12, 14, 16$) was prepared and characterized by elemental and thermogravimetric analysis, IR and NMR spectroscopy. The influence of the alkyl chain length on the structural and thermal properties was investigated by means of polarizing microscopy, differential scanning calorimetry and X-ray diffraction. All compounds exhibited a complex polymorphism and thermotropic mesomorphism from the stable crystalline form to the isotropic phase. On heating two main phase transition were observed for all compounds: solid to liquid crystalline phase transition and isotropization. The liquid crystalline phases exhibited textures characteristic for smectic A phase (S_A). The extent of crystallinity, temperatures of phase transitions, thermodynamic parameters, and basic lamellar thickness varied linearly with the increase of the alkylammonium chain length.

PHASE DIAGRAM OF THE AQUEOUS POLY(PROPYLENE OXIDE)-POLY(ETHYLENE OXIDE)-POLY(PROPYLENE OXIDE) TRIBLOCK COPOLYMER SYSTEM: A STRUCTURAL CHARACTERIZATION

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Structural studies are presented on the Pluronic R[®] copolymer 25R4 formed by a central poly(ethylene) block enclosed between two symmetric poly(propylene oxide) blocks [(PPO)₂₂-(PEO)₃₈-(PPO)₂₂]. Differently from direct Pluronic[®], at low temperature and copolymer concentration, 25R4 is present as a non-aggregated macromolecule in solution. This evidence is confirmed by several techniques such as NMR-PGSE, light scattering, hydrophobic probe solubilization, surface tension. Its gyration radius is about 30 Å as shown by SANS and SAXS. However, if temperature is slightly increased preliminary light scattering data show incipient aggregation.

In the whole composition range the studies have been carried out through small-angle neutron and X-ray scattering, as well as measurements of self-diffusion coefficients, rheology and quadrupolar splitting. A very detailed phase diagram was built. Evidences from SAXS, quadrupolar splitting and reology agree quite well. Complex aggregation has been observed as a function of temperature and concentration. The effect of temperature and composition on molecular aggregation has been investigated. By increasing the temperature of dilute solution, the neutron scattering shows the formation of micelle-like aggregates leading to the formation of a lamellar phase when the temperature is raised up to 60 °C. At 25°C and higher copolymer concentrations (20% -70%) an interconnected network of micelles is formed and the aggregates are arranged on a regular geometric lattice. By increasing temperature the interconnected micellar network rearranges in a lamellar phase. At concentration of about 70 wt % the system is essentially constituted by the lamellar phase. At this concentration the lamellar phase exist in a wide range of temperature (from -5 °C to 90 °C). Interestingly, the distance between the two layers in the lamellar phase is about 80 Å independently from the wt% composition of the system. Above 70% wt, probably a different, structure of the system is taking place. Rheological measurements of complex viscosity, viscous and elastic modulus at the same compositions and temperatures explored by SANS confirm our in progress structural characterization.

PHOTOMECHANICAL EFFECTS IN LANGMUIR MONOLAYERS OF POLYMERS CONTAINING AZOBENZENE GROUPS IN MAIN CHAIN

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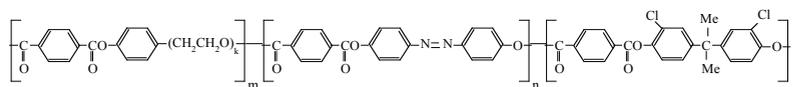
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The mechanical response produced by the *trans-cis* switching of photoirradiated spread monolayers of a series of amphiphilic polyesters containing azobenzene groups in the main chain was studied. These photochromic polymers ($M \approx 15000$) were synthesised by the acceptor-catalytic polycondensation [1] of terephthalic acid chloride with polyethylene glycol (molecular weight varying from 150 to 300), 4,4'-azophenol and 3,3'-dichloro-4,4'-dihydroxydiphenylmethane in dichloroethane in the presence of triethylamine and had the following structure



A considerable decrease in the surface pressure π (of the order of 5 mN/m for the initial surface pressure $\pi \sim 20$ mN/m and the area $A \sim 100$ cm²) was observed after illumination of the monolayers with 365 nm light that testifies for isomerisation processes in the monolayers. Incomplete reversibility has been found for the further illumination of the monolayer with visible light (440 nm). The delivered mechanical work per one macromolecule which could be recuperated due to the photoinduced deformation of the spread monolayer was estimated to be equal to $W \approx 10-100$ kT. The preliminary results on the photoinduced aggregative stability of nanoparticles and their adhesiveness to different solid substrates from aqueous solutions show the principal possibility to create smart polymer layers and colloidal systems with switching photosensitive properties such as wetting behavior, adhesion, permeability of membranes, interaction with biological objects, etc.

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FOAM FILMS STABILIZED BY DODECYL MALTOSE: STABILITY AND GAS PERMEABILITY

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The gas permeability behaviour of sugar based surfactant stabilized strongly depend on the type of the foam black foam film formed which also depends on the thermodynamic parameters: surfactant concentration C_s , electrolyte concentration C_{el} and temperature. For this reason we performed a series of measurements of one of these their parameters, while keeping both the other parameters constant. Long living bubble and very low permeability coefficients are reported for different single gases through such foam films. Nucleation theory of fluctuation formation of holes in amphiphile bilayer is used to fit the C_s dependent permeability which shows that the four vacancies clubs together to form a hole in Dodecyl maltoside stabilized foam films. Lifetime of the foam film films are measured and fitted with the theory and compared with permeability results. C_{el} insensitive gas permeability and non-monotonous changes of gas permeability with temperature are discussed in detail.

Key words: Sugar based surfactant, Foam film, Gas permeability, Life time, holes in bilayer film, amphiphile bilayers, and adsorption density.

ADSORPTION OF ORGANIC COMPONENTS ONTO SURFACTANT MODIFIED MINERAL OXIDES

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When ionic surfactants adsorb from aqueous solutions onto mineral oxide surfaces, the contribution from the hydrophobic bonding interaction among the adsorbed surfactant ions give rise to the formation of adsorbed aggregates termed hemimicelles or admicelles. These adsorbed aggregates contain liquid-like lipophilic regions. The incorporation of organic components into the lipophilic environment of the hemimicelles or admicelles is termed adsolubilization. The process where organic components adsolubilize into adsorbed surfactant aggregates has proven to be an effective separation method. Thus, the removal of organic pollutant components from aqueous solutions by adsolubilization presents a strong method for treatment of water. In this work, one has investigated the adsolubilization of benzyl alcohol (BA) and ethylcinnamate (EC) from water solutions into anionic surfactant aggregates on alumina and into cationic surfactant aggregates on silica. The data show an increasing degree of incorporation of BA and of EC in the adsorbed surfactant aggregates with an increasing concentration of the organic components. Moreover, the mechanism of adsolubilization and the degree of incorporation were strongly dependent on the system investigated. While the addition of BA gives a decrease in the amount of adsorbed anionic surfactant onto alumina, this was not the case for the cationic surfactant CTAB onto silica. The surface concentration of CTAB seems to be more or less independent of the presence of BA or EC. Moreover the degree of incorporation of BA and EC was strikingly higher for the cationic surfactant/silica system than for the anionic surfactant/alumina system. The anionic surfactant/alumina system reach a concentration ratio of $[BA]/[surfactant]$ equal to 0.5 at the alumina surface when the equilibrium concentration of BA is near to the saturation concentration. The corresponding value for the cationic CTAB/silica system is about 20, indicating that the mechanism of co-adsorption is different. The adsorption kinetic was quite similar for the various systems investigated. Approximately 80% of the number of adsorbed surfactants at equilibrium was reached after one hour in a thermostated shaking bath at 25 °C. Equilibrium concentration was reached after approximately 3-4 hours.

Spectroscopic and compositional properties OF LANGMUIR-BLODGETT FILMS OF PHOTOCROMIC BIOPOLYMERS

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Poly (L-glutamic acid) chemically modified with spiropyran units (PSG) exhibits, upon exposure to light, reversible modifications of its structure and conformation; such modifications are accompanied by variations of its physical and chemical properties. These photochromic features make PSG a suitable candidate in the development of highly promising material for devices that can be photomodulated [1].

We preliminary studied the spectroscopic behavior of PSG in solution by means of Electronic Spectroscopies. The screening of the influence of several parameters (polypeptide concentration, solvent composition, temperature) on the photochromic features of PSG solutions revealed that the temperature and the chromophore environment strongly influence the PSG electronic structure.

The examination of bulk PSG was followed by a characterization of the polymer in bidimensional systems. We found that PSG molecules form stable monolayers at the water-air interface and a thermodynamic and spectroscopic characterization of such photochromic systems was performed. Moreover, we transferred, with the Langmuir-Blodgett technique [2], polypeptide monolayers onto solid support in order to obtain ordered nano-films of controlled thickness and composition.

By means of surface techniques as well as electronic and vibrational spectroscopies, we investigated the surface composition and the architecture of the LB structure. The body of experimental data allows us to understand the distribution of the chromophores in the LB film and to clarify their photochromic behavior.

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SPECTROSCOPIC INVESTIGATIONS OF ANTIBIOTIC INTERACTION WITH PHOSPHOLIPID MONOLAYERS AND LANGMUIR BLODGETT FILM

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Rifamycin SV, Rifaximin and Rifampycin are macrocyclic antibiotics with a cromophoric moiety spanned by an aliphatic chain or bridge. These antibiotics are extensively used in veterinary medicine for the treatment of bovine mastitis. The presence of significant amounts of these drugs in animal-derived food is known to be harmful for the human health [1]. Current legislation imposes extremely low limits, i.e. 10^{-7} M, for these drugs in milk [2]; therefore a sensitive and fast determination method is needed to determine such small concentrations of the antibiotics. The long term goal of this work is the realization of a specific sensor for the rifamycin family by means of Langmuir-Blodgett (LB) nano-films of phospholipids. In fact, LB technology has been considered as a convenient tool for designing artificial system with biomembrane architecture and function on the other hand rifamycins are known to penetrate, by passive diffusion, the bacterial membrane interacting with its lipid constituents.

We preliminary studied the surface behaviour of the three antibiotics by means of Surface Tension and Surface Potential measurements at water-air interface. Moreover, investigation of Surface Pressure-Area and Surface Potential-Area isotherms of spreading monolayers of a variety of phospholipids in the presence of the antibiotics in the subphase allowed to select Dipalmitoyl Phosphatidyl Glycerol Sodium Salt (DPPG-Na), as the optimal matrix for LB films preparation. The interaction between the resulting LB films of DPPG-Na and the antibiotic molecules was characterized by UV-Vis spectroscopy, Fluorescence spectroscopy and Cyclic Voltammetry.

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SPECTROSCOPIC CHARACTERIZATION OF A STYRYL DYE IN MONOLAYER AT WATER-AIR INTERFACE

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The investigation of new amphiphilic fluorescent molecules has recently gained attention due to their interesting electric and optical properties.

The application of molecular assembly techniques has proven to be an excellent alternative to casting and evaporation methods in preparation of ultra-thin films for electro-optical and display applications. In particular, the Langmuir-Blodgett (LB) technique is still one of the most feasible processes for inducing order at the monomolecular layer level.

In this work, we focused on the monolayer behavior of a styryl dye, Di-8-ANEPPS, to evaluate its application in the electro-optical field. This molecule exhibits high non-linear properties [1] and it is known to modify its electronic properties with changes in the surrounding medium [2]. The film-forming properties of the molecule, mixed with a cationic surfactant, were evaluated by means of surface pressure – area and surface potential – area isotherms. The quality of the monolayer transfer on solid supports was estimated by contact angle and atomic force microscopy studies. The spectroscopic characteristics (UV-visible absorbance and fluorescence emission) of pure and mixed films at the water-air interface as well as LB films were investigated and compared with the spectroscopic behavior of Di-8-ANEPPS in solution.

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INFLUENCE OF CO-AGGREGATES ON J-AGGREGATE FORMATION IN MONOLAYERS AT THE GAS-WATER INTERFACE

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J-aggregates of cyanine and merocyanine dyes, due their unusual photophysical behaviour[1], are of particular interest as potential components of light harvesting systems. The formation of such aggregates in monolayers at the air-water interface using amphiphilic cyanine dyes is facilitated by co-aggregates (CA) like octadecane[2]. We have investigated the influence of slight chemical modification of the co-aggregate on monolayer organization and the resulting spectroscopic properties of the J-aggregates. The cyanine dye was N-octadecyl-N'-methyl-2,2'-cyanine perchlorate (S120), and the co-aggregates were octadecane (OD), chloro-octadecane (ClOD) and bromo-octadecane (BrOD). The monolayers were characterized by measuring surface pressure-area and surface potential-area isotherms as well as by reflection spectroscopy and Brewster angle microscopy. In the presence of the co-aggregates at molar ratio dye:CA = 1:1, the area per S120 increases (see Figure, left) and the surface potential (not shown) becomes slightly more positive. The area increase is somewhat unexpected, since the co-aggregates could be accommodated on top of the chromophores as has been observed with other additives like octadecanoic acid and methyl octadecanoate. Nevertheless, the co-aggregates do not interfere with the formation of J-aggregates observed immediately after spreading that are characterized by the strong and narrow absorption band (observed here as enhanced reflection ΔR from the monolayer-covered water surface, Figure right) shifted to longer waves with respect to the monomer absorption band. The position of the maximum and the intensity of the band depend on the slightly modified chemical structure of the co-aggregates used here.

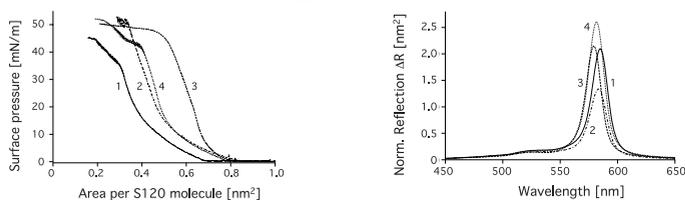


Figure: Surface pressure-area (π -A) isotherms (left) and reflection spectra at $\pi = 15$ mN/m, normalized to same surface density of S120 (right) of monolayers with the cyanine dye S120 on water; (1) pure S120, full line; (2) S20:OD = 1:1, dashed-dotted; (3) S20:ClOD = 1:1, dashed; (4) S20:BrOD = 1:1, dotted; 20°C.

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BIOPHYSICAL STUDIES ON THE PHASE BEHAVIOR OF A PROPANEDIOL BASED NON-PHOSPHOLIPID

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Since the applicability of natural phospholipids is limited due to several factors, such as low stability against oxidation and biodegradation, there is a growing interest in synthetic mimics of phospholipids. We report for the first time on the thermotropic phase behavior of a non-phospholipid based on lactic acid esters of 1,2-propanediol esters with fully saturated hydrocarbon chains. Though this compound is mainly used as an emulsifier in processed foods, the peculiarities of its molecular structure indicate that this non-phospholipid can be used as a building element of lipid self-assembled structures.

In order to fully understand the potential of this non-phospholipid for the formation of lipid mesophases, binary lipid mixtures were assembled by the addition of positively and negatively charged colipids of different geometrical shapes, such as dihexadecyl phosphate, dihexadecyldimethylammonium bromide and didodecyldimethylammonium bromide. Phase diagrams of these mixtures were established using polarized light microscopy, differential scanning calorimetry and small- and wide-angle X-ray diffraction techniques.

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SHEAR AND DILATIONAL VISCOELASTICITY OF MONOLAYERS

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We present a series of experiments on the dynamical properties of surface monolayers made of various different macromolecules: colloids, proteins and polymers. With different techniques we study both the dilational and shear viscoelastic responses of the systems.

At low concentration the shear modulus is negligible compared to dilation, on other words the layers are fluid-like. The monolayers of the polymer PVAc and proteins β -casein and β -lactoglobulin exhibit a semi-dilute regime for which the equilibrium properties are well understood from the theory of polymer scaling. We study the scaling of the complex dilational modulus at the air/water surface with a surface light scattering apparatus (SQELS). Both the elastic response and the dissipation follow power laws of the concentration and we explain this very general behavior in terms of a simple model [1].

Shear rheology measurements are performed on dense monolayers of micron sized colloidal spheres at the oil/water interface and of the protein β -lactoglobulin at the air/water surface with the oscillating thin rod technique [2]. As expected, the shear elastic modulus shows a changing character in the response, from a viscous liquid towards an elastic solid as the concentration is increased, and a change from elastic to viscous as the shear frequency is increased. Surprisingly, above a critical packing fraction, the complex elastic modulus curves measured at different concentrations can be superposed to form a master curve, by rescaling the frequency and the magnitude of the modulus. This provides a powerful tool for the extrapolation of the material response function outside the experimentally accessible frequency range. These results are discussed in relation to recent experiments on bulk systems, and indicate that at high concentration two-dimensional monolayers should be regarded as being close to a soft glass state.

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SURFACE INTERACTIONS AND ION TRANSPORT IN ELECTROLYTE FILLED NANOPORES

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We present a novel method for *in situ* investigation of surface charging and ion transport inside nanopores of titania-silica waveguides by means of the waveguide optical response. We use the Optical Waveguide Lightmode Spectroscopy [1] for kinetic and equilibrium measurements of processes leading to changes in the optical density near the waveguide surface. The main advantage of this technique is the ability to monitor on line various interfaces under non-idealized conditions, at chosen fluid phase compositions and temperatures. The optical sensor response is then used to evaluate the surface excess polarization density [2] and appropriate models are used to relate this thermodynamic quantity to surface properties of the system.

Porous oxide waveguides show a strong optical response when exposed to solutions of simple salts [3] or equally charged surfactants. A magnitude of the optical response for solutions of sodium chloride, sodium hydroxide and sodium dodecyl sulfate is consistent with oxide surface charging due to changes in ionic strength and pH of the solution in contact with the waveguide. For these systems, we found that the main contribution to the excess polarization density comes from the deprotonated silanol sites. However, the observed relaxation times were several orders of magnitude slower than expected from diffusion coefficients of electrolytes in neutral pores. These observations are compared to models of electrolyte diffusion in charged nanopores.

In contrast to solutions of simple salts, the optical response of the waveguide to solutions of tetrapropylammonium salts was qualitatively different, showing a steady increase of the waveguide optical density over several hours at ambient temperature. This allows us to monitor kinetics of surface interactions between tetrapropylammonium cations and silica, which are still poorly understood despite their postulated structure direction role in the synthesis of microporous molecular sieves [4].

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CHARACTERIZATION OF ALMOND SHELL CARBONS BY IMMERSION CALORIMETRY AND PHYSICAL ADSORPTION

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Activated carbons can be obtained from the biomass as raw material. The activation processes produce final materials with different surface properties and, then it is necessary to know if the resulting adsorbents have the appropriate characteristics for the purpose that was sought. The textural properties and the hydrophobic character of the carbon are fundamental parameters to be evaluated for the characterization of any adsorbent and then to foresee its behaviour as adsorbent. Both parameters can be determined by calorimetric evaluation of the solid immersion in different liquids. The modification of the immersion enthalpy in benzene for a set of activated carbons can be related to changes in the porosity and surface area of the original char during activation process [1]. Another method to evaluate the accessible surface area and porosity of a given solid is to study the physical adsorption of nitrogen at 77 K [2]. On the other hand, immersion calorimetry of the carbon in water also allows evaluating quantitatively the hydrophobicity of the solid [3].

The purpose of this work has been to obtain a description of the evolution of the porous texture, surface area and hydrophobicity of a set of prepared almond shell carbons as a function of the activation process from their heat of immersion in different liquids and adsorption of N₂ at 77 K. For this study four activated carbons have been prepared from carbonized almond shell. Two of them were prepared using carbon dioxide and air as activating agents, and the other two with water vapour under different experimental conditions.

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IMPACT OF HYDROPHOBIC AND ELECTROSTATIC INTERACTIONS ON THE INTERFACIAL AND BULK PROPERTIES OF WATER SOLUBLE ALKYLATED CHITOSANS

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Modification of chitosan by covalent binding of hydrophobic and hydrophilic functional groups to its macromolecular backbone, allow to significantly modify the functional properties of this natural cationic polyelectrolyte and thereby to extend the fields of their practical applications [1]. This presentation deals (1) with the synthesis of new chitosan derivatives (cationic polysoaps) obtained by simultaneous N-acylation (C_{12} , DS=2-25mol%) and N-carboxymethylation of the precursor chitosan ($M=300,000$ g/mol, DA=85 %), and (2) the study of bulk and surface properties of their aqueous solutions. Data obtained by different methods will be presented : steady-state shear stress and dynamic ($\omega = 1-10$ Hz) rheological measurements, isothermal titration calorimetry, dynamic light scattering, tensiometry based on the axisymmetric bubble shape analysis under dynamic ($\omega = 3.10^{-3}-10^{-1}$ Hz) and ramp type deformations.

Several physicochemical properties depend on the concurrence between hydrophobic and electrostatic interactions originating from the alkyl chains and ionic groups of polysoaps. This concurrence is controlled by the DS value and by pH and ionic strength I of the aqueous solution, and has been found to affect the conformation and solubility of the macroions, their adsorption kinetics at the air-water interface, their surface activity and viscoelastic properties of their adsorption monolayers, as well as the viscosity, enthalpic properties and foaming capacity of their aqueous solutions.

Particularly, rheological, calorimetric and DLS measurements show that the gradual increase of the hydrophobicity of the macroions (the increase of DS, pH or I) leads to the collapse (the coil-globule transition) of these latter in solution and their aggregation at relatively high bulk concentration. On the other hand, the kinetics of the structure formation in the adsorption layers of polysoaps and their resulting viscoelastic properties (two dimensional storage, G' , and loss, G'' , modules, relaxation times) are highly affected by the conformational state of the macroions in the bulk of solution.

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KINETICS OF THE PHYSICAL-GEL STRUCTURE FORMATION IN ADSORPTION MONOLAYERS OF HYDROPHOBICALLY MODIFIED CATIONIC POLYELECTROLYTES

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Hydrophobic modification of polyelectrolytes (PE) either by covalent alkylation or by electrostatic complex formation with oppositely charged surfactants in the mixed solutions highly increases the surface activity of PE [1]. At the same time, the hydrophobic interactions in the adsorption layers of alkylated polyelectrolytes (polysoaps) and surfactant-polyelectrolyte complexes (SPEC) lead to the formation of the gel-like interfacial films with anomalously high viscoelastic properties [2].

The dilatational rheological properties of adsorption monolayers of cationic polysoaps on the basis of chitosan, on the one hand, and of SPECS formed between chitosan and alkylsulphates, on the other hand, at the air-water interface have been studied by the axisymmetric bubble shape analysis under dynamic ($\omega=3.10^{-3}$ - 10^{-1} Hz) and ramp type deformations as a function of different physico-chemical parameters : concentration of PE, degree of alkylation of polysoaps or composition of SPEC, alkyl chain length, pH and ionic strength of the solutions. The gradual increase with the ageing time (at least up to 10 s) of two-dimensional storage G' and loss G'' elastic modules have been interpreted in terms of the formation of a gel-like structure in the adsorption layers of polysoaps and SPECS. It has been found that the elastic storage module G' increases with increasing alkyl chain content in the case of both polysoaps and SPECS, but unexpectedly, the kinetics of the adsorption and the elasticity of the SPEC adsorption layer are remarkable higher with regard to that of polysoaps. This is explained by higher diffusion mobility of alkyl groups of surfactants inside the SPEC with regard to that of polysoaps allowing the formation of more compact gel-like structure in the adsorption layers. It has been found that the conformation of the polysoap macroion and of SPEC in the bulk of solution has an impact on the kinetics of the structure formation in the adsorption layers.

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TYPES OF PHASE INVERSION OF SILICA PARTICLE-STABILISED EMULSIONS CONTAINING TRIGLYCERIDE OIL

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We report a detailed study of the inversion of triglyceride oil-water emulsions stabilised solely by nanoparticles of silica [1]. The majority of the data refers to pure tricaprylin, although similar findings are observed with the commercial analogue Miglyol 812. The effects of the initial particle location, oil-water ratio, emulsification time and particle concentration have been investigated for emulsions prepared in either a batch or a continuous manner. For particles initially dispersed in water, emulsions invert from simple water-in-oil (w/o) to oil-in-water (o/w) at low water content. For particles originating in oil, inversion occurs from w/o to multiple water-in-oil-in water (w/o/w) emulsions at high water content. Based on measurements of oil-water contact angles on treated glass substrates, the difference between preferred emulsions is argued to be due to the hysteresis in contact angle at the three phase line. For o/w emulsions, increasing the volume fraction of oil at constant particle concentration in water causes an increase in the average drop size and a concomitant decrease in polydispersity; interestingly monodisperse emulsions form in short time at high oil content. The appearance of multiple emulsions is shown to be linked to the coalescence of oil drops with inclusion of the continuous water phase during the process of emulsification. In other cases, fragmentation seems to dominate during emulsion formation.

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CHARACTERISATION OF OIL SOLUBLE AND WATER SOLUBLE NON-IONIC SURFACTANTS BY SURFACE VISCOELASTICITY MEASUREMENTS FOR EMULSION STABILITY STUDIES

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The surface rheological properties are very important for determining the emulsion stability-destabilisation conditions. Nevertheless, so far, a lack of experimental investigations in this field exists for liquid-liquid interfaces. This is due mainly to the intrinsic difficulties of this kind of systems to be modelled from the point of view of the adsorption, the mass transfer and the mechanical properties [1], which makes difficult the data interpretation.

In this work an oscillating drop technique [2] is used for measuring the surface viscoelasticity as a function of the frequency both for liquid-air and liquid-liquid systems, in a range of frequencies from 0.1 to 100 Hz. The same systems are studied with a drop shape technique [3], in a lower range of frequency.

The surfactants used are polyoxyethylene glycol ethers, C_nEO_m , with different ratio between the length of the hydrophobic and hydrophilic chains in order to have different partitioning properties in the water/alkanes systems.

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SURFACE DILATIONAL RHEOLOGY OF SOLUBLE MONOLAYERS IN THE PRESENCE OF CHEMICAL REACTIONS

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Developments of the classical approach for the surface dilation elasticity have been recently presented, to connect the dynamic surface elasticity to processes occurring within the monolayer [1] [2]. In this work the theoretical approach is extended to accounts for surface reversible chemical reactions involving surface active species in a soluble monolayer. A proper thermodynamic and kinetic model has been set up in order to link the physical parameters of the species involved in the process to the surface elasticity. According to the adopted rheological approach, the model yields expressions for the surface dilational elasticity ($\delta\gamma/\delta\ln A$) as a function of the frequency of applied perturbations. This provides the possibility to access the kinetic rates of the surface reaction by the experimental investigation of the surface rheology. Eventually, applications of the theory to specific reactions are discussed.

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COMPARISON OF DROP AND BUBBLE EXPERIMENTS IN STUDIES OF THE ADSORPTION BEHAVIOUR OF SURFACTANTS

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There are no simple experimental methods to determine the adsorbed amount of surfactants at fluid interfaces. In literature, essentially the radiotracer technique was successfully applied. More recently, neutron reflection and the improved ellipsometry proved to be suitable for direct adsorption measurements. All these methods require quite large experimental efforts, so that there is need for a much simpler methodology. The idea of the presented methodology here is based on findings obtained with experiments on drops and bubbles [1]. For sufficiently high surface active surfactants, the loss of molecules adsorbing at the surface of a single drop is remarkable. When compared with the adsorption at the surface of a bubble, immersed into a solution of respective volume, the difference gives direct access to the adsorbed amount.

An example is presented how the given methodology was applied to aqueous solutions of some model surfactants. The drop and bubble shape tensiometer used (SINTERFACE, Germany) allowed to keep the interfacial area constant, which is an important prerequisite of the experiment [2]. The agreement between the adsorbed amounts determined by the new method and on the classical way via a surface tension isotherm using a respective thermodynamic model is very good.

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CRITICAL ROLE OF THE CARBON SURFACE FUNCTIONAL GROUPS ON ADSORBED ENZYME IN BIOSENSORS

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The effective combination of biomaterials especially enzymes and electroconductive materials in analytical devices could provide the basis for direct electrical detection of a wide range analytes with great sensitivity and specificity. Carbon black have been demonstrated to be very useful as electrode material in biosensors due to this well known advantages such as low background current, wide potential window, possibilities of fast and easy preparation, modification and low cost. Data on the electron transfer of redox proteins and enzymes at electrodes indicate that efficiency of this process depends on the nature of proteins as well as on the electrode material.

In our work carbon black was synthesized from carbon monoxide precursor on a Fe catalyst with the aim to create promising electrode material for successful electrochemical reactions of adsorbed enzymes. Having an objective to obtain batches with different properties, the carbon black was modified; the modification protocol consisted of 11 technological operations, which can be divided into 3 blocks:

- a) delamination of graphite structure carried out using naphtalene, H_3BO_3 , KOH, H_3PO_4 and H_2SO_4 [1].
- b) tailoring of functional groups carried out in the presence of HNO_3 , $Br_2 + Fe$, N_2H_4 HCl and H_2O_2 [2].
- c) modification of particle shape carried out by melting with S and Zn [3].

Obtained batches of carbon black were analyzed for the surface functional groups by Boehm titration [4]. The particle size distribution was determined by sedimentation analysis. The correlation analysis between the carbon black parameters (amount and assortment of functional groups, particle size distribution and shape) and metrological results of enzyme biosensors made on the base of those carbons was made.

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ORDER AND DYNAMICS OF SURFACTANTS C₁₂E₅ IN MESOPOROUS SILICAS: A ²H NMR STUDY

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The aggregation properties of nonionic surfactants in mesoporous materials are investigated by ²H NMR. Selectively deuterated C₁₂E₅ was adsorbed from aqueous solution onto various porous silica surfaces (CPG, SBA15 etc). The pore structure of the silica varied in size from 1.88 to 35 nm for a selection of pore shapes (bicontinuous, hexagonal, ink-bottle-like etc). The surface aggregate spectra show an isotropically averaged Lorentzian line shape (or hyper-Lorentzian shape for pore size less than 5 nm), with R₂ relaxation rates of several kHz. The structural arrangement is discussed by studying relative order parameter profiles S_{rel} of the C-2H bond in dependence on the position along the chain. Typical values of S_{rel} were found to be around 1.05, suggesting that the structure of the surface aggregates is a bilayer. The dependence of S_{rel} and R₂ on both pore size and pore geometry are discussed in terms of different aggregate geometries. A most interesting discovery is that the linearly increasing relationship between S_{rel} and the distance of the 2H label position from the head group breaks down at a pore size around 5 nm (about the size of the C₁₂E₅ molecule). These observations suggest that a phase change is induced in the surface aggregate, induced by the confined geometry.

EVIDENCE OF AGGREGATES STRUCTURAL CHANGES DURING THE SOLUBILIZATION PROCESS OF TRIBUTYLPHOSPHATE IN AQUEOUS SOLUTIONS OF AMPHIPHILIC TRIBLOCK COPOLYMERS

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Amphiphilic triblock copolymers such as Pluronics® (polyethyleneoxide – polypropyleneoxide – polyethyleneoxide, $(\text{PEO})_n-(\text{PPO})_m-(\text{PEO})_n$) have been widely used so as to solubilize hydrophobic molecules in their supramolecular aggregates. Our work focuses on the solubilization of TriButylPhosphate (TBP), an organic solvent widely present in nuclear industry, in aqueous solutions of a Pluronic referred to as PE6400 ($(\text{PEO})_{13}-(\text{PPO})_{30}-(\text{PEO})_{13}$). The solubilization capacity of this typical non-ionic polymeric surfactant highly depends on the temperature. Actually, the increase of temperature leads to the PEO deshydration which favours the oil solubilization capacity due to the increase of the hydrophobic character in the micellar corona. In this study two significant temperatures are evidenced, the Solubilization Minimum Temperature (SMT) and the Cloud Point temperature (CP). The former corresponds to the lowest temperature allowing TBP solubilization in the aggregates. The well known later depends on the copolymer structure, and, more interesting, is directly related to the TBP concentration in the medium. The dependence of CP with TBP concentration is explained by both the variation of the aggregates curvature and the deshydration of the PEO chains following solubilization of TBP in the aggregates. A [Temperature - TBP concentration] diagram allows to delimit monophasic and diphasic domains. Turbidity, dynamic light scattering, viscosimetric, and ¹H RMN data suggest the occurrence of different structures of aggregates depending on the TBP concentration and inform on the location of the TBP molecules inside the aggregates. During the addition of TBP, the solubilized aggregates turn from spherical swelled micelles of amphiphile into nanophase of TBP (emulsion) stabilized by the copolymer, with an intermediate range of TBP concentration exhibiting more complex gel-like or precipitated structures.

INVESTIGATIONS OF PHASE TRANSITIONS IN THE ADSORBED MONOLAYERS OF AQUEOUS NONIONIC SURFACTANT SYSTEMS

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At the air/solution interface, the surface tension data for a single aqueous nonionic surfactant decrease smoothly with increasing bulk concentration up to the critical micelle concentration or the solubility limit. For several different types of surfactants, a clear break or transition region was detected in the surface tension - concentration curve, hinting to the possibility of a phase transition within the adsorbed layer. Such a transition cannot be fully elucidated from thermodynamic considerations alone; an analysis of the dynamic surface tension behavior is also required. Most analyses to date were based on the Frumkin (or similar) adsorption isotherm and the corresponding dynamic models for the surface tension evolution. This type of analysis does not allow for the possibility of more than a single stable monolayer phase to exist under equilibrium conditions. We propose a new type of analysis, an extension of the well-established nucleation and growth models used in electrochemistry for the characterization of phase transitions at the mercury/solution interface. In this type of analysis, the presence of dynamically stabilized islands is considered. Such a model is shown to well-describe the dynamic tension behavior of surface chemically pure monolayers of *n*-dodecanoic acid and *n*-dodecyl- β -D-glucopyranoside.

EFFECT OF STIRRING INTENSITY ON THE DYNAMIC CATASTROPHIC INVERSION LOCUS, FROM NORMAL TO ABNORMAL MORPHOLOGY

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Dynamic is the process in which an emulsion swaps its internal and external phases with a morphological change from oil-in-water (o\w) to water-in-oil (w\o) morphology or vice versa[1]. The stirring intensity has a complex effect on the dynamic catastrophic inversion of AN emulsion[2-4]. At low both and high stirring energy input, the emulsion inversion takes place early, after a low amount of internal phase has been added.

At some intermediate stirring energy the inversion appears to be delayed. This phenomenon has been reported before for the direction of change from abnormal to normal morphology[5]. In the present study a similar pattern is exhibited from normal morphology to abnormal one.

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SURFACE AGGREGATION OF CATIONIC SURFACTANTS FROM AQUEOUS SOLUTION ONTO ORDERED MESOPOROUS SILICAS AND ITS APPLICATION IN ADSOLUBILISATION

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The formation of surface-bound aggregates upon adsorption of cationic surfactants from dilute solution onto powdered silicas has been investigated in the laboratory for many years [1]. Very interesting results were obtained for periodic aluminosilicate materials with a hexagonal pore arrangement, issued from a surfactant-assisted sol-gel synthesis [2]. Since the pore size of such model adsorbents is comparable with that of a surfactant micelle, the question has arisen as to whether any surfactant aggregates can be formed on such substrates.

The influence of various factors on the adsorption mechanism was evidenced by measuring adsorption isotherms of the surface-active cations, differential molar enthalpies of displacement, changes in the supernatant composition upon adsorption on mesoporous aluminosilicates prepared with different structure-directing agents for a series of monomeric and dimeric cationics. The evolution of the differential enthalpy effect with surfactant adsorption was compared with the molar enthalpy of micelle formation in 'free' solution. Surfactant adsorption onto porous materials involved both the external surface and the pore walls. The ultimate compactness of the adsorbed phase and the energetics of its formation appeared to depend both on the extent of pore space available to the adsorbate and on the molecular structure of the surfactant.

Some interfacial aggregates may provide an environment for adsolubilisation of low molecular weight organic solutes from the aqueous streams [3]. Therefore, the uptake of phenol, butanol and heptanol molecules in surfactant-solid systems was quantified. The transfer of the solubilise from the aqueous phase to the interfacial aggregates was shown to be significantly exothermic, depending on the nature of the additive-surfactant-solid system. Compared to their monomeric homologues, dimeric cationics were much more efficient as adsolubilisation host systems.

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WATER-DISPERSIBLE POLYESTER RESINS CONTAINING HYDROPHILIC SULFONATE GROUPS

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Nowadays one of the most important problems related to the production of unsaturated polyester resins is an emission of organic solvents during their application. Those solvents are often very harmful for employee's health and for the environment. One of solutions of this problem is the production of water-soluble or water-dispersible polymers and resins. To obtain self-emulsifying polyester resins a suitable amount of hydrophilic groups should be introduced to polyester structure. There are many problems related to the incorporation of hydrophilic group into the polyester structure, their modification and neutralization (for example: carboxyl groups are neutralized by harmful volatile amines). The main problem is how to transform the solvent soluble unsaturated polyester resins into a resin able to form stable water dispersion. One of the concepts of the production of waterborne unsaturated polyester resins is the incorporation of highly hydrophilic sulfonate groups ($-\text{SO}_3\text{Na}$) into polyester chains. We have developed two methods of production of water-soluble polyester resins containing sulfonate groups. First one comprises the incorporation of the monomers carrying sulfonate groups into the polymer structure, the second one the synthesis of polyester having unsaturated bonds and then their sulfonation using sodium bisulfite. As far as concerns the first motif we developed methods of synthesis of various simple sulfonate derivatives containing functional groups such as vicinal dihydroxy, epoxy and allyl ones. These monomers were obtained from epichlorohydrin in the reaction with NaHSO_3 . The resulting chlorohydrin derivative, depending on a base used, gives sodium salt of 2,3-dihydroxypropane-1-sulfonic acid, 2,3-epoxypropane-1-sulfonic acid and 3-hydroxy-1-propene-1-sulfonic acid, respectively. These reactive hydrophilic sulfonate monomers were consequently incorporated into classical or modified unsaturated polyester resins structure in a relatively small amount (2-5%) in comparison to carboxylate based monomers. Waterborne polyesters with sulfonate groups should be very useful for a production of many type of polymeric emulsions, which can be applied mainly in the paint industry. All favourable ecological attribute mentioned above and refer to sulfonate monomers are transferred to the final emulsion product.

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Aggregation dynamics of dimer acid betaine solutions investigated by light scattering, surface tension, Electron microscopy, and rheology

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Dimeric (gemini) surfactants are designed out of two single surfactant molecules whose head or tail groups are connected by a spacer-chain. The structure of such a molecule is generally denoted by m - s - m where m represents the chaingroup (C_mH_{m+1}) and s the spacer length. These surfactants are now subject of increasing interest in academic and industrial research because they display some properties superior to those of conventional monomeric surfactants. Due to the structure of the supramolecular aggregates, their critical micelle concentration (cmc) is very low. Better wetting properties and greater efficiency in lowering of the surface tension is observed, and a comparably high viscosity of aqueous solutions is obtained [1, 2]. Rheological investigations of dimer acid betaine solutions (DAB) suggest a complex self-aggregation above the CMC in comparison to ionic surfactant forming a network of flexible or semi-flexible worm- or rod-like micelles [3, 4]. In the present work, the transient evolution of the aggregation was investigated by light scattering techniques, surface tension measurements, electron microscopy and rheology. It can be shown that DAB undergoes a transition from micelles ($CMC \approx 4 \cdot 10^{-4}$ mM/L) to vesicles above a concentration of 0.1 mM/L within the period of several hours. Above the mention concentration, aggregation continues and networks are built within weeks or months. The influence of such transient formation is seen in surface tension and rheological properties.

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INVESTIGATION OF THE SURFACE PROPERTIES OF SALT-TYPE MINERALS USING 12-s-12 GEMINI SURFACTANTS AS MOLECULAR PROBES

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The chemical composition of mineral surface is a significant parameter to improve the rheological properties and the stability (dispersion, flocculation...) of the solid-liquid dispersions in relation to their technological applications. In order to select the suitable additives (surfactant or polymer) used to adjust the suspension formulation, the identification and the characterization of active sites on the mineral surface remain a crucial preoccupation. According to a previous adsorption study of cationic dimeric surfactants on silica [1], it appears that these surfactants can be used as molecular rulers to probe the charged site distribution on silica surfaces. Indeed, the surfactant bindings to the surface involves one head groups for surfactants with a short spacer (12-2-12) and the two head groups as the spacer is enough long (12-10-12 surfactant) to interact with two charged sites.

The aim of this work is to give insight on the surface properties of calcium carbonate mineral using 12-s-12 gemini surfactants as molecular probes; “s” is the carbon number of polymethylene spacer. For sparingly soluble minerals, such as calcium carbonate, the mineral-water interface is strongly influenced by the surrounding dispersion media and particularly by the pH and the amount of lattice ions released from the surface. In fact, these lattice ions are known to affect the adsorption of ionic surfactants and consequently the efficiency of additives used as dispersant or stabilizing agent. In this way, the complex role of the solution chemistry of sparingly soluble minerals on the adsorption of surfactant has been investigated. The results were obtained from a microcalorimetric study completed by different physico-chemical measurements such as the adsorption isotherms, the evolution of the electrical conductivity of the supernatant and the amount determination of the ionic species during the adsorption process. The adsorption of the gemini surfactant on calcium carbonate occurs in two successive steps, an ion-exchange step following by a surface aggregation process. The number of adsorption sites and their distribution at the surface of calcium carbonate mineral have been estimated from the obtained results.

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Conformational changes of Proteins at the air/water interface

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Conformational changes at the secondary folding level of proteins adsorbed or spread at the air/water interface were determined from absorption spectra obtained with InfraRed Reflection Absorption Spectroscopy (IRRAS). In addition, information on the adsorbed amounts was obtained by means of spectral simulation. Adsorption behaviour and the conformational changes that may take place on adsorption were studied for β -casein, β -lactoglobulin and soy glycinin. The adsorbed amounts were determined as a function of time and the values found for the three proteins agree well with ellipsometry data. Only limited conformational changes in terms of secondary structure were found. Upon adsorption at the air/water interface $\sim 10\%$ loss of β -sheet structure was observed for β -lactoglobulin whereas the amount of unordered structure increased. For glycinin (pH 3) aggregation at the interface was observed by the appearance of an adsorption band at 1630 cm^{-1} , which indicates the formation of intermolecular anti-parallel β -sheet structures. This agrees with the fast formation of a strong protein network as determined by interfacial shear experiments. For β -casein and glycinin at pH 6.7 no conformational changes were observed. For glycinin at pH 6.7 interfacial network formation proceeds much slower; this may be related among others to the fact that it does not form intermolecular β -sheets at that pH. However, although of importance, conformational changes on adsorption including the formation of intermolecular β -sheets turned out not to be the most important factor determining the strength of an adsorbed protein layer. Likely 'hardness' of the adsorbed protein molecules is of greater importance. By comparing adsorbed and spread protein layers it was found that spreading of protein at an air/water interface leads to a somewhat different conformational state of the protein than when the protein is adsorbed from solution for similar adsorbed amounts. Upon compression of a spread layer changes in the conformational state could be detected for β -lactoglobulin and glycinin (pH 3).

PHASE TRANSITIONS IN THE CELLULOSE ACETATE SULFATE AQUEOUS SOLUTIONS

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We have developed new homogeneous way for the synthesis of mixed cellulose ester – cellulose acetate sulfate (CAS). Stable lithium Li, sodium Na, potassium K and calcium Ca salt forms of CAS have been obtained. Cellulose acetate sulfate is characterized by an extremely high solubility in water (up to 70 wt.% for the lithium form). There are liquid crystalline (LC) structures in its solutions at the definite polymer concentration range.

By means of polarizing microscopy technique the spontaneous formation of structural heterogeneities of colloidal size (10 -100 μm) as individual ring spherulites has been identified in CAS concentrated solutions. The spherulites formed are characterized by a well-pronounced annular structure cut by a Maltese cross. As for Li-, Na-, and Ca- forms of CAS these spherulites are aggregated into spherulite ribbons and more complex structural entities during the polymer concentration increases. It was shown that K-CAS is not able to form LC structures in aqueous solution. Rheological curves typical of lyotropic liquid crystalline systems were recorded. The corresponding concentration and temperature dependencies of shear viscosity prove the existence of liquid crystalline state in aqueous solutions of cellulose acetate sulfate [1].

The critical concentration corresponding to the transition of the sodium salt of cellulose acetate sulfate to liquid crystalline state at 20-50°C has been estimated at 52-52,5 wt.%. It has been found that concentration corresponding to the appearance of ordered structures in the solution rises with the increase of compensating ion radius.

In the temperature range between 18 – 26°C CAS solutions (C=42+58 wt.%) show the endotherms as it evident by the differential scanning calorimetry data. The T^* temperature does not depend on the concentration. The annealing of CAS solution (C=58wt.%) in the liquid crystalline state temperature range extends the first-order phase transition enthalpy (ΔH^*) 10 times. This fact suggests the increase of liquid crystallinity after annealing.

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POSTERS

7. Biocolloids & Biomaterials:

*Chemistry and Physics of biological colloids, design of biocolloids,
biomineralisation*

THE EFFECT OF TEMPERATURE ON THE FLUIDITY OF *E.coli* MEMBRANES AS DETERMINED BY ROTATIONAL DEPOLARIZATION OF FLUORESCENCE

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Many surfactants and biocides used in disinfectant formulations are believed to act upon the bacterial cytoplasmic membrane [1]. The process of disinfection is believed to involve diffusion of the active molecules through the outer layers of the cell and subsequent insertion into the lipid phase of the membrane. Insertion of the surfactant into the lipid phase is believed to result in the solubilisation of the membrane and an increase in its fluidity. This may lead to a conformational change in the lipid phase, perhaps through the melting of a gel phase. This change results in the rapid leakage of cellular contents followed by cell death [2]. Measurement of the fluidity of intact bacterial membranes is therefore relevant to studies of the mechanism of disinfection. The relative fluidity *in situ* has been determined by measuring the rotational depolarization of fluorescence of a probe in the membrane. In this work, the fluorescent probe DPH was incorporated into living bacteria cultured at different temperatures in order to study the effects on the cytoplasmic membrane [3]. The degree of depolarization of fluorescence by rotation was then determined using a novel polarimeter that uses a CCD camera to image a number of samples simultaneously. The fluorescence depolarization appears to be directly related to the fluidity of the membrane. The temperature of the samples can be varied during the experiment using a peltier pump. Results show that for *E.coli* the fluorescence depolarization strongly decreases with increasing temperature of the membranes and continues to decrease until well above the culture temperature. Temperature cycling measurements show hysteresis in the fluidity versus temperature curves suggesting the formation of separated gel lipid domains at low temperature. Similar results are observed for *Staph.aureus*. The fluidity at the culture temperature may indicate the coexistence of gel and lamellar phases under physiological conditions.

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DEVELOPMENT OF TARGETABLE IRON OXIDE BIOCOLLOIDS FOR MEDICAL APPLICATIONS

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Magnetoliposomes consist of subdomain magnetite cores which are camouflaged by a phospholipid bilayer. Upon incorporating some lipid molecules that are derivatized with poly(ethylene glycol) into the coating, so-called Stealth magnetoliposomes are generated, which, after intravenous administration, demonstrate an increased blood circulation time.

In this work, we further upgraded these structures for targeting purposes. This was done by using phospholipids which are covalently linked to a poly(ethylene glycol) chain which, in turn, possesses a so-called universal binder (e.g. a biotin residue) at its free terminus. In practice, phosphatidylethanolamine was quantitatively derivatized with α -biotinylamido- ω -*N*-succinimidinocarbonyl-poly(ethylene glycol) and the resulting conjugate was successfully incorporated in the magnetoliposome coat. Streptavidin-dinylated alkaline phosphatase, used as a model protein, strongly interacted with the resulting colloids.

This finding opens promising perspectives in various biomedical fields, dealing with colloid targeting. For instance, after binding of (strept)avidinylated monoclonal antibodies or specific ligands these biocolloids can be used for magnetic resonance imaging of malignant tissues, or, the presence of the magnetizable iron oxide core can be exploited to induce hyperthermia in the tissue envisaged.

THE INTERACTION BETWEEN A FLEXIBLE PROTEIN - PRP1 - AND A CHARGED SURFACE

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Due to the inherent surface activity of proteins, adsorption usually takes place at almost any type of surface in contact with a biological fluid. The process proceeds quickly and a monolayer is usually formed within seconds or minutes. It is well known that this initial layering monitors subsequent biocolloid adhesion and biofilm growth; hence the formation of the initial protein layer is an important clue in order to understand and control biofilm growth.

Oral biofilms, usually referred to as dental plaque, constitute a major research field due to the importance in dentistry in particular for the understanding of the development of plaque and related diseases, such as caries or periodontal disease. We have systematically over the last years studied key proteins in saliva and their role in the formation of the initial protein layer on surfaces in contact with saliva. One important protein group in this context is the so-called proline rich proteins (PRPs). These are known to be responsible for maintaining the calcium balance in saliva and hence to affect e.g. remineralisation of the enamel. In addition, they have also been reported to be involved in mediating specific interactions with oral microorganisms thereby modulating plaque growth.

As a first attempt to model protein adsorption to surfaces, we are using the primitive model and Monte Carlo simulation technique. The protein is modelled as beads on a necklace where each bead directly corresponds to an amino acid. Hence, the model will be very specific regarding the nature of the bead i.e., charged, neutral, or hydrophobic. A lot of work has so far been done regarding polyelectrolyte or polyampholyte adsorption to surfaces, but this project is novel in the sense, that we are not modelling “general” molecules; instead we will try to mimic a real protein and adjust/modify the model to experimental results.

We will show some preliminary results of protein adsorption to surfaces. The effect of the surface charge density, counterion valency, and the number of chains has been investigated.

INFLUENCE OF NANOPARTICLES ON THE SECONDARY STRUCTURE OF PEPTIDES

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Neurodegenerative disorders such as Alzheimer's disease and prion diseases are characterized by aberrant protein folding and aggregation, that results in the accumulation of protein fibrils. Although the mechanism of fibril formation is not fully understood, the protein conformation seems to play an important role in the pathogenic process of these disorders. In general, the monomeric native protein is in α -helical or unordered structures, whereas the protein fibrils are rich in β -sheets. The stabilization of the native protein structure or the inhibition and reversion of conformational transitions are therefore possible approaches for the treatment of such disorders.

In this work, we study the influence of negatively charged nanoparticles on two different peptides, the fusogenic peptide B18 and the amyloid β -peptide (1-40). The fusogenic peptide B18 is a distinct amphiphilic sequence of 18 amino acids of the sea urchin protein bindin. The peptide per se forms β -sheet amyloid fibrils at pH above 7, both in aqueous buffer and in lipid membranes. Additionally, it has the ability to aggregate and fuse vesicles [1]. Fusogenic properties have been identified in peptides involved in neurodegenerative disorders [2]. Therefore, B18 is a simpler model peptide to study conformational changes that lead to aggregation of proteins. Amyloid beta-peptide (1-40) is the major component of the neuritic plaques observed in Alzheimer's disease. The peptide, consisting of 40 amino acids, has high propensity for aggregation and form amyloid fibrils. The nanoparticles consist of a compact core, which is formed by hydrophobic surfactant chains and a hydrophilic shell like a typical surfactant micelle, but in this case the low molecular counter ions are replaced by the polyampholyte [3]. The influence of fluorinated and non-fluorinated nanoparticles on the peptides structure will be discussed.

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HYDROPHOBIC BEHAVIOUR OF THREE STRAINS OF STAPHYLOCOCCUS EPIDERMIDIS AT DIFFERENT TEMPERATURES

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Bacterial adhesion to biomedical devices is a subject of great interest due to the increasing number of clinical practices which require the use of them. One of the most important bacteria involved in such processes is *Staphylococcus epidermidis* due to the ability of some strains to segregate a polymeric substance known as "slime" which becomes an authentic adhesive between cells [1].

There is a clear relationship between the "slime" production and the biofilm formation. This process starts with an initial phase, inespecific adhesion, between the bacterium and the substratum, where the physico-chemical parameters of both surfaces play an important role. In this context, the cellular surface hydrophobicity seems to be a relevant factor in many adhesion processes.

The methods generally employed to measure such a hydrophobicity are MATH (Microbial Adhesion to Hydrocarbons) as proposed originally by Rosenberg et al. [2] and with the later modifications of Lichtenberg et al. [3] (kinetic MATH) and Bellon-Fontaine et al. [4] (MATS, Microbial Adhesion to Solvents) and also contact angles on lawns of filtered bacteria. This property is usually determined at room temperature, far away from that inside the human body.

Therefore, the aim of this work is to compare the hydrophobicity, measured by the former methods, of three strains of *S. epidermidis* with different slime production, at 22°C and 37°C. We found that the measurement temperature has a great influence on the results obtained, changing the initial adhesion rates to p-xylene, n-hexadecano and chloroform. These variations are also related to the different slime production of the strains. Also, the changes in contact angles and surface tensions of bacteria are in general agreement with the above results.

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Contact angle characterization of biomaterials under in vitro conditions

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Nowadays there is a sharp increase of the usage of biomaterials for prosthesis, implants, catheters and a large number of devices which are in contact with body fluids. Despite the important advances in their design to avoid the unwanted biofilm formation by bacteria or yeasts, causing infection and then the need to removal of the device, the risk of such processes increases with the resistance of microorganisms to antimicrobial agents [1].

Microorganism adhesion to the biomaterials surface can be modelled by the interfacial free energy between them [2-3]. However, once a device is inserted inside the patient body, an adsorbed layer from the components of the body fluid is formed on the surface. On this basis, a more accurate evaluation of the interfacial free energy between microorganisms and biomaterial surface needs the characterization of the biomaterial surface in such a conditions that reproduce as close as possible the *in vivo* state.

Composition of body fluids is very complex, besides the inorganic salts, there is a mixture of different proteins and molecules emerging, in some cases, from metabolic processes. Also, the risk of infections gives place to the presence of antimicrobial agents solved in the fluids.

In this work we are focused on the changes introduced in the surface free energy of some biomaterials (polymeric and metallic) after the contact with an aqueous solution of an antibiotic.

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MISCIBILITY OF CHOLESTEROL IN DIPALMITOYL PHOSPHATIDYLETHANOLAMINE MONOLAYERS

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Monolayers composed of cholesterol and phospholipids constitute the molecular model system commonly found in eukaryotic cell membranes. There are the structural similarities between monolayers and bilayers and it is assumed that cholesterol interacts with membrane phospholipids in monolayers in the same way as in the natural membranes. The nature of the interactions between cholesterol and phospholipid as well as their bidimensional miscibility mainly depend on the phospholipid polar head group structure and the hydrocarbon chain composition.

In the present work we have studied the influence of cholesterol (CHOL) on structure and properties of dipalmitoylphosphatidylethanolamine (DPPE) model membranes. The interactions between lipids have been examined at the air/salt solution interface using the monolayer technique. Surface pressure/area isotherms of pure and mixed monolayers were recorded at 20, 25 and 30°C. The two-dimensional miscibility of cholesterol in phospholipid membranes was discussed in light of the nonideal behaviour of mixed monolayers. For the analysed binary mixtures both components show a mutual miscibility under all the employed conditions, confirmed by the negative deviations from additivity of the areas in the mixed monolayers and the negative values of excess free energy of mixing. Moreover, these results indicate that the attractive intermolecular forces were dominant in the mixed monolayers. Based on the thermodynamic of mixing between cholesterol and phospholipid we have characterized the stability of the monolayers at the air/liquid interface. The DPPE/CHOL mixtures form more stable monolayers than that of pure component. The role of cholesterol in phospholipid monolayers was considered in the context of the biological applications.

DETERMINATION OF CELLULOSE SURFACE ENERGY BY IMBIBITION EXPERIMENTS IN RELATION TO BACTERIAL ADHESION

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Control of microbial contamination in paper and board industry is limited by bacterial adhesion to cellulose fibres. The adhesion process results from interactions between the cell surface, the liquid and the fibres. In this context, we determined the cellulose surface energy to better understand these interactions in the aim to control bacterial adhesion and slime formation.

As contact angles cannot be directly measured on cellulose fibers, experiments involving liquid imbibition into cellulose pulp sheets were performed. The variation of mass observed when a piece of cellulose pulp is brought into contact with the liquid was recorded with a tensiometer. The mass measured accounts for the mass of the liquid meniscus formed on the solid and the mass of liquid absorbed in the cellulose pulp [1]. The liquids studied were two apolar liquids, decane and dibromonaphtalene, and three polar liquids, water, ethylene glycol and formamide. Capillary absorption of apolar liquids into cellulose pulp followed the classical Washburn law. Concerning polar liquids, the interpretation of kinetics of capillary rise was not as straightforward as liquid absorption and swelling of the fiber matrix occurred simultaneously. Analysis of the results allowed the determination of the Lifshitz-van der Waals (γ_s^d), electron donor (γ_s^-) and electron acceptor (γ_s^+) components of the surface energy following the approach developed by van Oss et al [2].

Results evidence that cellulose fiber surface is a strong electron donor surface, as is the cell surface of the bacteria in the chosen growth media. Bacterial adhesion was shown to be optimal in moderate ionic strength solution and to increase with increasing temperature [3]. These results suggest the importance of hydrophobic – non specific type of interactions between the cell surface and cellulose in this case.

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MORPHOLOGIES OF AQUEOUS DISPERSIONS OF BRAIN LIPIDS

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Brain lipid extracts (porcine sphingomyelin and bovine brain lipids (Folch fraction 1)), dispersed in physiological NaCl solution (0.9wt.%) with and without added CaCl₂ (1mM), were investigated by cryo-TEM. The effect of solubilization of cholesterol, an important constituent in brain lipids, into these lipids was also investigated.

In sphingomyelin dispersions, liposomes were always formed with multilamellar liposomes being most prominent in the case of the Na⁺-solution (see figure). Cholesterol induced the formation of large (of the order of 1 μm) multilamellar liposomes although smaller liposomes were still present. The liposomal unit layers consist of two rippled bilayers consistent with the findings by Meyer et al [1] and show an angular appearance.

The bovine brain extract shows a very different morphology with large connected liposome structure. Also in this case we could detect an influence of Ca²⁺ and cholesterol. Cholesterol seems to induce lamellar-like sheets.

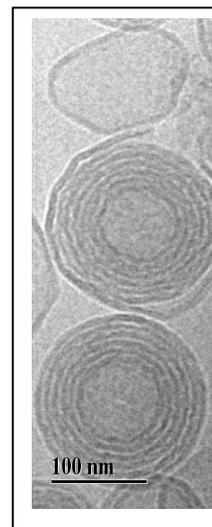
The variety of morphologies, which are dependent on the sample composition, implies the importance of these lipids for the function of the physiological processes [2]. For instance the importance of the cholesterol to membrane lipid ratio has been pointed in connection to so-called functional membrane rafts for e.g. transport of lipids and proteins as well as signal transduction [3].

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THE STABILITY OF AIR BUBBLES BENEATH A PLANAR AIR-WATER INTERFACE

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Foam, a dispersion of gas bubbles, is a non-equilibrium system in which each gas cell is encapsulated by a thin film of adsorbed surface active material. In many commercial food products foam is a major component and the stability of the bubbles has a significant influence on the quality of the product. Disproportionation, i.e., the diffusion of gas from small bubbles into large bubbles, is an important instability mechanism. Various theories have been developed to describe disproportionation in foams and emulsions (where it is usually referred to as Ostwald ripening). Recent theoretical work indicates that adsorbed films with high enough interfacial dilatational elasticity should mechanically arrest bubble shrinkage and therefore disproportionation. In this paper we describe the results of experiments used to test this idea, using the more accessible practical case of a bubbles beneath a planar air-water interface, the planar interface acting as an infinitely large bubble. Bubbles stabilized by a range of proteins (caseinate, gelatin, β -lactoglobulin and soy glycinin), hydrophobically-modified silica nano-particles and sucrose esters were studied.

It was found that proteins forming films with nominally very different interfacial rheology behave rather similarly [1, 2]. No protein produced a very marked slowing of disproportionation and no protein could completely stop bubble shrinkage at any visible size (above *ca.* 1 μm diameter). The system of sucrose esters in a high viscosity dextran syrup did, however, produce a marked slowing of disproportionation that could not be accounted for by the higher viscosity of the aqueous phase alone. On the other hand, bubbles stabilized by silica nano-particles in water could be produced that were almost indefinitely stable to shrinkage. The production of stable bubbles in the last instance was critically dependent on the degree of hydrophobicity of the silica particles and the ability to coat the bubbles rapidly with a sufficient surface density of particles [3].

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ANALYSIS OF THE PHYSICO-CHEMICAL PROPERTIES OF DILUTE SUSPENSIONS OF SPHERICAL PARTICLES COATED WITH CHARGED MEMBRANES

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It is well known that the electrokinetic properties of colloidal suspensions provide powerful analytical tools for the characterization of colloidal systems. This is why, considerable efforts have been made in the last century for the understanding of the behavior of charged solid spherical particles in suspension, as a first approximation to real colloidal suspensions. However, in the last years, several authors extended the rigid spherical particle model to more realistic physical situations, e.g., spheroidal particles, particles with dissociable functional groups on their surface, solid particles covered with ion-permeable membranes, etc. In particular, the case of colloidal particles coated with a charged permeable membrane (soft particle) is specially important in many biological aspects. However, since there are no general analytical solutions for this problem, a number of methods have been devised in order to obtain either approximate [1-3] or numerical solutions [4,5]. In previous works, we used the network simulation method to analyze the electrophoretic mobility [4] and the dielectric properties [5] of colloidal suspensions of rigid spherical particles coated with charged membranes, and compared our results, whenever possible, with existing analytical solutions. The aim of the present communication is to use the network model developed in these previous works to study in depth the physico-chemical properties of the system, analyzing the electric potential, concentrations of ionic species, and fluid velocity profiles for different parameter values of the model used to characterize the suspension.

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THE EFFECT OF BACTERIORHODOPSIN, DETERGENT AND HYDRATION ON THE CUBIC-TO-LAMELLAR PHASE TRANSITION IN THE MONOOLEIN-WATER SYSTEM

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Understanding the mechanisms of proteins requires their structures to be elucidated to high resolution by *e.g.* x-ray crystallography. In 1996, Landau and Rosenbusch demonstrated that the cubic phase of monoolein (MO) could be used for crystallization of membrane proteins [1] but since then, only a few membrane proteins have been crystallized *in cubo*. One reason for the low output may be the narrow aqueous pores, but the underlying mechanism for crystal growth is still unclear. Phase behavior of MO have been extensively studied [2,3]. At high water contents, the diamond (C_D) cubic phase is present, while at lower water content the gyroid (C_G) cubic phase is formed. The C_G phase can be transformed into a lamellar phase (L_α) upon dehydration and it is possible that this cubic-lamellar phase transition has an important role in the *in cubo* crystallization process. It is also likely that the dimensions of the phases are crucial for the inclusion and the diffusion of membrane proteins. There are several possibilities to increase the aqueous pore width of the cubic phase as well as to incorporate other lipids in the bilayer. We have used distearoyl phosphatidyl glycerol (DSPG) that in addition to the C_G and the C_D -phases forms a primitive (C_P) cubic phase that can contain substantially more water. We used bacteriorhodopsin (bR) as our model protein and observed that crystals appeared more readily in the MO-DSPG cubic phase than in the MO cubic phase [4]. We have also focused on different aspects of the equilibrium between cubic and lamellar phases [4], and are presently investigating other bicontinuous lipid systems with respect to membrane protein compatibility and subsequent crystallizability.

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IMMOBILIZATION OF GLUCOSE OXIDASE IN POLYACRYLAMIDE-POLYPYRROLE MICROPARTICLES

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Some enzymes, like glucose oxidase, maintain the enzymatic activity for long time when they are encapsulated in polyacrylamide microgels. For this reason, microgels with entrapped glucose oxidase have been used as biological component in amperometric biosensors showing a remarkable stability and reproducibility. Recently we have reported the performance of this type of glucose sensors [1] and the structural modifications induced by the glucose oxidase in the polyacrylamide microgels [2]. With the aim to decrease the biosensor response time and reading potential, polypyrrole was incorporated inside the polyacrylamide microparticles. The synthesis of these microparticles was carried out in two steps: First, soluble polypyrrole was prepared and stabilized in aqueous solutions by the addition of polystyrenesulfonate during the polymerization. By this method a stable and soluble polystyrenesulfonate-polypyrrole complex is obtained. Second, the synthesis of microparticles was performed using a concentrated emulsion (W/O) polymerization method. The W/O concentrated emulsion was prepared by dropwise addition of the aqueous phase (a solution of polypyrrole-polystyrenesulfonate, acrylamide, bis-acrylamide, ammonium persulfate and glucose oxidase at pH 7) to the continuous oil phase (Dodecane and Span 80). The polymerisation of the emulsion produces conducting microparticles with average size of 4.5µm. Microparticles with 50/50, 70/30, 80/20 and 90/10 polyacrylamide/polypyrrole (w/w) were produced and their structure was investigated by DSC, X-ray diffraction and scanning electron microscopy. Furthermore, microparticles with encapsulated enzyme have been used as the biological component of an amperometric glucose sensor that presents good response under aerobic and anaerobic conditions.

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ZETA POTENTIAL AND ESR SPECTROSCOPY OF DOTAP/DOPE AND DC-CHOL/DOPE LIPOPLEXES FOR GENE DELIVERY

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Non-viral vectors represent an important alternative in gene delivery. Among these vectors, cationic liposomes are widely studied, because of their ability to form stable complexes with DNA fragments (lipoplexes), thanks to electrostatic interactions.

In the present communication we report on the characterization of cationic liposomes and homo-oligonucleotides complexes. Liposomes were made by the zwitterionic lipid dioleoyl-phosphatidyl-ethanolamine (DOPE) and the cationic lipids dioleoyl-trimethylammonium-propane (Cl⁻ salt, DOTAP) and dimethylaminoethane-carbamoyl cholesterol (DC-Chol). Oligonucleotides were the 20-base single strand deoxyadenosine monophosphate (Na⁺ salt, polyA), the 20-base single strand deoxythymidine monophosphate (Na⁺ salt, polyT) and the corresponding double strand (dsAT). Lipoplexes formation was followed by zeta potential measurements. In each case an S-shape titration curve was observed, and a well defined surface potential drop took place upon charge compensation between the cationic lipid heads and the phosphate groups on oligos. The inversion point depended on the specific system under study. In the case of DOTAP/DOPE liposomes the two single strands gave an inversion point that corresponded to the exact charge balance between all the oligo phosphate groups and the external lipid heads alone (charge ratio +/-=1/0.50). This indicated that liposomes were not disrupted upon the complex formation. dsAT behaved in a more complicated way. Titration of DC-Chol/DOPE liposomes with polyA and polyT showed a peculiar trend, which depended on the basis type and was different from the case of DOTAP/DOPE liposomes. The bilayer properties and the changes that occur with DNA fragments addition, were monitored by ESR spectroscopy of appropriately tailored spin probes. This is a very useful tool to investigate the dynamics and ordering of lipids-based structures on a molecular scale. We used stearic acid derivatives with a nitroxide paramagnetic unit placed in different position of the hydrocarbon chain. These probes were able to insert in liposome double layer and gave details on the environment sensed by the nitroxide. For all the systems investigated, either 5- or 16-doxyl stearic acids showed that no major alteration took place after lipoplexes formation and molecular packing remained substantially unchanged.

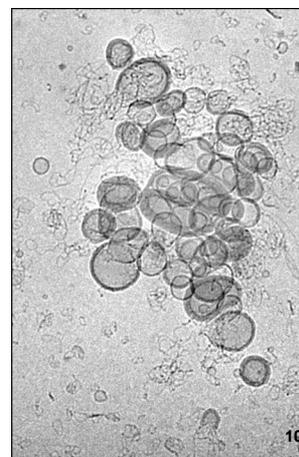
COMBINED CRYO-TEM AND ESR STUDIES OF EPC LIPOSOMES LOADED WITH A CARBORANYL COMPOUND INTENDED FOR BNCT

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Substituted glycosyl carboranes are amphiphilic boron-containing compounds intended for *Boron Neutron Capture Therapy* (BNCT). BNCT requires that the tumour cells accumulate large amounts of the boronated compound and the use of liposomal carriers has been suggested as a possible way of increasing the uptake. Cryogenic Transmission Electron Microscopy (cryo-TEM) was used to investigate the effects of the glycosyl carboranes on the structure and properties of extruded egg phosphatidylcholine (EPC) liposomes. Only at carborane mole fraction $x_{\text{LCOB}} \geq 0.44$ significant changes of the liposome size distribution and the overall structure were observed. Extremely small liposomes with diameters ranging from 10 to 30 nm were found to coexist with the original 100 nm liposomes. The fraction of small liposomes increased with increasing glycosyl carborane concentration. In a limited concentration regime the boronated compounds were found to induce aggregation of the liposomes. These effects were verified by turbidity measurements. In addition, cryo-TEM revealed that the structure of the liposome membrane became more irregular with increasing glycosyl carborane concentration. At concentration above 0.82 the boronated compounds induced formation of open liposomes and thread-like micelles (see figure) and, with time the sample displayed a macroscopic phase separation. More details on the molecular interaction between the carborane derivatives and the liposome membranes were obtained by Electron Spin Resonance (ESR) spectroscopy. Two different *n*-doxyl stearic acid spin probes, (*n*-DSA), were used to measure the dynamics and the degree of order in the mixed systems. The results using 5-DSA indicated that carborane insertion into the phospholipid bilayer increased the packing order in the vicinity of the water/hydrocarbon interface. In contrast, no effects on the membrane dynamics were detected with 16-DSA, which monitored the inner hydrophobic region of the bilayer.



LIPOSOMAL FORMULATION FOR A NUCLEOSIDE CONTAINING CARBORANE TO BE USED IN BNCT: AN ESR STUDY

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5-carboranyl-2'-deoxyuridine (CDU) is a non-toxic boron containing pyrimidine nucleoside that was studied extensively for its cytotoxicity, anticancer, antiviral activity and cellular uptake[1]. This compound may be used in the treatment of gliomas by *Boron Neutron Capture Therapy* (BNCT). The basis of this therapeutical method is the production of high linear energy transfer (high-LET) particles (${}^7\text{Li}^{3+}$ and ${}^4\text{He}^{2+}$) upon capture of a slow (thermal) neutron by the structurally unique ${}^{10}\text{B}$ nucleus, and spontaneous fission of the resulting excited ${}^{11}\text{B}$ nuclei. The intracellular ionisation tracking that results from the release of the heavy ion fission products, provides a cell lethality mechanism that is potentially effective up to $\sim 10\ \mu\text{m}$ (cell diameter). Therefore, irradiation of sufficient quantities of the ${}^{10}\text{B}$ isotope in the tumor cells should result in the destruction of the tumor cells, while healthy neighbouring cells remain unaffected. Unilamellar liposomes of specific size and composition can be used as carriers of boron therapeutical concentrations to neoplastic cells[2].

In this study the effect of CDU on phospholipid phase behaviour and on phospholipid dynamics were investigated using Electron Spin Resonance (ESR) spectroscopy. Fatty acid spin labels (*n*-doxylstearic acid, *n*-DSA) and the nitroxide-labeled cholesterol analogue cholestane (CSL), were incorporated into liposomes built up with saturated distearoyl phosphatidylcholine (DSPC), unsaturated egg yolk phosphatidylcholine (EPC) and mixtures of DSPC/Cholesterol (55-45%mol), EPC/Cholesterol (55-45%mol). The CDU content in the liposome dispersion was determined by measuring UV absorption at 274 nm. The data clearly show that CDU insertion has a significant influence on the lipid bilayer structure and temperature dependent phase behaviour. The analysis of the ESR lines by spectral simulation supports the increase of membrane fluidity and the ordering effect of the carboranyl-nucleoside into the lipid packing over the whole temperature range. The differences in the interaction and organisation between the boronated nucleoside and both the cholesterol free-, and the cholesterol-containing liposomes have been also discussed.

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COPPER(II)-NUCLEOSIDE COMPLEXES: C.W. AND PULSED-WAVE ESR STUDY OF THE EFFECT OF SURFACES OF POROUS SOLIDS

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The effects of surface of porous solids is of interest in the formation of biomacromolecules. This communication reports on copper(II)/nucleosides complexes which were studied in water at high pH and after contact with the cavity walls of 13X-zeolite. The results were mainly collected by electron spin resonance in continuous (cw-ESR) and pulsed (ESE) wave. Adenosine was used as the nucleoside model for the formation of compounds which were fully characterized in alkaline water solution and after adsorption on commercial 13X-zeolite. In aqueous solution adenosine was coordinated to copper(II) through deprotonated hydroxyl groups in the 2' and 3' positions of the ribose unit, with the formation of Cu(II)/ads = 1/2 compound. When adsorbed on zeolite, both cw-ESR and ESE showed that a fraction of the adsorbed complexes did not change structure and underwent to high mobility into the interzeolite cavities cavity. The remaining fraction directly interacted with ²⁷Al nuclei of the zeolite framework. Other copper(II)/nucleosides behaved in the same manner.

Surprisingly enough, alkaline solutions of nucleosides were able to remove copper(II) from zeolite under the form of [Cu(ads)₂(H₂O)₂]²⁻ which freely moved in the supernatant aqueous liquid.

ENTROPIC FORCES IN BIOLOGICAL SYSTEMS

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In colloid-polymer mixtures free volume effects are well known to lead to entropic interactions which are responsible for rich phase diagrams in such situations. While the understanding of entropic forces in model systems, e.g. colloidal suspensions, has considerably put forward during the last years, only little is known about the importance of those forces in biological systems where entropic forces are also assumed to play a major role. We investigate by means of fluorescence microscopy and dynamic light scattering experiments the bundle formation of actin filaments in the presence of uncharged polymer coils of polyethylene glycol (PEG). Our results demonstrate that addition of PEG enhances the formation of actin bundles which is interpreted in terms of entropic forces. Because cytoplasmic proteins might have a similar effect as PEG, the actin filaments may form bundles in the cytoplasmic matrix more readily than expected.

STRUCTURE OF PROTEINS/POLYELECTROLYTES COMPLEXES

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The mixture of proteins and polyelectrolytes of opposite charges lead to the formation of different types of complexes. Such complexes may be either soluble, either lead to solid/liquid or liquid/liquid phase separation. The occurrence of these transitions depends on the structure of the complexes. The knowledge of such structures is important as proteins/polyelectrolytes complexes are often encountered in real situations in biology, food industry, controlled flocculation... Though the number of studies concerning the mechanisms driving the formation of complexes has grown to a large extent these last years, there is a lack of structural studies on complexes. We present here a SANS study on a system constituted of a globular protein, lysosyme, and of a model polyelectrolyte, PSSNa. SANS is very powerful in such system as contrast matching enables us to study either the signal from lysosyme, either from PSSNa in complexes. Phase diagrams have been built for different molecular weights of PSSNa in the semi-dilute regime at pH 4.5 where lysosyme bear a net charge of + 11 and all PSSNa monomers are negatively charged. All diagrams present an aggregated area when the ratio lysosyme/PSSNa is important and a soluble area when the ratio lysosyme/PSSNa is weak. Aggregated suspensions are gel-like for large polyelectrolytes and liquid turbid for short ones.

In the aggregated regime, we only match the signal of PSSNa, looking to the signal of lysosyme. At large q where intensity is $I(q)$ is proportional to the form factor of objects, $I(q)$ decays as q^{-4} indicating that lysosyme keep its globular shape. For turbid samples (large molecular weight), an important correlation peak corresponding to the contact of two lysosyme is observed and $I(q)$ decays again as q^{-4} at small q , showing that the complexes are made of dense globular aggregates of lysosyme, stuck by PSSNa. For gelled samples (small molecular weights), the correlation peak at intermediate q is no longer observed and $I(q)$ decays as $q^{-2.5}$ at small q , indicating that lysosyme and PSSNa form a fractal network. In the soluble regime, we perform both measurements on matched lysosyme and matched PSSNa. At large q , PSSNa intensity decays as q^{-1} as expected for a polyelectrolyte. Contrary to the aggregated case, Lysosyme intensity decays as $q^{-1.7}$, indicating a change of conformation of the protein. This exponent, characteristic of an excluded volume chain, is found for denaturated proteins. Both signals from PSSNa and lysosyme are flat at low q (no more aggregation in the system) and show a small peak at the same q , remaining of the polyelectrolyte effect.

LYSOZYME CRYSTALLIZATION IN CUBIC PHASES

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We studied the crystallization of lysozyme in lipid cubic phases upon the addition of salt (sodium chloride). The structure of the cubic phase strongly affects the crystallization of lysozyme; lysozyme crystals were found to nucleate at salt concentrations well below the nucleation boundary for bulk solutions without cubic phase present. We analyse these findings in terms of the reduced volume accessible to the lysozyme molecules and the elastic energy needed to deform the cubic phase in an attempt to accommodate single lysozyme molecules or lysozyme clusters.

EQUILIBRIUM AND NON-EQUILIBRIUM BEHAVIOUR OF MIXED LIPID MEMBRANES

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There has been a long-standing interest in lipid bilayers due to their relation to cell membranes. We are particularly interested in giant unilamellar vesicles (GUVs) whose membranes are formed by a mixture of lipids. In these mixed membranes separate domains with different lipid compositions can exist. Using confocal microscopy, we not only systematically investigate the shape and size of these domains, but also follow their formation after a temperature quench. These observations are then analysed in terms of the equilibrium phase behaviour and current theories on domain formation.

NOVEL PATTERNING OF POLYMER SUPPORTED LIPID MEMBRANES

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Lipid bilayers membranes supported by a hydrophilic polymer cushion at the interface between a solid substrate and an aqueous phase have reached a level where they are important novel model membrane systems with the potential for practical applications. Recently, we have prepared different suitable polymer cushions and investigated these for the build up of polymer supported lipid membranes [1-3].

However, the important step towards an application of supported membranes is the patterning of these bilayer-substrates. Only some approaches have been described so far in the literature ranging from scratched glass slides over micro-contact printing to photopolymerization [4 and references in there].

Here, we present a novel way of patterning polymer supported lipid membranes. The successful direct micro-contact printing of the hydrophilic polymer cushion is followed by a controlled water condensation on these transferred areas. In a second step polystyrene is dewetted on the substrate resulting in a regular array of the hydrophilic polymer cushion. These hydrophilic areas are now accessible to a following vesicle fusion to build up the polymer supported lipid membrane.

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INFLUENCE OF SC3 HYDROPHOBIN ON THE STRUCTURE OF MODEL MEMBRANES

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Hydrophobins are fungal proteins which have a high affinity for various types of surfaces [1]. While it is well established that covering of fungi hyphae and of the air/water interface is crucial for fungi growth and proliferation, no detailed mechanism of this phenomenon is available. In order to get more insight into the interactions of hydrophobins with these interfaces, we studied the behavior of SC3 hydrophobin at the air/water interface, as well as its impact on model lipid membranes. Dynamic surface pressure measurements, circular dichroism, small angle X-ray scattering (SAXS), Langmuir film technique, grazing incidence X-ray diffraction (GIXD), Brewster angle microscopy (BAM) and polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS) were used in our experiments. The results obtained showed that SC3 hydrophobin covers densely the air/water interface. While the impact of SC3 hydrophobin on model membranes, namely the cubic phases of monoolein (MO) and monomolecular films formed with dipalmytoylphosphatidylcholine (DPPC) at the air/water interface is clearly visible, the basic structure of the membranes are preserved. These findings indicate that the SC3 hydrophobin undergoes conformational modifications in membrane-like environments. The interactions established by SC3 with lipid structures used as model membranes are non-destructive. This observation may explain the absence of toxic effects in this highly tensioactive protein.

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BIOPHYSICAL LAYERS: ELABORATION OF SENSING SURFACES USING HYDROPHOBIN

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Small, interfacially active proteins called hydrophobins have the remarkable property of adhering to almost any surface [1]. A *Schizophyllum commune* hydrophobin (SC3) has been used to coat glassy carbon electrodes, Teflon[®] and polystyrene surfaces. The structure of the hydrophobin films was studied using Transmission Electron Microscopy (TEM). Six different enzymes adsorbed to the hydrophobin-modified surfaces are stably immobilized and remain active for long time, allowing detection of the enzyme substrates in aqueous solutions using electrochemical and spectrophotometric techniques [2]. Our approach shows a way to an easy manufacturing of catalytic surfaces for applications in biosensing and in biotransformations. Indeed, the SC3 hydrophobin can be used as a molecular bridge between solid surfaces and enzymes. The enzymes, immobilized via the SC3 layer, remain active over several months. Both modification and functionalization of the surfaces are simple and the systems obtained are long-lasting.

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COATED PARTICLES FOR STUDIES OF LIPID-POLYMER INTERACTING IN LAYERS

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The coupling of the lipid head groups to various polymer components constitutes an essential point in biological systems. Furthermore, in order to create biomimetic systems e.g. by self-assembly, the interaction between subsequent layers is a crucial issue.

As model systems, colloidal particles (silica particles or polystyrene latex particles) or planar SiO₂ substrates have been coated with a polymer cushion using the layer-by-layer technique, which enables the alternative deposition of positive and negative polyelectrolytes on surfaces [1]. Phospholipid bilayers were prepared by adding an unilamellar vesicle solution [2].

In the case of the colloidal systems, ζ -potential measurements and single particle light scattering showed that the adsorption of the polymer layers was successful (alternating positive and negative surface potential during the depositing process, regular increase of the thickness of the deposited material). Employing fluorescently labelled lipids, confocal laser scanning microscopy indicated that the lipid layer was deposited on the polymer-coated particles. ²H NMR transverse relaxation of the water in aqueous dispersions of coated colloids allows then to investigate the hydration water within the layers [3], and in the studied case, the influence of the phospholipid on the hydration of the polymer layers.

In the case of the planar systems, fluorescence spectroscopy as well as neutron reflectivity indicated the successful deposition and the swelling properties.

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A PRELIMINARY STUDY OF THE FENGYCIN-LIPID INTERACTION AT AN INTERFACE IN ORDER TO GAIN MORE INSIGHT IN THE ACTION MECHANISM OF FENGYCIN IN BIOLOGICAL MEMBRANES

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Fengycin is a lipopeptide produced by *Bacillus subtilis*. Its structure is composed by a β -hydroxylated fatty acid linked to a peptide part comprising 10 amino acids including 8 in a cycle.

It has been shown that it has antifungal activity against filamentous fungi and that its haemolytic activity is 40-fold less than one of the surfactin, another lipopeptide produced by *Bacillus subtilis*. It could be supposed, as it was shown for surfactin, that its activity is due to its interaction with the target membrane leading to the alteration of the bilayer properties. But no detailed mechanism has already been suggested in the literature.

In a previous work [1], we have shown that fengycin is able to inhibit the fusion of vesicles induced by the Simian Immunodeficiency Virus (SIV) tilted peptide without affecting the permeability properties of the membrane. We suggested that lipopeptide-lipid interactions interfere with the ability of membranes to form highly curved “stalk” intermediates which are necessary for the fusion of the vesicles.

In this work, in order to gain more insight about the lipopeptide-lipid interactions, surface pressure (Π) – area (A) isotherm coupled with Brewster angle microscopy were applied to analyze the effect of fengycin on the structural and morphological characteristics of DPPC monolayer, as a simple model of biological membranes.

When fengycin is mixed with DPPC monolayer, clear deviation from pure DPPC behavior is evident. Isotherm shape and domains lack the characteristic features of pure DPPC. This work constitutes a preliminary study of the membrane perturbative properties of fengycin. Further investigation will be necessary to obtain the detailed mechanism.

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LIVING POLYMERS: WORMLIKE MICELLES FORMED BY THE SELF-ASSEMBLING OF DI-LAUROYL-PHOSPHONUCLEOSIDES

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The aggregation properties of phospholiponucleosides, lipids bearing a nucleoside moiety on their polar head, with various acyl chain lengths, are current subject of study in our group. While these compounds do have a potential application as prodrugs in gene delivery therapy, their phase behavior is enriched by the presence of a polar head capable of selective attractive interactions. We have found that the self-assembling of the phospholiponucleosides triggers molecular recognition properties similar to those observed in nucleic acids between the bases.

This contribution concerns a structural and dynamic investigation of di-lauroyl-phosphonucleosides aggregates in aqueous solutions as a function of the surfactant concentration and of the ionic strength.

Small Angle Neutron Scattering (SANS), Static Light Scattering (SLS) and Quasi Elastic Light Scattering (QELS) have been employed to assess the structural evolution of the binary system as a lipid concentration is increased [1]. A merging of SANS and SLS provides in fact a spectral window corresponding to all the relevant length scales of the system in the direct space. The data show the formation of cylindrical aggregates rather flexible and remains essentially unchanged during the micellar growth. Above a surfactant concentration threshold, the scattering properties do not follow the monotonic behavior, suggesting the onset of a novel cooperative structure, where the micelles become entangled. In this concentration regime the system shows a distinct viscoelastic behavior that suggests the presence of a polymerlike network. The similarity with the polymers in the semi dilute regime has suggested a successful interpretation for scattering data. In our case the correspondence is not limited to the mesoscopic structural scale, since the micelles have nucleic functionalities, so that they can be considered as the first example of *micellar polynucleotides*.

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PolyAT CHEMICAL DENATURATION IN W/O MICROEMULSION

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The study of polynucleotides in microemulsion has offered in the past years several unexpected results [1,2]. First of all, the stabilizing effect of the micellar medium on the polyAT double helix, that did not show thermal melting even at temperatures well above the melting temperature in solution (318K in 10 mM NaCl; no melting up to 336K at the same ionic strength in microemulsion). In addition, the microemulsive medium induces the formation of aggregate species (ψ -forms) of polyAT modulated by the NaCl concentration in the aqueous microdomain. Such compaction occurs in solution in the presence of high molecular weight polymers and high salt concentrations. In microemulsion, a $\psi(-)$ form, characterized by an intense negative CD band at 280nm, is observed when the endomicellar concentration of NaCl exceeds the threshold value of 0.35 M. We have now extended our investigations on the properties of polyAT in microemulsions to verify the possibility of its chemical denaturation, by addition of a strong acid or a strong base, as a function of the endomicellar salt concentration. The results are, once more, considerably different from those obtained in solution. In particular, *ca.* one mole of strong acid (HCl) per mole of polyAT monomer units is required for half-denaturation by protonation of adenine N1, and *ca.* 2.5 moles of strong base (NaOH) per mole of monomer units for half-deprotonation of thymine N3. These quantities are practically independent of the ionic strength of the aqueous pool, at variance with the solution behaviour (manuscript in preparation). The results will be discussed in terms of screening of the negative charges on the polynucleotide.

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MICELLES OF diC₈P-NUCLEOSIDES AND THE HOFMEISTER SERIES

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Diocanoylphosphatidyl-uridine (diC₈P-Uri) and diocanoylphosphatidyl-adenosine (diC₈P-Ade) belong to the class of phospholiponucleosides. They are a class of synthetic amphiphiles formed by two biological subunits, where the phospholipid group is connected to a nucleobase, with the same chemical functionality and charge of the repeating units in nucleic acids. From previous studies we know that diC₈P-nucleosides form micelles in water solution. These self-assembled structures mimic quite well the molecular recognition properties of polynucleotides. In fact both, stacking and H-bonding, are present between the bases at the micellar surface [1].

Aim of this work is the investigation of the effect exerted by the anions of Hofmeister series both on the surfactant and on the aggregational behavior of diC₈P-nucleosides. These effects are typical non-DLVO, and their investigation in colloidal science is currently gathering considerable interest. A surface tension study yields different cmc curves for different Hofmeister aqueous media, so that a specific ion interaction between surfactant's polar head and anions can be hypothesized. To compare the structural properties of such micellar systems Small Angle Neutron Scattering (SANS) experiments have been performed on diC₈P-Uri, diC₈P-Ade and their 1/1 mole ratio mixture in aqueous solutions 0.18M of Na₂SO₄, NaBr, NaNO₃, NaSCN, NaClO₄. SANS spectra depend on the anion kind in low-q and high-q regions, suggesting that micellar properties are affected both on a local and on a global structural scale. A correlation between base polarizability and efficiency of the Hofmeister effect can be inferred from the experimental data.

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BIOINTERFACES: PHYSICAL CHARACTERISATION AND PERFORMANCE OF IMMOBILISED LIPASES

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The new product Accurel MP1004, is a porous polypropylene powder used as support for enzyme immobilisation. The particle size of MP1004 ranges between 40-80 mesh, corresponding to a particle diameter of 420-177 μm . The pore distribution of MP1004 falls between macroporous and mesoporous regions. By measuring the variation of pore volume and of pore size distribution of mesopores as a function of enzyme loading it was found that they are penetrated by enzyme molecules during the adsorption process.

The characterisation of three commercial lipase preparations (CLP), A Amano 6, M Amano 10 and R Amano, showed that their protein content varies between 8-27%. They are comprised of at least five proteins.

The various proteins of the CLPs are quickly adsorbed by the Accurel MP1004. However they are progressively substituted by the lipases because of their greater affinity for the support. The immobilisation process has the effect of differentiating between the activities of M Amano 10 and A Amano 6 CLPs. The immobilisation process modifies the thermal resistance of the lipases in different ways for the three CLPs.

Recently, immobilised lipase Novozym 435 was used for the enzymatic synthesis of sugar esters, which are non-ionic, biocompatible and environmental friendly surfactants. To overcome the problems related to the different polarity of the reagents, two strategies were used: the first involves the use of a polar organic solvent, able to dissolve both the sugar and fatty acid, while the second requires the protection of some hydroxyl groups to reduce the sugar polarity. The second path was followed in this work for the synthesis of a sugar alcohol fatty acid ester (mannitol laurate). The synthesis started from vinyl laurate and different mannitol isopropylidene derivatives in the presence of the commercial immobilised lipase Novozym 435. The acylation was carried out either with solvent (hexane and 2-methyl-2-butanol) or in solvent free conditions at 50°C and at atmospheric pressure. The use of the vinyl ester was important to force the equilibrium towards products formation.

CHARACTERIZATION OF THE CUBIC PHASE AND THE RELATIONSHIP WITH THE NEIGHBORING PHASE IN ANIONIC/AMPHOTERIC SURFACTANT/OLEIC ACID/DECANE/WATER SYSTEM

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Discontinuous aqueous micellar cubic phase and the relationship with the neighboring phase was investigated with polyoxyethylene (1.5 mol) myristylether sulfate sodium and tri-ethanol amine salt (PMST)/N'-carboxyethyl N'-hydroxyethyl N-aminoethyl dodecylamide [Imidazoriumbetain (IB)]/oleic acid/water/decane system[1] by means of phase study, small-angle X-ray scattering (SANS), rheological measurement, and transmission electron microscopy observation with freeze fracture replication method (FF-TEM). In the ternary phase diagram, the cubic phase region has a large extension with respect to the content of decane, from 25 to 45 % at approximately constant surfactant/water ratio of 4/6. Characteristics of the cubic phase changed continuously depending on the concentration of decane. By swelling the spherical micelle of the cubic phase, the size of the micelle increased and eventually reached 35 nm that is approximately 9 times larger than that of the micelle without oil (approximately 4 nm). In the meantime, the packing fraction of the micelle in the phase is calculated to be 72 volume %, very close to the maximum value for a packing of spheres, suggesting it is well organized. The neighboring phases are a L1 phase on the water rich side (beyond small 2-phase region), a 2-phase region (cubic + oil) on the oil rich side, and a lamellar phase on the surfactant rich side. Characterization on the very narrow L1 phase channel from the water corner to the cubic phase performed by FF-TEM observation and static light scattering measurement showed that the packing of spherical micelles became denser with increasing concentration of the total surfactant and decane, and the cubic phase appeared as a result. The important thing is the adjacent phase on the surfactant rich side is a lamellar liquid crystal with flat bilayer. Although it has been tacitly assumed that the cubic phase in the close neighborhood with a lamellar phase has a bicontinuous structure, the cubic phase found in this study was not the case. The FF-TEM observation revealed a network-like arrangement of the spherical micelles followed by a layered structure of the lamellar phase suggesting a model of a phase transition process between a cubic phase and a lamellar phase.

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LATERAL MOBILITY OF PROTEINS ADSORBED ON OR EMBEDDED IN POLYELECTROLYTE MULTILAYERS

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We present results relative to the diffusion process of proteins (Human Serum Albumin, HSA) adsorbed on or embedded in Poly(sodium 4-styrenosulfonate)/Poly-allylamine hydrochloride polyelectrolyte multilayer films by using Fluorescence Recovery After Photobleaching. At least two populations of adsorbed proteins exist on the top or within the multilayer architectures. One population, that represents typically 50-70 % of adsorbed proteins, corresponds to proteins that are able to diffuse laterally along the surface or in the multilayers, while the others diffuse more slowly or appear almost immobile over the experimental time scale. Special attention is brought to the evolution of the diffusion coefficient with the surface HSA concentration. We find that while on PSS terminating films the diffusion coefficient of adsorbed HAS is independent of the protein surface concentration in the explored range, it decreases strongly with the surface concentration when HSA is adsorbed on PAH ending films. On both films, the mobile fraction of adsorbed protein molecules decreases when the surface concentration increases. At low surface coverage, up to 90% of the adsorbed protein molecules are mobile both on PSS and PAH terminating films. The decrease of the mobile fraction with the HAS surface concentration is more pronounced on PSS than on PAH reaching, respectively, 50% and 70% of mobile HAS molecules at high surface coverage. This behavior is typical for protein aggregation. Infrared spectroscopy in the ATR mode confirms the presence of protein interactions but also rules out that this constitutes the unique reason for the evolution of mobile fraction with surface coverage. We also find that the diffusion coefficient, at small surface concentration, is more than 1 order of magnitude smaller on PSS than on PAH ending films. A tentative model based on the wrapping of HSA molecules by PAH chains and bringing between the chains by both polyelectrolytes is proposed to explain the observed features. Finally we also determine the diffusion coefficient of HAS embedded in PSS/PAH multilayers. We find that the diffusion coefficient of HSA embedded in -PAH-HSA-PAH- type multilayers is close to that determined when HSA is adsorbed on PAH terminating films.

SMALL-ANGLE SCATTERING STUDIES OF THE SILICATE NANOSTRUCTURES FORMED BY USING DNA AS TEMPLATES

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Recently, small-angle X-ray scattering method was used to investigate the nanostructures of silicates formed by using the DNA as templates. The DNA has a diameter of about 2 nm and lengths in the micron range and it is very useful as nanowire templates. DNA has been widely used as templates to form conducting nanowires by metalization [1,2]. In this study the DNA was used as templates to form silicate nanowires or nanotubes. Experimentally, mixtures of H₂O/TMOS/DNA/HCl in different ratios were prepared. The incubation time for each sample was 2 days at 80 °C. It was found that cylindrical nanostructures with a diameter of 4 nm were formed. Their diameter is larger than the DNA diameter and it indicates that thin layer of silicate was deposited on the DNA. After calcination at 450 °C for 4 hours, the diameter of the cylindrical nanostructure was reduced to 3.2 nm. More detailed analysis as well as electron microscopy studies will be reported.

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CHARACTERISATION OF CARRAGEENAN AND WHEY PROTEIN GELS USING NMR PGSTE DIFFUSION EXPERIMENTS

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NMR PGSTE [1] diffusion experiments are used to characterize the gelling behavior of carrageenan mixtures and whey protein mixtures. Restricted diffusion measurements, so called q-space imaging [2] is used to characterize the porous structure and the interfaces between the pores. The structure of developing networks can be observed as a function of the composition of the mixture (concentration of hydrocolloid, sugars and salts), the measuring temperature and the protein denaturation dependent on the denaturation temperature and duration. Besides the fundamental aspects of these studies these data are required in order to model processes sufficiently precisely for industrial production, to guarantee specific properties concerning the flow-, gelling- and syneresis/storage-behaviour, the texture and sensorial behaviour of food-products and to realise a process and quality control of thermal protein denaturation- and hydrocolloid gelling-processes. Therefore, further quantitative correlations between macroscopic quantities and the available NMR parameters have to be established for an industrial application of NMR diffusion experiments.

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RECONSTITUTION OF ATPase ACTIVITY IN PROTEOLIPOSSOMES OF MOUSE MDR3 P-GLYCOPROTEIN

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Members of the ABC (ATP binding cassette) superfamily of proteins are responsible for moving many different types of compounds across biological membranes. The substrates moved by ABC proteins range from chloride ions, drugs, amino acids to large proteins. The 170-130 kDa multidrug transporter P-glycoprotein is one of its most representative members. This plasma membrane protein confers multidrug resistance (MDR) on mammalian cells, representing a major obstacle to successful chemotherapy. Transport occurs against a concentration gradient is driven by ATP hydrolysis at the NB domain. Here we describe an efficient purification and functional reconstitution of ATPase activity in proteoliposomes of mouse P-glycoprotein. Metanotrophic yeast *Pichia pastoris* expressing mouse P-glycoprotein (MDR3-His₆) was grown in 1-Liter flask cultures. Plasma membrane proteins soluble in 23.5 mM *n*-dodecyl- β -D-maltoside were purified on a Ni-NTA agarose resin (Qiagen), using a method adapted from Lerner-Marmarosh *et al.* [1]. The fraction eluted with 200 mM imidazole contained highly purified (90-95%) His-tag P-glycoprotein. Reconstitution of this preparation into phospholipid bilayers was carried out by detergent dialysis at 4°C in a Snake Skin Dialysis tubing with 10.000 MWCO (Pierce). Detergent removal was also accomplished with detergent-absorbing beads, Bio-Beads[®] SM -2 (BioRad). The capacity to hydrolyse ATP was used to assess functional reconstitution of P-glycoprotein in proteoliposomes. The ATPase activity was determined by a colorimetric method that measures the release of inorganic phosphate from ATP.

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DIRECT OBSERVATION OF DNA COMPLEXATION WITH POSITIVELY CHARGED LATEX PARTICLES

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The complexation of charged particles with oppositely charged polyelectrolytes has attracted great interest due to its importance in many industrial and biological systems. Recent theoretical and simulation studies show that these complexes can form rich structures, depending on the conditions of the considered systems. Herein, we present the direct observation of the complexation of positively charged polystyrene latex beads with negatively charged DNA by using fluorescence microscopy.

Fixing the concentration of positive latex beads, first single complexes are formed, then they condense into big aggregates, and reenter into single complexes when the charge ratio of DNA to latex beads (-/+) is increased from 1:4 up to 50:1. Huge complexes are found in the charge ratio regime close the isoelectric point. Typical complexes with special structures, named as beads-on-a-string complex and one-tail complex, which are expected by the theoretical and simulation studies, are experimentally observed at a charge ratio of 50:1. Our results also indicate that complexes of different structures can coexist in polydisperse polyelectrolyte systems.

PHASE BEHAVIOUR OF COLLOIDAL LIPID A-DIPHOSPHATE

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Monodisperse colloidal particles, having a spherical symmetric interaction potential, are known to crystallize as colloidal crystals in several structures, depending on the range of their mutual interaction potential. Moreover, molecular systems of nanometric sizes have attracted increasing interest due to their application in high-performance materials, coatings, photonics, and bioactive glasses and in pharmaceutical formulations [1]. Lipid A-diphosphate obtained from E.coli can form nanometric structures in aqueous solutions including the formation of colloidal crystals in the absence of salt [2, 3]. The formation of colloidal crystals has been observed for volume fractions of lipid A dispersions ($3.50 \times 10^{-4} < \phi < 5.15 \times 10^{-4}$). These solutions have been analyzed by SAXS, SANS, TEM, LS, and the data was used in the calculation of $\overline{S}(Q)$. At volume fraction ($4.15 \times 10^{-4} < \phi < 5.15 \times 10^{-4}$), the spectra indicate the presence of long-range order and the observed peaks were found to be reflections originating from a face-centered cubic (fcc) lattice with a unit cell dimension of $a = 57.25 \pm 1.5$ nm. The formation of colloidal crystals ($3.75 \times 10^{-4} < \phi < 4.15 \times 10^{-4}$) in the presence of $1.0 \mu\text{M}$ NaCl, may be indexed on the basis of a bcc lattice with $a = 36.14 \pm 1.3$ nm. The diffraction lines are clearly distinguishable for both structures. These two colloidal crystal forms are apparently in equilibrium when grown and appear within a time period of 6-8 weeks. The ultimate size and shape of the lipid A-diphosphate aggregate in the form of a colloidal crystal, determines the geometrical arrangement, e.g. whether they are rounded, spherical or ellipsoidal or faceted shapes (cubic, hexagonal). The Q dependence ($0.1 \leq Q/Q_{110} \leq 0.75$) of the scattering of the liquid phase and the crystalline bcc phase are very similar, i.e. the peak in $S(Q)$ for the liquid is close to Q_{110} and suggests a similarity in the structure of the liquid and the bcc crystal phase. But, taking the bcc structure, Q_{110} , to be at the first peak in $S(Q)$, we would expect the second peak located at $Q = \sqrt{2} \times Q_{110}$. However, only a shallow peak in the liquid structure factor at $Q = 1.67 \times Q_{110}$, has been noted as an indication that the Q dependence of the liquid dispersion of lipid A-diphosphate exhibits some common features with that for the longitudinal 110 lattice vibrations in the bcc crystal.

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ELECTROPHORESIS OF IONIC MICROGEL PARTICLES

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Application of electric fields yields motion of charged objects. However, the dynamics of such phenomena is a complex problem involving both the properties of the system under consideration and those of the medium in which it is immersed. Ionic microgels form a set of interesting systems that are charged and possess variable internal structure and size due to their swelling capability. As a result, their electrophoretic behavior is extremely rich; and important, since they can be thought of realizing simplified versions of more complex biological systems. In this work, we study electrophoresis of an ionic microgel whose equilibrium size can be controlled by the network charge and the liquid ionic concentration. Interestingly the electrophoretic mobility μ of the particles is controlled by both charge density and hydrodynamic friction when the gel is swollen. For deswollen states, μ is controlled by the surface charge density that assures the dispersion colloidal stability. The effective charges responsible for the particle motion in the swollen and deswollen phases can be accounted for with simple thermodynamic models residing on the idea of counterion condensation. Finally, we observe that upon swelling, the maximum in the μ -salt curves observed in the shrunken phase and for most hard colloids is removed. We account qualitatively for most of the phenomenology with Ohshima theory for soft particles [1]. We kindly acknowledge financial support from project MAT2001-2767.

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SWELLING BEHAVIOUR OF CHARGED POLYMER NETWORKS

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The swelling and deswelling of microgel particles (gels with mesoscopic dimensions) can be described by means of state equations that predict first order phase transitions. The influence of the counterions is accounted for with the Donnan theory, resulting in a qualitatively good description of the colloidal gel swelling behaviour [1].

In this work, we study by Dynamic Light Scattering the swelling induced by charge of a polyelectrolyte (poly-L-Lysine) used in the formation of colloidosomes [2] whose structure can be controlled by changing the solvent pH. The aim is to understand the influence of direct Coulombic interactions between charged groups of the uncrosslinked polymer, and compare its behaviour with crosslinked polymeric structures, as in the case of microgels. We present a preliminary study of the poly-L-Lysine behaviour with pH and temperature variations.

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POSTERS

8. Colloids in Nature & Art:

*clays, food, conservation of cultural heritage, new application of colloids
and interfaces*

VESICLE TO CYLINDER TRANSITION IN EXTREMELY DILUTED ARGININE BASED SURFACTANT SYSTEMS INDUCED BY pH-CONCENTRATION EFFECTS

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A VESICLE TO ROD TRANSITION HAS BEEN OBSERVED IN EXTREMELY DILUTED 1, 2 DIDECYL-3-O-(L-ARGINYL) RAC-GLYCEROL · 2HCl SURFACTANT SYSTEMS BY MEANS OF STATIC LIGHT SCATTERING. AT CONCENTRATION AS LOW AS 0.005mM THE SOLUTIONS SCATTERED SIGNIFICANTLY. FROM THE ANGULAR DEPENDENCE AND MOLECULAR WEIGHT OF THE AGGREGATES A VESICULAR STRUCTURE IS SUGGESTED. INCREASING SURFACTANT CONCENTRATION IN WATER INDUCES THE VESICLE TO ROD TRANSITION AT CONCENTRATIONS AS LOW AS 0.5mM. THIS TRANSITION IS ACCOMPANIED BY A STRONG DECREASE OF SCATTERED INTENSITY AND CHANGE IN ANGULAR DEPENDENCE. OWING TO THE PRESENCE OF TWO CATIONIC GROUPS WITH A WEAK ACID CHARACTER, LOWERING THE pH AT A FIXED CONCENTRATION CAN INDUCE THE SAME TRANSITION. BOTH PARAMETERS CHANGE THE PROTONATION OF THE SURFACTANT, INDUCING A DECREASE IN PREFERRED SURFACTANT HEAD-GROUP AREA. THOSE FINDINGS ARE CONGRUENT WITH THE OBSERVED SURFACE TENSION BEHAVIOUR AS A FUNCTION OF SURFACTANT CONCENTRATION AND SUGGESTS AN EXPLANATION FOR THE WIDELY DIFFERENT CMC (CRITICAL MICELLAR CONCENTRATION) AS DETERMINED BY DIFFERENT TECHNIQUES.

THE ASSESSMENT OF THE INFLUENCE OF HYDROCOLLOIDS ON THE RELEASE OF FLAVOUR COMPOUNDS FROM FOOD MODEL SYSTEMS

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Hydrocolloids have become widely used in numerous food applications as thickeners, stabilizers or fat substitutes covering a broad range from traditional foods to new, convenient and low-calorie food products. However, the presence of any hydrocolloid in foods may influence the rate and intensity of flavour release which depends on the availability of the aroma compounds to be in the vapour phase above the product. An understanding of how hydrocolloids influence the flavour of a product can aid in optimizing product quality.

The major factors affecting flavour release from foods are phase partitioning and mass transport [1]. The partitioning between product and air phases can be expressed as partition coefficient $K_{gp}=C_g/C_p$, ratio of flavour concentration in air phase C_g with concentration in product phase C_p at equilibrium. The analysis of headspace concentration above the product at equilibrium leads to estimation of the level of interaction between flavour and matrix. However, when food is eaten the equilibrium is not achieved, since both aqueous and gas phases are undergoing dilution. In this case, the key parameter influencing the rate of release of volatiles from aqueous to air phase, is mass transfer, which is determined by diffusion coefficient and thus viscosity [2].

This work is aimed to investigate the effect of hydrocolloids on flavour release from viscous food model solutions in relation to the concentration of hydrocolloid and rheological properties of the model system. Static headspace – gas chromatography was used to measure interactions between hydrocolloids and aroma compounds in thickened solutions. Time dependant flavour release measurements by dynamic headspace – gas chromatography were performed in order to evaluate mass transfer of volatiles from aqueous to air phase in hydrocolloids solutions of different viscosities.

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FIVE-COMPONENT FOOD GRADE OIL-IN-WATER NONIONIC MICROEMULSIONS: STRUCTURAL CHARACTERIZATION

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MICROEMULSIONS HAVE ATTRACTED CONSIDERABLE ATTENTION IN MANY INDUSTRIAL APPLICATIONS SUCH AS COSMETICS, FOODS, PHARMACEUTICALS, PESTICIDES AND COATING MATERIALS IN THE LAST DECADE. THERE IS CURRENTLY A SIGNIFICANT INTEREST IN FORMATION OF OIL-IN-WATER MICROEMULSIONS FOR FOOD APPLICATIONS. ONE OF THESE APPLICATIONS IS UTILIZING O/W MICROEMULSIONS AS A MICROREACTOR WHICH OFFERS A NEW OPPORTUNITY FOR THE GENERATION OF FOOD ACTIVE MATERIALS SUCH AS THE FORMATION OF FLAVORS FROM MAILLARD REACTIONS. VERY LITTLE WORK HAS FOCUSED ON RESEARCHING THE FORMATION AND THE PHASE BEHAVIOR OF FOOD-GRADE MICROEMULSIONS.

The phase behavior of the system of R(+)-limonene, ethanol, (1/1) water/propylene glycol (PG) and polyoxyethylene sorbitan monostearate (Tween 60) containing a 1:1:3 R(+)-limonene:ethanol:surfactant weight ratio is characterized by an extended single continuous isotropic region starting from an oil-rich solution containing no aqueous phase (reverse micelles) to the water/propylene glycol (1/1) corner (swollen direct micelles). The microemulsions seem to be attractive for food applications. Along this dilution line, NMR self-diffusion, viscosity, and conductivity measurements indicate that the microstructure changes gradually, smoothly and continuously upon increasing the aqueous phase content. The microemulsion transforms from a water-in-oil (W/O) microemulsion, to a bicontinuous phase and to an oil-in-water (O/W) microemulsion. The so-called L-ratio of the water self-diffusion coefficient (D_w), to the PG self-diffusion coefficient (D_{PG}), was found to be sensitive to the aqueous phase content. In the O/W microemulsions, the water/PG mixture diffuses as hydrogen bonded entity (molecular diffusion controlled), while in the W/O microemulsions, the PG partitions, in part, at the interface and the dominate diffusion process is neither aggregate nor molecular controlled. The microstructure of these temperature insensitive systems have been studied also using small angle scattering techniques (SAXS, and SANS), and dynamic light scattering. The maximum dimension of these systems in the aqueous-rich region (≥ 60 wt% aqueous phase) is about 8-10 nm. Their $p(r)$ functions have the typical shape for globular, almost spherical systems. We conclude that the ethanol penetrates into the surfactant interface and acts as a cosurfactant, while it appears that PG behaves as a cosolvent and acts to change the polarity of the water.

CATIONIC SURFACTANTS FROM ARGININE: STRUCTURE-ACTIVITY RELATIONSHIP

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Owing to the trend toward greater environmental awareness and protection, there is a pressing need for high-performance surfactants that are multifunctional, biodegradable and biocompatible. Lipoaminoacids and glycerolipids are natural compounds that can be considered environmentally friendly surfactants with low toxicity when the length of alkyl chains is in the range of eighth to sixteen carbon atoms.

In the last decade our group has developed three families of novel cationic surfactants derived from arginine which exhibit properties of both lipoaminoacids and glycerolipids. The first family includes N^α-acyl-arginine methyl esters which are antimicrobial compounds with low toxicity profiles.

The second family are gemini cationic surfactants from arginine, which can be considered dimeric of the N^α-acyl-arginine methyl esters. The new compounds improve the effectiveness and efficiency of their single chain homologues.

The third family includes two groups of compounds: cationic monoglycerides and diglycerides, both derived from arginine. These new surfactants show similar aggregation behaviour to those of diglycerides and phospholipids, easy formation of liposomes and antimicrobial activity due to the presence of aminoacid arginine as polar head.

We have studied the influence of the alkyl chain length and the chemical structure on two physicochemical properties, and on two biological properties. The first group includes critical micellar concentration and qualitative phase behaviour. The second group includes antimicrobial activity and acute toxicity against *Daphnia magna*. The critical micellar concentration was determined applying three different techniques: surface tension, conductivity, and fluorescence measurements. Qualitative phase behaviour of binary water/surfactants systems as a function of temperature was studied by optical microscopy. Antimicrobial activities were determined in vitro on the basis of the minimum inhibitory concentration MIC values.

INTERACTIONS OF RUTIN WITH ANIONIC MICELLES

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FLAVONOIDS ARE POLIPHENOLIC TYPE COMPOUNDS, PRESENT IN PLANTS IN SUBSTANTIAL AMOUNTS (0.5-1.5%), WITH ANTIOXIDANT PROPERTIES. GROWING EVIDENCE ABOUT THE RELEVANCE OF HUMAN DIET AND SUPPLEMENTATION WITH VITAMIN TYPE ANTIOXIDANTS IN THE PREVENTION OF AGE RELATED DISEASES, NAMELY CERTAIN CANCERS, CORONARY THROMBOSIS, DIABETES OR CATARACTS HAS LEAD TO EXTENSIVE STUDIES OF THESE NATURAL ANTIOXIDANTS, EVER SINCE THEIR DISCOVERY[1].

THESE COMPOUNDS ARE CHARACTERIZED BY A C₆-C₃-C₆ FLAVONE OR FLAVANOL LIKE SKELETON, WHERE THE THREE CARBON BRIDGE BETWEEN PHENYL GROUPS IS COMMONLY CYCLIZED WITH OXYGEN. DIFFERENTIATION IN TERMS OF THE DEGREE OF UNSATURATION/OXIDATION OF THIS SEGMENT, AS WELL AS TERMS OF THE NUMBER AND TYPE OF SUBSTITUENT GROUPS (HYDROXYL, SUGAR, METHYL GROUP, ETC) HAS ALLOWED THE IDENTIFICATION OF OVER 5000 DIFFERENT SPECIES. *IN VITRO* STUDIES HAVE SHOWN THE RADICAL SCAVENGING ABILITY OF THESE COMPOUNDS BUT NUMEROUS IRREGULARITIES HAVE BEEN OBSERVED IN TERMS OF STRUCTURE-PERFORMANCE RELATIONSHIPS EVALUATIONS, AN ASSESSMENT ATTRIBUTED TO THE WIDE RANGE OF PROCESSES THAT MAY BE INVOLVED NAMELY HYDROGEN DONATION, METAL CHELATION, OR DIFFERENCES IN HIDROFOBICITY WITHIN THE FAMILY [1]. CONSEQUENTLY PARTITION/ADSORPTION/INTERACTION STUDIES OF THESE COMPOUNDS TO/ON/WITH BIOLOGICAL MEMBRANES ARE ESSENTIAL IN TERMS OF A MOLECULAR COMPREHENSION OF THE FLAVONOIDS' PROTECTIVE MECHANISMS.

In this work anionic micelles of sodium dodecylsulfate and octylsulfate were used as membrane mimetic systems and micelle interactions with rutin (3-*O*-rutinoso-3',4',5,7-tetrahydroxiflavone), within physiological concentrations evaluated[1]. Conductance and density measurements were performed and the experimental data assessed in terms of surfactant critical micelle concentrations (cmc) and apparent partial molar volumes (V_{ϕ}). Micelization shifts, solute-micellar aggregate interactions and solute-monomer interactions were rationalized in terms of the surfactant head group as well as the two moieties of this particular flavonoid [2,3].

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PRECIPITATION OF CALCIUM CARBONATE POLYMORPHS BY ENZYME-CATALYZED REACTIONS

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The present study deals with the influence of two different types of urease: plant and bacterial enzymes fractionated from *Canavlia ensiformis* and *Bacillus pasteurii*, respectively, on the precipitation of calcium carbonate polymorphs in solutions of calcium salts and urea at room temperature. Our previous investigations have shown that calcium carbonate polymorphs and strontium and barium carbonates can be precipitated by the activity of enzyme urease, added to solution containing calcium, barium, and strontium salts, and urea at room temperature [1-3]. In this study it has been shown that the formation of different polymorphs and morphologies of calcium carbonate precipitates was affected by the type and concentration of enzymes. Despite similarity in their amino acid sequences and in catalytic decomposition of urea, these enzymes caused precipitation of different calcium carbonate polymorphs. Thus, under the same experimental conditions, the presence of *Bacillus pasteurii* enzyme in reacting solutions governs precipitation of vaterite, while calcite was formed in the presence of *Canavlia ensiformis* urease. In addition, these enzymes exert different influence on development of calcite faces, and significantly modify the morphology of obtained particles. These results offer insight into the role of enzyme macromolecules in the precipitation of calcium carbonate polymorphs in some biogeochemical processes in natural environments.

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INORGANIC NANOMATERIALS: SYNTHESIS, CHARACTERIZATION, AND APPLICATION IN WORKS OF ART CONSERVATION

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In the field of porous materials conservation, nanosized inorganic consolidating agents can have much better performances than traditional products, in terms of efficacy of the treatment and durability. Considering the different typologies of manufacts that can be affected by degradation (frescoes, carbonatic stones, lime and gypsum plasters), we selected two kinds of binders: $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. The aim of this work was to synthesise and characterize nanosized particles of these materials and test them on real specimens.

Both $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (precursor of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, plaster of Paris) were obtained by reaction in aqueous phase containing sucrose as an additive: sugars can have a retarding action on nucleation and growth of crystalline phases and affect their size and morphology. Several syntheses were conducted by adopting different concentrations of sucrose: the formation of solid phase and the size of $\text{Ca}(\text{OH})_2$ particles were strongly affected by the concentration of sugar, and crystallinity of the products was confirmed by XRD. No influence was observed on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ size (20-100 microns needles). Addition of 2-propanol to water dispersions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ caused the average length of needles to lower: 2-5 microns. Ortorhombic, 50-100 nm particles of plaster of Paris were obtained after partial dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

2-propanol dispersions of nanosized $\text{Ca}(\text{OH})_2$ particles obtained by a previously developed synthesis (ethylene glycol as a reaction medium [1]) were applied on degraded stone samples (*Gallina* and *Alberese* carbonatic stones) and on specimens simulating flaking of the paint layer, with positive results assessed by capillary rise measurements, SEM, and EDX analyses.

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NANOSIZED Ca(OH)₂ PARTICLES: SYNTHESIS, CHARACTERIZATION, AND REACTION WITH CO₂

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The purpose of this project was to investigate the synthesis and the characterization of nanosized Ca(OH)₂ particles, with the aim of studying their behaviour against carbonatation in view of potential applications in the field of frescoes conservation. At first we synthesized nanoparticles from water-in-oil (w/o) microemulsions trying to develop the suitable microemulsion system that could allow to reach high concentration of the reactant species into the core of the droplets. The selected system was the ternary Igepal-CO520/cyclohexane/water [1] at various water concentrations and temperatures; the phase diagram at 25°C was investigated too. The synthesis of Ca(OH)₂ nanoparticles [2] was carried out as a function of the w_o parameter. The obtained nanoparticles were characterized by TEM and SEM microscopy: the particles showed as hexagonal platelets with a thickness of a few nanometers and sizes around 60 nm.

The second part of the research concerned the study of the behavior of Ca(OH)₂ nanoparticles synthesized from homogeneous phase at 90°C [3] against carbonatation by atmospheric CO₂. The carbonatation of the particles was morphologically followed by SEM and TEM microscopy in different conditions of relative humidity and CO₂ concentration; FTIR spectroscopy allowed to detect the calcite formation [4].

The same carbonatation reaction was studied by spreading Ca(OH)₂ dispersions in 1-propanol on the calcite {101} crystallographic plane; we found that the most of Ca(OH)₂ hexagonal platelets oriented parallel to the {101} plane. Moreover, after carbonatation this configuration was retained showing calcite particles oriented parallel of same plane.

All these results presents particular interest in the field of frescoes conservation, since the reaction of Ca(OH)₂ nanoparticles with atmospheric CO₂ is responsible for fixing the coloured pigments onto the wall surface.

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SALT CRYSTALLIZATION IN POROUS MATERIALS: PHYSICOCHEMICAL ASPECTS

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This study dealt with the problem of crystallization within porous materials. Growth of salt crystals in the pores of stones or wall paintings generates stresses that can lead to serious damages. This effect is similar to the one observed in freeze/thaw phenomena.

The aim of the present work was to study these processes of crystallization and the mechanisms that originate stresses within the pores. The porous supports studied were: *Firenzuola* stone (sandstone), *Lecce* stone (carbonatic stone), brick, two types of ceramic material, and some kinds of mortar. The salts chosen were among those more commonly present as degrading agents of monuments: Na_2SO_4 and KNO_3 . The solutions of these salts were prepared near the saturation.

We report the characterization of the supports and the study of the effects on the processes of crystallization within the porous structure. We followed the crystallization of the pure solutions and of the same solution in the presence of particular compounds, namely organo-aza-phosphonates that inhibit the crystal growth. In particular, we used the following additives: 1,5,9,13-tetraazatridecane (name trades Dequest 2086) and 1,4,7,10,13,16-esazaesadecane (Penten). The stone samples were characterised with respect to porosity by Hg pycnometer, He pycnometer, and Hg porosimetry. The morphology were studied by SEM and ESEM.

The final purpose was to find a way to prevent or reduce the crystallization effects causing the damage on the architectonic/artistic materials.

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NANOSIZED PARTICLES OF Mg(OH)₂: SYNTHESIS AND APPLICATION IN PAPER CONSERVATION

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PAPER DE-ACIDIFICATION IS A FUNDAMENTAL PROCESS FOR THE CONSERVATION AND RESTORATION OF PROBABLY THE MOST IMPORTANT MATERIAL USED TO TRANSMIT CULTURAL HERITAGE.

BASICALLY, THE PAPER DEGRADATION IS DUE TO THE DE-POLYMERIZATION OF CELLULOSE FIBERS, AND THIS PROCESS IS PROMOTED BY ACID PH.

Nanosized particles of Mg(OH)₂ have been synthesized in order to prepare basic nonaqueous nanodispersions, to be used for deacidification treatment.

Two different reaction pathways have been studied: (i) high temperature and supersaturation degree was selected as control parameters to increase the nucleation rate in order to reduce the particle dimensions; (ii) sugar additives of varying concentration and different Mg-source salts were used for the synthesis at room temperature. Both methods show that inorganic particle size and shape appear to be very easily adjustable with great yield. SEM, TEM, XRD, Z-potential, and surface area analysis provided a physico-chemical characterization of the nanoparticles.

Finally, deacidified paper samples, dating from 19th century, were submitted to artificial aging by hydrothermal treatment and light exposure. The kinetic of paper degradation was checked by colorimetry and measurements of the polymerization degree. The experiments showed that this deacidification treatment worked with efficacy. Finally, Mg(OH)₂ nanodispersions can be applied to paper, by using conventional procedures. This new method is environmentally clean, inexpensive and can be also used for industrial processes.

EFFECT OF GALACTOMANNAN'S MOLECULAR WEIGHT ON THE HEAT-INDUCED GELATION OF WHEY PROTEINS

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Several polysaccharide-protein systems are used in the food industry to improve functionality and to develop new gelling and thickening systems. Their properties have been explained either by demixing due to thermodynamic incompatibility or by the formation of complexes by electrostatic interactions [1].

It was previously shown that the presence of a neutral polysaccharide has a significant effect on the formation and viscoelastic behaviour of whey protein gels, an effect strongly dependent on the structural organisation of the protein network [2]. The aim of the present work was to study the influence of the molecular weight of the galactomannan sample on the rheological behaviour and microstructure of whey protein/galactomannan mixtures, under gelling conditions close to the electroneutrality of the protein component.

Under the pH conditions used in this study (pH=5), close to the protein isoelectric conditions, the whey protein network corresponds to a particulate gel [3]. The galactomannan samples, having a mannose-to-galactose ratio of 3.8 and different molecular weights, ranging from about 300 to 2000 kDa, were obtained by controlled enzymatic hydrolysis with β -mannanase, from a purified locust bean gum sample.

The effect of the galactomannan samples on the viscoelastic behaviour and microstructure of the protein system, during its thermal-induced gelation and after curing, has been monitored by dynamic oscillatory measurements and by transmission electron microscopy.

Under the studied ionic conditions, the galactomannan addition can have either a detrimental effect on gelation, at low protein concentrations, or a positive influence on the gelation process at higher concentrations. The magnitude of both effects is clearly influenced by the polysaccharide molecular weight, increasing as the molecular weight increases. An explanation is given based on the structure of the particulate network (pore and particle size), the expected biopolymer segregation and "local" concentration of each component, and the consequences of the filling effect on the gel viscoelasticity.

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EFFECT OF COMMERCIAL C₁₂E₃, METHYL OLEATE ON THE PHASE TRANSITIONS OF CARNAUBA WAX

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Additives present in agrochemical formulations play a very important role in promoting the effects of chemicals such as insecticides and herbicides [1]. One possible mechanism is that the additives increase the permeability of the epicuticular wax of the insect or plant species through plasticisation [2]. To examine this mechanism, the effects of two popular additives in agrochemical formulations, C₁₂E₃ and methyl oleate, were investigated. DSC, FTIR, X-ray diffraction and NMR were employed to study the phase transitions in the wax. Carnauba wax, which comes from palm tree leaves, was chosen to simulate the natural epicuticular wax of cereal and grass species.

On the carnauba wax DSC curves of the second heating runs, there are three distinguishable peaks at 58.9, 77.1 and 81.9 °C respectively which correspond to the first solid-solid (s-s) transition, the second s-s transition and the normal melting transition [3]. Their enthalpy changes are 8.7, 81.29 and 97.94 Jg⁻¹ correspondingly that sum up 187.93 Jg⁻¹. This contrasts with previous reports on the melting behaviour of this wax [4]. The presence of C₁₂E₃ or methyl oleate reduced the melting point and the second s-s transition temperature. Small additions of these additives increased the first s-s transition temperature of the wax. X-ray diffraction showed no structural changes in the carnauba wax with increasing temperature. The same phenomena were observed in the presence of C₁₂E₃ or methyl oleate except for the lowered melting point of the carnauba wax. FTIR and NMR were used to measure the percentage of liquid in the mixtures (sometimes referred to as the amount of amorphous material). The amorphous content is thought to be important in determining the rate of diffusion of xenobiotics through cuticular surfaces.

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