

RHODIA & PLENARY LECTURES

LIQUID CRYSTAL PHASE TRANSITIONS IN SUSPENSIONS OF INORGANIC ROD AND PLATELIKE COLLOIDS: NEW LIFE FROM OLD ROOTS

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One of the most remarkable phenomena exhibited by concentrated suspensions of colloidal particles is the spontaneous transition from fluid-like structures to those exhibiting long-range spatial and/or orientational order (colloidal crystals and colloidal liquid crystals). The fact that such ordering can occur in suspensions in which interparticle forces are purely repulsive provides a dramatic realization of the predictions made by Lars Onsager in the 1940's and later substantiated by computer simulations. From these studies it is clear, that the ordering is driven by entropy.

Liquid crystalline phases in suspensions of mineral colloidal particles have been known for a long time. Zocher reported in 1925 on the observation of a nematic phase in suspensions of V_2O_5 and a smectic phase in suspensions of β -FeOOH.

Later in 1938 Langmuir reported on sols of California bentonite clay particles that after standing for several 100 hours separated into an isotropic and nematic phase.

In recent years the number of mineral colloidal liquid crystals has steadily increased. These systems are interesting due to the fact that size and shape of the particles can be tuned by dedicated chemical synthesis methods leading to novel and interesting phase behavior. Modern optical microscopy and Synchrotron X-ray scattering techniques allow these systems to be studied in detail. Furthermore the electric magnetic and optical properties can be varied over a wide range leading to interesting phenomena. In this talk I will review the phases formed and their structural characteristics and compare the results with computer simulations and theoretical predictions.

MAGNETIC COLLOIDS AT THE AIR/WATER INTERFACE

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We have developed a system of super-paramagnetic colloidal particles confined by gravitational pinning at the free water-air interface in a hanging drop geometry. The interface is essentially flat making the system truly two-dimensional. Inter-particle (dipole-dipole) interactions are controlled by a vertical external magnetic field and time dependent particle positions are measured by video-microscopy.

In this contribution I will review several recent investigations which highlight that this system is an almost ideal model system for fundamental issues in 2D solid state physics. (a) The two step melting scenario of hexagonal crystals [1,2] including their elastic properties as measured from strain fluctuations [3] and deformations using optical tweezers [4] (b) local and non-local structural and dynamic features near the glass transition in binary mixtures [5,6], the role of hydrodynamic interactions [7,8] and higher order correlations [9] in the 2d fluid phase.

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NANOSCIENCE – BRIDGING FOOD MATERIAL SCIENCE WITH NUTRITION AND CONSUMER SCIENCE

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The challenge of future food production lies in providing healthy and delightful foods. In the realisation of this goal, it is crucial that nutrition and food material and consumer science are working hand in hand. Nutritionists will tell us what is good for us and how foods are metabolised in our bodies. Consumer scientists elaborate what is liked and elucidate the underlying perception mechanisms. Food scientists will be challenged to translate the know-how we have from consumer science and nutrition into new food structures providing the necessary sensorial and health benefits. Applying nanoscience concepts, i.e., structure formation on a nanometer length scale, will allow us to design novel structural elements with properties specifically tailored to the required functionalities such as carriers for flavour release or targeted delivery of functional molecules. Of specific interest are nanostructures formed via self-assembly processes from food ingredients.

In the present paper we will discuss strategies for applying self-assembly structures in food systems. A prominent class of food ingredient with self-association behaviour are emulsifiers such as monoglycerides and phospholipids, which are widely used in the food industry [1]. Monoglyceride self-assembly structures were shown to be an excellent entrapment medium for flavour molecules [2] and can be used as carrier systems for insoluble nutritionally active compounds. Self-assembly nanostructures can also be used to control chemical reactions occurring during Maillard reaction. The yield in Maillard reaction products between amino-acids and sugars in monoglyceride w/o microemulsion (L_2 phase) and in a bicontinuous cubic phase is remarkably higher in these nanostructured fluids than in water.

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GENE DELIVERY WITH CATIONIC POLYMERS

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GENE THERAPY AIMS TO TREAT INHERITED OR ACQUIRED GENETIC DEFICIENCIES BY INTRODUCTION OF DNA ENCODING FOR A THERAPEUTIC PROTEIN INTO THE TARGET CELL. HOWEVER, A CARRIER SYSTEM IS REQUIRED TO DELIVER DNA INTO THE RIGHT CELL. CATIONICALLY CHARGED WATER-SOLUBLE POLYMERS FORM AN ATTRACTIVE CATEGORY OF DNA DELIVERY SYSTEMS. IN THIS PRESENTATION SOME RECENT DATA OBTAINED WITH METHACRYLATE-BASED POLYMERS AS NON-VIRAL GENE CARRIER ARE DISCUSSED.

EM STUDY ON STRUCTURAL CHANGE OF SILICA MESOPOROUS CRYSTAL WITH SYNTHESIS PERIOD

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Three dimensional (3d-) structure of silica mesoporous crystals can be controlled by choosing proper synthesis conditions such as amphiphilic molecules and their compositions, temperature and basic or acidic media. An important aspect is that the mesoporous silica system is formed not in equilibrium but in kinetic, therefore their structures are dependent not only on thermodynamic parameters but also on history of the synthesis.

Recently we have developed a method to solve 3d-structure of silica mesoporous crystals uniquely and straightforwardly based on electron crystallography (EC) through Fourier analysis of HREM image, which carries both phase and amplitude information of crystal structure factors. By the EC, we solved 3d-structure of SBA-1, where two cavities with different sizes, A and B, are arranged periodically in a SG of $Pm\bar{3}n$ at a composition of A_3B . High quality cubic $Pm\bar{3}n$ mesoporous SBA-1 crystal shows a highly isotropic morphology with fifty-four or seventy-four crystal faces indicating PG of $m\bar{3}m$.

I will report at the Conference structural changes with synthesis period, e.g., the initially formed 2d-hexagonal crystal of $p6mm$ to the cubic $Pm\bar{3}n$, and others. I will also try to discuss a role of EM for observing Micro-, meso- and macro-scale structured materials.

FORMATION OF CARBONATE-SILICA “BIOMORPHS”

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Novel self-assembled colloids are prepared by precipitation of barium carbonate (witherite) in the presence of silica under alkaline conditions. The particles exhibit complex structuring, with the smallest building blocks consisting of nanometric witherite crystallites encased in silica. The crystallites are orientationally ordered, resembling chiral liquid crystals. Larger scale shapes vary depending on the formation conditions, from spherulites to beautiful twisted filaments. Carbonate species can be selectively dissolved, leaving a templated silicate skin, whose micron-scale morphology resembles primitive bacteria. The work has major implications for current understanding of the emergence of life on earth, dated by Archean era “microfossils”, whose features we have reproduced in every respect abiotically [1].

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COLLOID DYNAMICS IN CONFINED MEDIA

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The transport properties of adsorbed or confined colloids can be very different from the bulk transport properties.

We present a review of our work on the interfacial rheology of soap films containing polymers, of surfactant and polymer monolayers and on the diffusion and transport properties of beads and DNA molecules embedded in soap films or between two glass plates.

We shall discuss the potential applications of the developed measurement set-ups.

HIERARCHICAL STRUCTURE AND MECHANICAL PROPERTIES OF NATURAL MINERALIZED TISSUES

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Natural mineralized tissues such as bones or teeth are hierarchically structured and optimized for mechanical performance at all levels of hierarchy [1]. The basic unit is a collagen fibril reinforced with calcium phosphate nanoparticles. Such fibrils are assembled into a complex composite structure [2] which is far from being completely understood. A successful approach to study hierarchical structures is scanning microfocus x-ray scattering complemented with scanning electron microscopy and nanoindentation [3]. These techniques allow simultaneous characterization of the nanometer scale structure, via x-ray scattering, and of the micrometer scale by scanning the specimen across the narrow x-ray beam, which has a diameter of a few μm or less. The size, shape and arrangement of the mineral nanoparticles are essential for the mechanical performance of the composite [4]. They are seen to vary systematically with age [5], at the interfaces between dentin and enamel [6], or bone and cartilage [7]. One essential structural feature is the elongated shape of the mineral particles, which allows the transmission of considerable shear forces by the organic matrix between the particles [5]. A second is the size and local orientation of nanoparticles, whose variation on a length scale of several tens to hundreds of micrometers results in graded mechanical and structural properties of the tissues [6,7].

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SELF-ASSEMBLED ICOSAHEDRA: A MICROCRYSTAL, A CLEAVED IONIC SOLID OR A “GIGAMOLECULE”?

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Mixing slowly poorly soluble anionic and cationic amphiphiles, in the absence of any counterion other than H^+ and OH^- , is a general way to produce in a reversible manner a new type of molecular aggregates only bound by non-covalent interactions with peculiar properties:

- sandwich structure of the bilayer, with two hexagonal surface lattices of alternated charges embed crystallized chains produces colloids with the stiffness of clay, so this is a new and general method to obtain synthetic purely organic flat whiskers.

- once formed, these micro-cystals can be diluted, each aggregate behaving like a molecule, with a characteristic mass up to 10^9 Dalton.

- the aggregates formed can be considered as an infinitely cleaved ionic solid, with interesting properties related to intra- as well as inter-particle long range electrostatic interaction, i.e. a two dimensional analogue of a polyelectrolyte. The net charge is controlled by initial mole ratio.

We propose that shapes and topologies produced (punctuated planes, faceted objects including regular icosahedra and nano-discs of controllable size) are all produced by a general principle of molecular segregation during co-crystallisation. This in-plane molecular segregation molecular is closer to mechanism of formation of rafts and bicelles than the quasi-equivalence principle, which is the molecular motor for self-assembly of viral aggregates.

KEYNOTE LECTURES

PHASE DIAGRAMS, MICROSTRUCTURES AND INTERACTIONS IN ALKYL GLUCOSIDES

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Alkyl glucosides (AG) are non-ionic surfactants derived from sugar. They have some definite advantages as compared to more traditional surfactants such as good biodegradability and dermatological properties.

In this communication I will attempt to summarize our work on this interesting class of surfactants. Thus I will discuss the appearance of phase diagrams, both from binary AG/water and ternary AG/water/additive (where additive is a hydrocarbon or co-surfactant) systems. The phase diagrams have been derived from D₂O NMR experiments but also using both differential scanning calorimetry and a novel sorption calorimetric method, that allows the determination of very accurate phase diagrams in concentrated systems. The latter technique also conveys information about interactions in the investigated systems.

I will further describe the microstructure of the phases found, focusing on the connection between the microstructure and the characteristic liquid-liquid phase separation, which occurs in some AGs. The experimental technique used to determine the microstructure in solution phases is NMR diffusometry, while SAXS experiments have been used to characterize liquid crystal phases.

PARTICLES AND POLYELECTROLYTES: CONTROL OF NANOPARTICLE FORMATION AND CRYSTALLIZATION IN WATER

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Organic and inorganic nanoparticles find use as paints, food additives, adhesives, dispersion colors, and UV-absorbers; in industry they play an important role in the formulation of pigments and in the production of catalysts. Furthermore, nanoparticles occur as intermediates in crystallization processes; in seawater desalination plants as well as in the washing machine these nuclei must be stabilized by suitable polymeric additives in order to prevent encrustation.

The *formation* of organic and inorganic nanoparticles and crystals from highly supersaturated solutions is a complex process that often proceeds via various intermediate stages [1] - and not by simple nucleation/growth processes. Precursor structures such as amorphous and/or hydrated nanoparticles may occur, which aggregate and/or dissolve before finally recrystallizing. Structural information on these intermediates is essential when developing polymers to control crystallization processes - either to achieve particles of a certain size or to prevent crystallization on surfaces [2].

We review the state of knowledge with respect to precursor structures that occur in particle formation processes from the aqueous phase. Emphasis is put on how to obtain time-resolved data by combining microscopic and scattering methods.

It will be discussed how particle formation/crystallization can be controlled by the use of polyelectrolytes, where several modes of action can be identified: (i) stabilization of the intermediate nanoparticles, (ii) prevention of recrystallization due to the effective wrapping in of the nanoparticles, (iii) impediment and modification of crystal growth by blocking the respective growing crystal surfaces. Which of these mechanisms is active depends on the type and the amount of polymer used.

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ENGINEERING ADVANCED LIPID-BASED DELIVERY VECTORS BY APPLICATION OF COLLOID & INTERFACE SCIENCE PRINCIPLES: TRANSITIONS FROM GENE TO CANCER THERAPEUTICS

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Construction of novel delivery vehicles toward optimization of therapeutic agent transportation and release at the desired diseased site is a challenging technology, requiring a multidisciplinary knowledge-base. Manipulation and application of fundamental colloid chemistry and particle engineering principles to modify and design delivery systems, constitutes a direction that can lead to novel biomaterials useful as delivery devices for various therapeutic or diagnostic applications. In the present communication, recent efforts of different approaches in engineering lipid-based delivery systems will be described, each focusing on improvement of a specific pharmacological obstacle before achievement of a therapeutic goal, in this way transcending from gene therapy to tumor therapeutics. First, by manipulating the surface, aggregation and flocculation behavior, and physicochemical interactions with other molecules of a genetically modified, replication-defective virus population, novel gene delivery vectors were engineered. The new molecular complexes exhibited altered biological and pharmaceutical profiles *in vitro* and *in vivo*, constituting a distinct class of gene transfer vectors. Towards a different therapeutic approach, the interaction of physicochemically different liposome systems with multicellular spheroid tumor models illustrates the effect their surface characteristics have on their intratumoral transport and diffusion, factors extremely crucial in determining the overall therapeutic efficacy of any cancer drug. Throughout those studies one fundamental issue is asserted: the opportunity to rationally design optimum delivery systems for gene therapy or other therapeutic applications by simply exercising colloid and surface engineering principles and techniques to manipulate established and powerful agents (biological, radiological, chemical) towards their transformation to effective therapeutics.

DRY EMULSIONS: PHYSICAL-CHEMISTRY, PROCESS AND APPLICATIONS

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Water transportation, emulsion metastability, premature reaction between two reactive oils during storage, handling, toxicological issues, are key problems in the industry. One of the answers is from a liquid make a powder by obtaining dry emulsion.

Principle to manufacture a dry emulsion is the following: add a natural or synthetic polymer to an oil-in-water emulsion, then dry this emulsion containing additives – by spray drying for example, finally collect and store a free flowing powder. This powder is redispersible in water and the emulsion is recovered, ready for application.

Of course, dry emulsions are known since powder milk or dried aroma are used for food applications [1]. Main limitation to a larger use of these dry emulsions has been for years the limited pay load in encapsulated liquid (30%) [2]. One will show that this limitation is due to emulsion unstability upon drying. The aim of this study was to closely link physical-chemistry to process and to demonstrate how with new developments, pay load up to 65% in encapsulated liquid can be achieved [3].

Various applications are targeted for these new dry emulsions. Markets like Agrochemical are specifically developed [4].

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INELASTIC X-RAY SCATTERING STUDY OF PHONONS IN LIQUID CRYSTALLINE DNA

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A high resolution x-ray scattering method is used to measure spectra of the collective density oscillations propagating along the axis of a rod-like supra-molecular system made of a shear-aligned columnar hexagonal liquid crystalline phase of DNA dispersed in water. The dynamic structure factor is extracted from the spectrum using a Generalized Three Eigenmode theory developed by one of us earlier. The dynamic structure factor consists of three Lorentzian lines, one central Rayleigh and two symmetrically shifted Brillouin peaks, from which the thermal diffusion coefficient, the phonon frequency and damping can be obtained. We investigated three systems: a 40 wt % calf-thymus DNA of molecular weight 8.4×10^7 Daltons (13,000 base pairs) in water; and 40% DNA in water with 8.5 mmol of $MgCl_2$ and $ZnCl_2$ respectively added. The phonon dispersion relations obtained show an oscillatory behavior in the Q (magnitude of the scattering vector) range of 2 nm^{-1} to 30 nm^{-1} , similar to that obtained from lipid bilayers before. The dispersion relation of 40% DNA rods in pure water, for example, starts with a linear dispersion at low q with a high-frequency sound speed of about 3100 m/s, similar to that observed in bulk water, reaching a maximum of $\omega = 12 \text{ meV}$ at $q = 9 \text{ nm}^{-1}$, going down to a valley at $q = 18 \text{ nm}^{-1}$, coming up to a secondary (lower) maximum at $q = 25 \text{ nm}^{-1}$ and eventually going down to zero at $q = 30 \text{ nm}^{-1}$. One major distinctive feature of the DNA systems from liquids is that the dispersion relation in the shear aligned DNA extends to a considerably higher q than that observed in liquids. The extended range of q includes q values corresponding to that in the second Brillouin zone in a crystalline system. This latter feature implies that a DNA rod can be regarded approximately as a one-dimensional crystal, as far as the density oscillations are concerned. This signifies that one ought to be able to extract the stretching force constant of a single DNA molecule from the analysis of the dispersion relation. The details of the analyses of the three systems studied will be presented.

STRUCTURAL AND FUNCTIONAL FEATURES OF THE BICONTINUOUS CUBIC PHASES OF LIPIDS WITH ENTRAPPED BIOMOLECULES: SPECTROSCOPIC AND ELECTROCHEMICAL APPROACH

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Interactions of lipids with proteins and low-molecular-weight lipophilic biomolecules play a significant role in many biological systems and biochemical processes. The digestion of fats, transport of lipids, and, of course, biomembranes should be considered as the prominent examples of the above statement. In biomembranes, lipids and proteins are the dominant constituents. On the average, proteins account for about half of the membrane mass in eukaryotic cells. In parallel with these biopolymers, biomembranes contain several functionally important molecules of lower molecular weight – ubiquinones, plastoquinones, lipophilic vitamins. Thus, not surprisingly, the efforts to explore the unique features of biomembranes have stimulated a considerable body of work performed on the biomimetic lipidic systems with entrapped guest-biomolecules. In this respect, there is no doubt that the reversed bicontinuous cubic (Q_{II}) phases of lipids are among the most elegant models of the lipid bilayer. Moreover, as pointed out in several studies, a number of cubic mesophases have been observed in conditions close to those prevailing in living organisms, and seem to be involved in different biological processes. In parallel with the biomimetic value, the Q_{II} phases are also gaining in practical importance. These functionalized 3D-structures may be used as matrices for membrane protein crystallization, protein and drug delivery systems for pharmaceutical applications, and also as biocatalytically active layers in biosensors.

In our research, the principal emphasis has been on two topics:

(i). Structural features of the functionalized Q_{II} phases of lipids have been studied by X-ray diffraction, Raman and FT-IR spectroscopic techniques. Among the entrapped biomolecules were: proteins lysozyme, cytochrome c and glucose oxidase; lipophilic biomolecules vitamin K_1 and ubiquinone-10. In these studies, the focus was on the phase types, their stability, crystallographically determined parameters, and interactions at a molecular level.

(ii). In the area of electrochemical and bioanalytical applications of the bicontinuous Q_{II} phases with entrapped biomolecules, we cover amperometric and potentiometric systems. To this end, the phases were functionalized by cytochrome c, glucose and L-lactate oxidases, urease, creatinine deiminase, microperoxidase-11. All these systems were characterized in terms of macrokinetics and practical significance.

WHAT IS THE COLLOIDAL TEMPLATE ROLE IN CONTROLLING THE SIZE AND SHAPE OF NANOCRYSTALS?

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In this presentation we will discuss the role of the template to control the particle size and shape [1]. This will be based on reverse micelles and other templates. With some discrepancies, reverse micelles are a rather good candidate for controlling the size of spherical nanocrystals. However, they are not the determining factor in controlling the shape of inorganic materials. Crystal growth on the nanoscale seems to follow behavior similar to that of the bulk phase with a marked dependence on pH. The latter is particularly important when some impurities are present in the growth medium because it influences, e.g., the formation either of zwitter-ions or of complex ions, the efficiency of which is greater than that of the initial impurity. These elements lead to a decrease in the growth rates of certain crystal faces. These conclusions are based on data obtained with copper nanocrystals produced by using $\text{Cu}(\text{AOT})_2$ -isooctane-water solution as a template. Even if the template does not change with various salt additions, the nanocrystal growth markedly depends on the salt used. It is demonstrated that chloride ions enable the growth of nanorods with an aspect ratio varying with chloride concentration. Conversely, only a slight amount of bromide ion is needed to increase the nanorod aspect ratio from 3 to 5 without any changes when increasing the bromide ion concentration. A rather large number of cubes are produced. Formations of nanorods and cubes are explained in terms of anion adsorption on (111) and (100) faces, respectively. By replacing chloride by other ions, the morphology of copper nanocrystals drastically changes. In all cases the nanocrystals formed are fcc single crystals with a polyhedral shape or crystals composed of fcc tetrahedra (deformed or not) bounded by (111) faces. Some cylinders are formed by the connection of 2 different crystals with different 5 fold axes and/or with additional planes. This gives rise to various particle shapes.

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SPECIFIC ION EFFECTS IN THE FORMATION OF INORGANIC COLLOIDS: INSIGHTS FROM MODEL SYSTEMS

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Specific ion effects are ubiquitous in colloid science. In recent years, with the great increase of activity in the area of colloidal (wet chemical) production of new inorganic materials, “spectator” ions have been found to play significant – and some times unexpected - roles in materials syntheses. The situation respecting the production of mesoporous solids was recently reviewed [1], but similar phenomena have been found in the production of metal or semiconductor particles. Specific ion effects are particularly important in procedures that make use of surfactants or polymers as templates, stabilizers, or habit-modifiers. Such ionic effects are closely related to the Hofmeister series of ions, which was created on the basis of salt effects on protein solubility in water [2]. The Hofmeister series appears in a wide range of chemical and biological phenomena, but its exact origin is not quite understood to date, since it stems from the interplay of ion-surface and ion-water interactions. In this presentation, I will try to make the connection between the two worlds: that of inorganic colloid production and that of specific ion effects at surfactant interfaces. To understand the basis of specific ion effects in the complex systems of inorganic colloid synthesis it is useful to consider much simpler model systems. I will discuss two model systems that are currently being exploited both experimentally and theoretically. One is the free surface of electrolyte solutions, with emphasis on the effect of electrolytes on the surface tension of water [3,4]. The other is a sequence of precisely controlled phospholipid structures (micelles, monolayers, and bilayers). The emerging picture supports the notion that specific ion effects act through binding or specific interactions at interfaces, and not through a – more or less obscure – modification of the structure of water, as was believed until recently in the biological community.

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INTERACTIONS BETWEEN IONS, COLLOIDS AND SOLVENTS

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Interactions in colloids and with surfaces are usually modeled with (charged) hard-sphere potentials, eventually completed with chemically mysterious Yukawa or similar potentials. Counterions or added electrolytes are supposed to modify colloidal properties via their charges and, in advanced models, via their sizes. Solvent properties are usually taken into account via the dielectric constant.

However, such simple models never can explain the specificity of ions and solvents, although the influence of ions and solvents beyond their size, charge and macroscopic dielectric constant can be huge. As long as no predictive theory is available, it is difficult to take profit of such specificities for the design of new materials.

The present contribution gives examples of specific ion and solvent effects in complex liquids, especially in colloidal and biological systems. Furthermore, the state of art of the theory of complex electrolyte systems is summarized.

PHOTO-SURFACTANTS

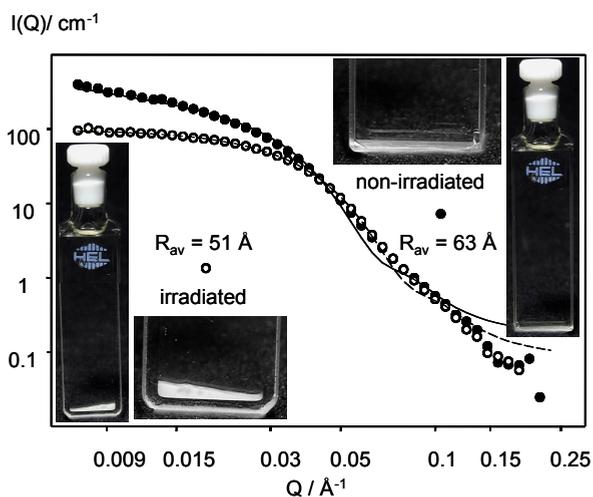
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For surfactants containing a suitable chromophore, light can be used to trigger changes in aggregation and adsorption. The advantage of this approach is it eliminates, or minimizes, the need for composition or temperature changes. New photosurfactants have been synthesized, and photoreactions in water, water-in-oil microemulsions, interfacial properties and changes in aggregation characterized [1]. As such changes in activity under wide range of colloiddally relevant situations has been demonstrated: air-water, oil-water and solid-liquid interfaces, as well as aggregation in aqueous and microemulsion dispersions. These results highlight the importance of molecular design for generating effective and efficient photosurfactants.



Appearance, SANS data (symbols) and analysis (lines) from photo-shrinkable microemulsions.

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INTERFACIAL ENZYMES IN TARGETED LIPOSOME-BASED DRUG DELIVERY

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Secretory phospholipase A2 (sPLA2) refers to a large class of water-soluble interfacially active enzymes that function mainly on organized types of substrate, e.g. micelles and lipid bilayers. The activity of the enzyme is strongly controlled by the lateral organization and the physical properties of the substrate, in particular the structure in the nano-meter range. Lipid bilayers are prone to such small-scale structuring due to their intrinsic softness that implies formation of lipid domains near lipid phase transitions and in phase-separation regions. Results obtained from a variety of experimental and theoretical studies of PLA2 activity on lipid-bilayer substrates will be presented which provide insight into the biophysical mechanisms of PLA2 activation on lipid bilayers and liposomes of different composition. The insight into these mechanisms has been used to propose a novel principle for liposomal drug targeting, release, and absorption triggered by secretory PLA2.

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NANOSCIENCES FOR THE CONSERVATION OF CULTURAL HERITAGE

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Nanotechnology, usually portrayed as the futuristic pursuit of molecular-scale machines, has something to offer to the conservation of Cultural Heritage. As illustrative examples we report some recent methods for the restoration of works of art where microemulsions and nanoparticles of calcium hydroxide have been used to restore frescoes (Beato Angelico, Sogliani, Taddeo Gaddi, Piero della Francesca, etc.), or to de-acidify papers and canvas.

DESTABILISATION OF COLLOIDAL DISPERSIONS BY POLYMERS THROUGH THE MECHANISM OF CAPILLARY- INDUCED PHASE SEPARATION (CIPS)

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Polymers added to a particle dispersion can either increase or decrease the stability of the dispersion.[1] The increase in stability is often a consequence of steric stabilization by adsorption of polymer molecules to the surfaces of the colloidal particles. Two well-known polymer destabilisation mechanisms result from depletion or bridging interactions between the colloidal particles. Recently, a third type of destabilising mechanism has been found in polymer solutions that are close to phase separation, namely the capillary-induced phase separation (CIPS). CIPS induces a long-ranged attractive force between the colloidal particles. The phenomenon of CIPS is driven by the formation of a new phase in the gap between the colloidal particles, as in a capillary condensation, where the new phase has a lower surface energy than the bulk phase.[2]

We have studied the CIPS phenomenon in polymer solutions with dispersed colloidal particles, both experimentally and theoretically. Previous surface force measurements have shown that CIPS occurs both in quasi-binary and in ternary polymer solutions.[3-4] This has been confirmed theoretically by mean-field lattice studies.[5-6] The occurrence of CIPS depends on parameters like the affinity of the polymers to the surfaces, the distance between the colloidal particles and the molecular weight of the polymers. Experimentally, studies of the influence of dispersed colloidal particles on the phase behaviour of quasi-binary and ternary polymer solutions have been carried out, and the results agree qualitatively with the theoretical mean-field studies.[7] However, in some ternary polymer solutions, the phase behaviour changes dramatically by the dispersed colloidal particles, which is not predicted by the CIPS mechanism.

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STRUCTURE AND PHASE STABILITY OF POLYELECTROLYTE-MACROION SOLUTIONS

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polyelectrolytes are polymers bearing ionisable groups, which, in polar solvents, can into charged polymer chains (polyelectrolytes) and small counterions. In aqueous polyelectrolytes interact strongly with other macroions and in particular they tend to form objects of opposite charge and form complexes.

The complexation of linear flexible polyelectrolyte and *one or several* oppositely charged macroions has been studied by employing a simple model system with focus on the electrostatic interaction. [1,2] The composition and the structure of the complex as well as conformational data of the polyelectrolyte were obtained by using Monte Carlo simulations. The binding isotherms Langmuir-like, and in excess of macroions the polyelectrolyte-macroion complex shows a large reversal. These properties were investigated at different linear charge densities, and flexibilities of the polyelectrolyte, and different macroion charges, all at different concentrations of macroions at constant volume. The effect of adding simple 1:1 salt has also been studied. [3]

Complexation, phase separation, and redissolution of concentrated polyelectrolyte solutions have also been examined. [4] As oppositely charged polyelectrolytes were mixed in a macroion solution with repelling macroions became successively less stable. The electrostatic attraction brought macroions and polyelectrolytes closely together and slightly reduced the molecular charge equivalence, distinct and repelling complexes were established. At different charge equivalence, the system became unstable and a large and loose cluster of polyelectrolytes was formed. Finally, in excess of polyelectrolytes, the large cluster of polyelectrolytes and the macroions were dispersed again – a redissolution had occurred. The effect on radius, the chain length, and the chain flexibility on the phase separation has also been studied.

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INTERACTIONS BETWEEN CHARGED COLLOIDS AND SURFACTANTS IN FREE-STANDING LIQUID FILMS

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Polymers can be used as stabilizers of foams. To use polymers in an efficient way in surfactant systems, it is necessary to control and to manipulate the building blocks, i.e. the single free-standing surfactant films of a foam. In our experiments the film thickness is controlled on a mesoscopic length scale (5-100 nm) by varying the outer pressure in a thin film balance. The sum of interactions (DLVO, steric, structural forces) between the film surfaces is determined quantitatively by the disjoining pressure. The addition of polyelectrolytes affects the (de)stability of the film due to complexation between polymer and surfactant at the film surfaces [1, 2]. This complexation occurs at lower surfactant concentrations than the bulk complexation and is caused by electrostatic attraction or hydrogen bonding. The polymer/surfactant complexation at a single interface is studied by surface tension measurements, e.g., and the results are correlated to the disjoining pressure isotherms. In dependence on the composition either a Newton Black Film (NBF, stabilized by steric repulsion) or a Common Black Film (CBF, stabilized by electrostatic repulsion) occurs at high outer pressure. In the case of pure surfactants the NBF presents the more stable film, while in the case of mixed polyelectrolyte/surfactant films the CBF is more stable.

Furthermore, the films are functionalized by the addition of thermosensitive polymers. In order to study the effect of geometrical confinement on the LCST either a thermosensitive homopolymer or a diblock containing a thermosensitive block has been used.

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ION EXCHANGE KINETICS AND STRUCTURE OF POLYMERIC MICELLES

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Recently, we have developed a time-resolved Small Angle Neutron Scattering (SANS) study of the long time stability and chain exchange kinetics in block copolymer micelles in various conditions [1]. The system under investigation, poly(ethylene-*alt*-propylene) oxide (PEP-PEO), forms micelles in mixtures of water and dimethyl formamide (DMF) and both good solvents for PEO and non-solvents for PEP. An important difference is more compatible with PEP than water. This allows to tune the interfacial free energy contribution we focus on the structure and exchange kinetics of highly asymmetric 20k block copolymer micelles in water/DMF mixtures by SANS. Special attention is given to the role of the interfacial tension. We show that the micelles are kinetically frozen in mixtures above 20 mole% DMF and can thus be considered as form stable hairy

scattering curves show characteristic features for diffuse star-like structures. Analysis of pure water, the micelles have an aggregation number, P , of 120 which steadily increases with increasing DMF. Corresponding interfacial tensions, γ , were measured using a tensiometer. We obtained good agreement with the scaling law $P \sim \gamma^{0.65}$ proposed for spherical micelles in particular at high aggregation numbers. Furthermore the SANS results show a significant shrinking (more than expected from steric effects) of the coronal PEO chains with increasing DMF. SANS measurements of the 2nd virial coefficient, A_2 , of linear PEO chains showed that in good correlation with the other results, the exchange rates were found to be ideal for the SANS study in the range between 25 and 50% DMF. The obtained relaxation curves could not be described by a single exponential decay from unimer exchange only. Two exponentials or stretched exponentials were observed, however the interpretation is unclear.

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SURFACTANT UNDER SHEAR IN AQUEOUS MEDIA: TOWARDS UNDERSTANDING BIOLUBRICATION

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The effortless ease with which some biological tissue surfaces slide past each other has long puzzled tribologists in engineering and puzzled physicists studying friction. What is the molecular mechanism of biolubrication? Although many models have been proposed, focusing on the roles of various components of biological tissues, *i.e.*, proteins, poly- or oligo-saccharides, and phospholipids, the underlying physics of biolubrication is yet to be well understood. In the current study, we examine a physiological oligolamellar model [1], which ascribes biolubrication to the presence of surface active phospholipids on tissue surfaces, a model that has been intensively investigated.

Our experimental investigation is carried out with a surface force balance (SFB), in which two surfaces are brought into intimate contact in aqueous media and the friction between them measured with sub- μN sensitivity as they shear past each other. The surfaces are coated with various surface active molecules, *i.e.*, cationic surfactants and phospholipids, and the effects of the molecular structure of these molecules, the applied load, the shear velocity, and the presence of electrolytes are systematically investigated. Our results have revealed remarkable lubrication properties of some cationic surfactant molecules in aqueous media, which allows us to examine critically the postulated role of lipids in biolubrication.

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ELECTROSTATIC EFFECTS IN EQUILIBRIUM ELECTROLYTE BLOCK COPOLYMER MICELLES

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diblock copolymers of vinyl acetate and acrylic acid PVAc-b-PAA have been controlled radical polymerization via the Madix process [1]. The relatively low T_g effects on the micellar structure and check recent theoretical predictions [2]. Self-scattering (SANS), Fitting the SANS patterns with recent models [3] indicates that consist of a PVAc swollen spherical core surrounded by a PAA weak polyelectrolyte VAc as already observed for several neutral amphiphilic micelles [4]. At low pH, the PAA chains adopt an ideal gaussian conformation, but rising the pH (i.e. charge density of the PAA) induces a progressive stretching as evidenced by a rise of both the hydrodynamic radius (DLS) and the scattered intensity at large angles (SANS). Concomitantly, the micellar aggregation number decreases (SANS and DLS) and the hydrodynamic radius increases (DLS) and the scattered intensity at large angles increases (SANS and DLS). When the ionic strength of the solution increases, the micelle core radius increases monotonously. The micelle hydrodynamic radius is first constant at low salt concentrations, then increases until reaching a plateau when all charges are screened, and finally starts to decrease at higher concentrations, a peak appears in the structure factor. The peak height varies weakly with the polymer concentration.

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REAL-SPACE DYNAMICS AND AGING IN CONCENTRATED COLLOIDAL SUSPENSIONS

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Dynamics in concentrated colloidal suspensions (close to and beyond the glass transition) were studied by means of real-space fluorescent recovery after photo bleaching, using Confocal Laser Scanning Microscopy. This method provides information on collective particle movements up to timescales as long as 10⁸ Brownian time steps. We also investigate "aging" phenomena in glassy systems using this technique.

LANDING BULK ELASTICITY OF MONODISPERSED SOLID-STABILIZED EMULSIONS

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study silicone-in-water emulsions stabilized by partially hydrophobized silica. We produce calibrated emulsions in a large range of diameters (1µm to 1 cm) by the phenomenon of limited coalescence. The large monodisperse emulsion drops form the laws governing the size evolution. Stabilized such emulsions, exhibit exceptionally high bulk elasticity. Their elastic modulus G' and the loss modulus G'' have been measured for different oil volume fractions over the random close packing concentration. The G' data were normalized by the sure of the non-deformed droplets and compared with the literature data obtained for surfactant-stabilized emulsions. For the same oil volume fraction, the elasticity of bilized emulsions always exceeds that of surfactant-stabilized emulsions. We discuss considering the rigidity of particle layers and state of flocculation of the particles in

INFLUENCE OF CLUSTER INTERACTIONS ON AGGREGATION AND GELATION KINETICS IN CONCENTRATED COLLOIDAL DISPERSIONS

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This work aims at developing kinetic models for the irreversible aggregation and gelation in colloidal dispersions at moderate solid volume fractions. Using light scattering and linear rheology experiments combined with population balance modeling [1,2] we study aggregating colloidal dispersions in a range of solid volume fractions (0.01 to 0.1) and primary particle stability ratios under reaction-limited aggregation conditions.

Cluster-cluster aggregation leads to a progressive increase in the volume fraction occupied by clusters and ultimately to the formation of a colloidal gel. A realistic description of such a process has to account for spatial correlations between clusters and direct and hydrodynamic interactions. Specifically, transport properties of the clusters, i.e. the apparent self and collective diffusion coefficients, for the short and long time behavior, can be distinctly affected by severe crowding of the aggregating clusters (caging effect), especially close to the gel point.

In order to study these effects, mobility of aggregating clusters was monitored by angle-dependent dynamic light scattering using two approaches: 1) off-line by diluting the aggregating dispersion to quench the aggregation at desired times, and 2) online with suppressed multiple scattering. The stability ratios (ranging from 10^4 to 10^5) were estimated from the initial aggregation rates and the aggregation kinetics were accurately modeled by a RLCA kernel. The parameter of the kernel was found to be dependent on the solid volume fraction, reflecting transport nonidealities. The gelation kinetics were monitored with linear rheology to obtain the elastic modulus (G') as a function of time. The gelation times investigated range from $t_g=10$ min to $t_g=16$ h. Using the stability ratios determined from DLS to scale process time, both aggregation and gelation kinetics resulted in master curves for a given solid volume fraction.

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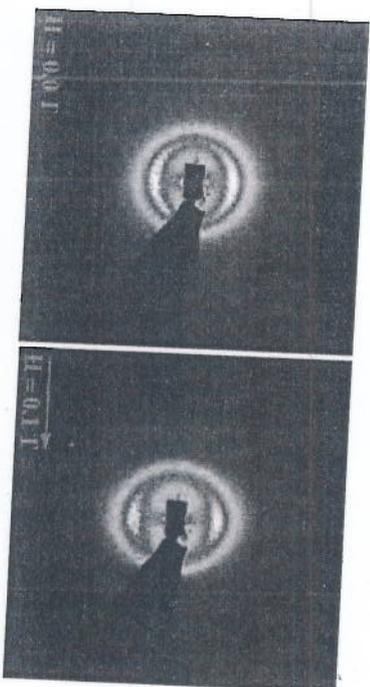
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STRUCTURE AND DYNAMICS OF COMPLEX LIQUIDS IN MAGNETIC DIPOLE-DIPOLE INTERACTION BY MEANS OF SAXS AND XPCS

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Complex liquids consisting of spherical colloidal core-shell particles with a magnetic core and a silica shell are studied by means of static and dynamic X-Ray small angle scattering in dependence of an external magnetic field. Different to conventional ferrofluids, our system nearly monodisperse and self organises to liquid like mesostructures and even to crystals [1]. Due to the combination of a magnetic core and a silica shell carrying charged particles on its surface, these particles interact via a sum of an isotropic screened Coulomb field and an anisotropic magnetic dipole-dipole interaction. In presence of an external magnetic field, all particles arrange parallel to the field direction. In this configuration, an additional repulsion perpendicular to the external field induces a liquid-like ordered structure visible as an anisotropic small angle scattering pattern. The sum of a screened monopole and a dipole interaction. Monte Carlo simulations of collective diffusion studied by means of X-Ray photon correlation spectroscopy significantly influenced by the magnetic contribution to the interaction: both the parallel and perpendicular to the external field.



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ATTRACTIVE INTERACTIONS IN DROPLET MICROEMULSIONS

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The effects of temperature changes and polymer addition on the behavior of nonionic surfactant, decane and water microemulsions are analyzed and reported. Dilution viscometry and dynamic light scattering were used to confirm earlier studies by Olsson and Schurtenberger [1] that found these microemulsions to behave essentially as hard spheres, providing us with an ideal reference system. Addition of poly(ethylene glycol) (PEG) lowers the emulsification failure boundary, where excess oil is expelled, which can be qualitatively understood by a 1st-order perturbation calculation of the available volume for the polymer. Sufficient addition of PEG causes a fluid-fluid phase separation at higher temperatures, in qualitative accord with experiments on mixtures of colloidal hard spheres and non-adsorbing polymer [5]. Addition of PEG or raising the temperature causes the collective diffusion coefficient (D_c) to decrease. From theory [2], the initial linear slope of D_c versus droplet concentration can be used to discriminate between attractions and repulsions in a similar manner as the second virial coefficient. The measured D_c data for the droplets in the presence of PEG are modeled using the Asakura-Oosawa theory of depletion [3]. Fitting the theory to the measured D_c data permits for extracting the only unknown parameter, the polymer radius of gyration. Quantitative agreement is found with literature data [4], demonstrating that polymer depletion occurs in the system and that the Asakura-Oosawa theory provides a good description of the phenomenon.

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GLASSY STATES IN HARD SPHERES WITH SHORT-RANGE ATTRACTION

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studied glass formation in hard spheres with short-range attraction [1]. The system nearly-hard-sphere polymethylmethacrylate (PMMA) particles and non-adsorbing polystyrene, which induces a depletion attraction between the particles, dispersed in The experiments reveal a re-entrant glass transition and two qualitatively distinct Dynamic light scattering, covering many orders of magnitude in time, gives insight of particle motion responsible for these observations.

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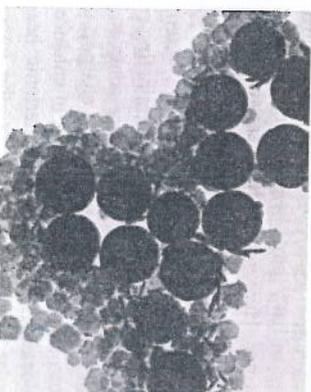
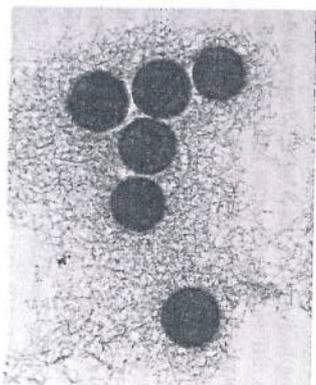
PHASE BEHAVIOUR OF MIXTURES OF COLLOIDAL SPHERES WITH RODS OR PLATES

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Mixtures of colloidal particles with different size and shape are ubiquitous in industry, food science, and the biological realm. Knowledge of the stability of those systems is therefore essential. Here we study the behaviour of mixtures of colloidal spheres with rods or plates theoretically as well as by means of confocal microscopy.

We calculated from the free-volume theory, using scaled-particle theory, that already low volume fractions of hard rods [1] or plates will lead to phase separation. This makes them more efficient depletion agents for spheres than, e.g., polymers.



Well-defined mixtures of FITC-labelled core-shell silica spheres with silica-coated boehmite rods as well as silica-coated gibbsite plates were prepared in dimethylformamide with little salt, such that the interactions of the particles may be considered to be hard. For low rod volume fractions (< 0.015), in the one-phase region of the calculated phase diagram, a crystalline sediment is formed slowly. Although the total crystalline area grows upon increasing rod volume fractions, as also observed in sphere/polymer mixtures [2], the number of grain boundaries rises as well. Samples with higher rod volume fractions (> 0.020), within the predicted two-phase area, form aggregates during sedimentation which drop down and remain glass-like.

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WATER SWELLING OF PHOSPHOLIPID-POLYELECTROLYTE INTERFACES: LOCAL INTERACTIONS AND LAYER DISTANCES

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e dynamics of lipids in a monolayer coupled to polymer layers is studied. The lateral f lipids serves as a parameter characterizing the local interaction of the lipids with a polyelectrolyte surface.

e lateral lipid diffusion is studied by means of fluorescence recovery after pattern ing (FRAP). The polymer support is formed by layer-by-layer self-assembly of charged polyelectrolytes.

viously, we have measured lipid diffusion coefficients in air [1], which are on the $D = 1.2 \text{ cm}^2 \text{ s}^{-1}$, indicating strong electrostatic coupling of the lipid head groups and the D . Thus still reduced in their dynamic behaviour as compared to a free monolayer on a

fusion coefficients are determined in dependence of chain order, the head group charge of the terminating polyelectrolyte layer. The major findings include the fact and polyelectrolyte dynamics are completely dominated by electrostatic interactions between lipid interaction results in enhanced monolayer stability and reduced mobility of the lipid ionic versus zwitterionic headgroup binding can be described by Coulomb versus reactions, however, the interaction strength depends on both, the local dielectric the distance of the binding charges and is not trivial to separate.

interfacial distance between lipid and polyelectrolyte transfer (FRET) is measured to evaluate the . FRET experiments performed in air and in solvent provide evidence that water diffuse into the interface of lipid and polyelectrolyte and cause an increase of interlayer ch leads to a reduction of the interfacial interaction.

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THE ANOMALOUS ELECTRIC BIREFRINGENCE OF POLYELECTROLYTES: NEW LIGHTS ON AN OLD MYSTERY

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Since many years ago, a bizarre phenomenon has been observed in the behavior of dispersions of rod-like polyelectrolytes: their electro-optic susceptibility (e.g. electric birefringence) changes its sign when the dispersion concentration is increased [1, 2]. This evidence indicates that at high concentration the particles longest axis align, on average and quite surprisingly, perpendicularly to the electric field, while it is universally true that diluted rod-like particles orient along the field direction. This phenomenon, usually referred to as the "Anomalous Birefringence" of polyelectrolytes, has been reported in literature about a hundred times, but no explanation has yet been offered.

In this work we present an experimental and theoretical investigation of the anomalous birefringence that provides a new ground to interpret the whole body of recent and older observations. At variance with previous understanding, we provide new experimental evidence indicating that the anomalous birefringence is a pseudo-collective effect that can be interpreted in terms of single particle electrokinetic behavior: the high concentration of polyelectrolytes effectively modifies the mobility of co-ions and counter-ions, in turn changing the anisotropy of the polarizability of each single particle.

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AGGREGATION AND GELATION IN COLLOIDAL DISPERSIONS: FROM MODELING TO COAGULATOR DESIGN

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Aggregation of colloidal particles dispersed in liquids can be carried out under various processing conditions leading to formation of either slurries with significantly larger particle size or particulate gels. However, modeling tools available in the literature have so far provided only limited predictive capability, beyond very dilute systems [1], to describe either the kinetics of aggregation or qualitative features, such as the appearance of a particulate gel, under realistic conditions relevant for industrial applications. At the same time, quantitative modeling of aggregation and gelation kinetics in colloidal dispersions is an important prerequisite for optimization and design of various industrial processes in chemical, food and pharmaceutical industries.

We have investigated experimentally processes of aggregation and gel formation in both static [2] and turbulent flow conditions and have developed and validated corresponding kinetic models based on population balance approach taking into account an interplay between the fluid flow, aggregate structure and aggregation kinetics. We use distributed population balance modeling to describe aggregation kinetics in various experimental devices, where flow patterns and energy dissipation rates are obtained from computational fluid dynamics. Our final aim is to develop methodologies for design of industrial processes and equipment for production of materials through controlled aggregation and gelation of colloidal particles dispersed in liquids.

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DROPLET SIZE MEASUREMENTS AND FAT STALLISATION IN HEATED PROTEIN-STABILISED OIL-IN-WATER EMULSIONS

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omogenised acidified protein-stabilised oil-in-water emulsions can be seen as model fresh cheese products. Recently, two techniques were evaluated to measure fat droplet emulsions: Static Light Scattering (SLS) and pulsed field gradient NMR [1]. In the present work, these techniques are applied to liquid oil emulsions (20-40% fat, 2-8% whey protein) and good correlation between SLS and pfg-NMR results was observed. Droplet size distribution after homogenisation at 300 bar was found to decrease with increasing amount of WPC, with increasing WPC/oil ratio. This suggests that transport of protein to the droplet interface during homogenisation is limiting the final droplet size rather than the total amount of protein. The presence of crystalline fat in the o/w emulsion affects the stability and rheology of emulsions considerably [2]. Firmness of the emulsion increases with increasing protein content and fat droplet size were sometimes found to be sensitive to temperature cycling to and from room temperature. Tailored investigations on polymorphic transitions during the fat (re-)crystallisation in the emulsion (x-ray diffraction, SFC measurement, polarised light microscopy) were carried out.

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HEAVY OIL EMULSIONS

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Very viscous heavy-oil deployment is a topic that the oil companies will have to face with in the next future to compensate the production decline of conventional light hydrocarbons. Among the technologies developed to manage such viscous hydrocarbons (very often solid at room temperature), the emulsification with water is one chosen for production. According to that oil in water emulsions must fulfil precise technical and economical requirements, mainly related to the need to have as much oil fraction as possible, stability under flow and temperature, and oil/water separation before oil treatment at the refinery.

The presentation will briefly describe the constraints, the technical solutions adopted, a discussion of the principle on which the technology is based on. Emulsions properties will be described in relation to oil composition, water salinity and dispersant structure. The main idea is to stabilise the (heavy) oil in water emulsions with low molecular weight polynaphthalensulphonate dispersants.

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USE OF ALTERNATIVE OLIGOMERIC NONIONIC SURFACTANTS TO SLOW ADSORPTION DYNAMICS IN OILS SOLUTION AND IMPROVE CONTROL OF POST COATING FLOW

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Large part of what might be termed the conventional nonionic detergent industry is the use of polyethyleneoxide as the hydrophilic headgroup, although more recently headgroups have become increasingly popular on environmental grounds. However, derived from a 'dynamic adsorption' perspective in aqueous gelatin solution, these two monionic surfactant behave very similarly and not too dissimilarly from conventional surfactants. In this context it is believed that the dynamics of conventional nonionic surfactant systems are mostly diffusion controlled, and therefore relatively rapid in action. In the photographic industry, and as such are very effective at coating of aqueous solutions in the parts of the process where surface ages are short. However, these materials are not so effective at controlling coating uniformity at the longer surface ages encountered during the 'post coating flow', i.e. for the duration the coatings remain fluid. This presentation addresses the problem and how the situation can be significantly improved by the use of oligomeric nonionic surfactants based on polyacrylamides [1]. A hypothesis will be put forward for the mechanism behind the improvement.

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CONTROL OF THE CRYSTALLIZATION OF PARAFFINS IN DIESEL FUEL

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Major troubles occur in diesel fuel at low temperatures because of the crystallization of long chain alkanes (paraffins). "Cold weather performance additives" keep the engine operability by controlling the crystallization of paraffins when the temperature becomes lower than the cloud point of the fuel. The work deals with physical chemistry investigations into the mechanism of action of two types of such additives: Cold filter plugging point improvers which are ethylene - vinyl acetate copolymers (EVA), and wax anti-settling additives (WASA) which are surfactant-like molecules that are soluble in the fuel.

Diesel fuels are mixtures of n-paraffins in a partly aromatic liquid matrix containing some surface-active materials (asphaltenes and malenes). A fraction of the n-paraffins centered on tetraacosane crystallize between 0 °C and - 5 °C. The physico-chemical studies of such very complex and variable systems have required the correct choice of representative model systems. Models were validated by comparisons with standard characterizations of additives. Paraffins crystallized below the cloud point were filtered at low temperatures and subsequently analyzed for their size, shape and chemical composition. Interactions between EVA and paraffins were evidenced by means of infrared spectroscopy and X-ray diffraction. Studies of WASA's were complemented by measurements of settling rates at low temperatures.

The main results are the following: Depending on the paraffin lengths distribution and liquid matrix, EVA can act as a nucleating agent or as a growth inhibitor. There is a favourable interaction between EVA and paraffins since EVA is able to co-crystallize with paraffins. A reduction of crystals size and a modification of their morphology result from the co-crystallization at the surface of the growing crystals. The WASA's adsorb on the crystals surface, allow a supplementary reduction of crystals size and lower their sedimentation by preventing their aggregation.

NEW COLLOIDAL GELS FOR NUCLEAR DECONTAMINATION

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Within the context of nuclear plants maintenance, a new process based on the use of silica gels was developed to decontaminate metallic surfaces [1]. This process is applied as follows: First, the gel is sprayed onto the surface to be cleaned. Next, during the gel drying, a thin layer of the contaminated surface is corroded, the gel cracks and leads to the formation of a porous layer that is brushed away.

The gel was composed of silica particles suspended in an aqueous acid solution with a small quantity (< 1% weight) of an organic surfactant. Silica acts as a viscosifier and the gel having a thixotropic behavior which is necessary for a good spraying. The viscosity under 100 mPa.s under a shearing rate of 700 s⁻¹ to succeed in good spraying and above 10 s⁻¹ to perform a perfect adhesion to the surface. The surfactant is a non-ionic, provides a good wettability on the surface and a sufficient stability in a strong acid medium. Rheological studies showed that a few amount of surfactant was necessary to obtain a gel viscosity after shearing. Adding a surfactant in the suspension had a huge effect on the other hand, under a 700 s⁻¹ shearing rate the viscosity is still below 100 mPa.s on the other hand, under 10 s⁻¹, the viscosity increases by a factor 10 compared to the surfactant.

The aim of this work is to determine the effect of the surfactant on the silica suspension rheological scale. Surfactants are classified according to the ionic charge present on the molecule. Three classical surfactants - a cationic: CTAB, an anionic: SDS and a nonionic: Triton X-100 - were examined. The researches will be particularly focused on the size of the aggregates, the pH of the solution and on the dispersive forces that occur in the medium. The first experiments using light scattering and microscopic observations are currently in progress.

These first experiments using light scattering and microscopic observations are currently in progress and the results will be described and discussed at the 10th International Extension in Progress.

DROPLET DEFORMATION UNDER SIMPLE SHEAR FLOW: INFLUENCE OF SURFACTANTS PRESENT AT THE INTERFACE

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We present experimental investigations on droplet deformation under simple shear flow conditions, using a computer-controlled parallel band apparatus and an optical device which allows us to record the time dependence of the droplet shape for indefinite times. In contrast to previous work by many authors [e.g. 1-3], the steady state deformation of sheared droplets as well as other complex flow profiles can now be achieved accurately.

The measured systems are Newtonian, both droplet and fluid phase, and consist out of a solution of polyethylene glycol-ethanol-water as continuous phase and several silicone oils (Wacker, Germany) as the dispersed droplets. Droplet deformation, orientation angle and retraction are studied for interfaces covered with and without different surfactant systems (Kolb, Switzerland). The influence of surfactant concentration, adsorption kinetics of surfactant on the droplets interfaces is studied and compared to several models.

The surface tension of the different systems is calculated using the theories of Taylor, Rallison, and Hinich et al. [4-6]. The results obtained are in very good agreement with detachment experiments as reported in literature [7]. The analysis of the deformation and orientation angle show qualitative agreement to the theory from Hinich et al. [6] but unveil larger quantitative discrepancies for several empirical fitting parameters of the used model. Since the manifold properties of surfactants present at droplet interfaces are not discussed by the mentioned models, the observed shortcomings and possible modifications are discussed in detail.

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TRANSFORMING W/O MICELLES IN STRUCTURED NETWORKS OF H-BONDS USING "MODIFIERS": A SAXS STUDY

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conding solvent are industrially used as "modifier" in liquid/liquid extraction ural processes. Addition of octan-1-ol, a "modifier" prevents the problem of "third nation": the splitting into two phases of the organic phase. We studied by SAXS ; the effect of the addition of octan-1-ol on the structure of the extractant organic phase h diamide extractant molecule.

is known [1] that diamide molecule diluted in dodecane are organised in reverse hich have many features in common with reverse micelles. Octan-1-ol is also known iate in alkane solution [2].

e presence of a broad peak in the SAXS pattern obtained for octanol/dodecane veals the apparition of electronic density heterogeneities, in agreement with literature nol/alkane mixtures.

diamide/dodecane solution, it is shown that for addition of a small amounts of alcohol, r acts as a co-surfactant, i.e. it swells the reverse micelles by adsorbing onto the nd increases the surface per extractant polar head. When n-octanol is added in larger 1 new microstructure appears and the amount of octanol required for this transition he amount of diamide in solution (for example: [octanol] \geq 1M for 0.7M of diamide). 1 hydrogen bond network is present in solution and the presence of areas of high nsity separated by a distance varying from 15 to 20 Å is found to explain the items.

; structuration of the solvent octanol/dodecane can be compared to the one observed trope" molecules in water.

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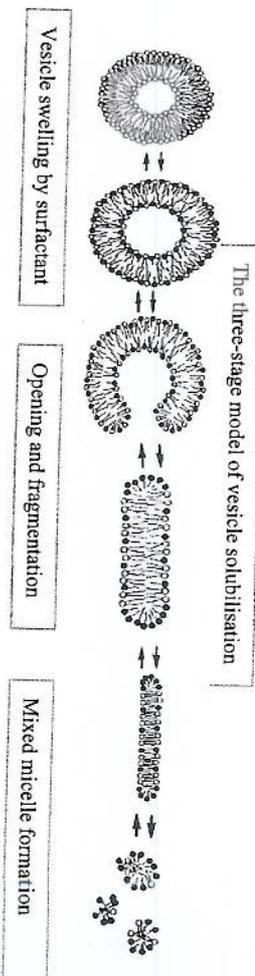
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PHASE BEHAVIOUR AND COLLOIDAL STABILITY OF SURFACTANT-CATIONIC LIPID MIXTURES USED IN COMMERCIAL FABRIC SOFTENERS

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The fascinating phenomenon of vesicle to micelle transition in mixed phospholipid-surfactant systems first discovered in membrane research has enabled the formulation of concentrated fabric softener liquids with attractive flow and optical properties for the domestic market. After an introduction to the world of fabric softeners and a review of the science of vesicle to micelle transition this presentation focuses on the understanding of the viscosity stability of a mixture of di-chain cationic softeners and ethoxylated non-ionic surfactants. The liposomal (multilamellar vesicle) microstructure of cationic lipids transforms to an intermediate liposome fragment phase and eventually to a mixed micelle phase with the increasing proportion of nonionic surfactants. This phase transition manifests itself in the bulk as changes in the rheo-optical properties - reduction in viscosity, and opacity with the appearance of a pearly luster and finally a transparent liquid. Such rheo-optical transformation has made the launch of concentrate fabric softer liquids which flow with ease and show pearlescence under flow a possibility. However one major draw back of these liquids has proved to be their instability at elevated ambient temperatures where their viscosity increases with time leading to the formation of a non-flowing gel phase. We argue here that this gelling process is associated with the familiar phenomenon of 'cloud point' depression in ethoxylated nonionics. At elevated temperatures the ethoxylate chains become dehydrated and hydrophobic leading to the weakening of the steric repulsion they provide between the exposed edges of the liposome fragments. This facilitates the aggregation and coalescence of the fragments entailing the bulk viscosity increase and gelling with time.



TIME DEPOSITION FROM RINSE-OFF CONSUMER PRODUCTS

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Fragrances have long been associated with cosmetics and toiletries and the choice of fragrance has become a highly important aspect in the development of any new product in this industry. Fragrance materials into these products not only produces a 'pleasant' fragrance but may also be required to perform other roles. This can include 'masking' of base odours, 'fixing' of the raw materials, and while the fragrance may not contribute to the properties of the product, it can, by its very nature, influence the consumer's expectations of the product. Therefore, the initial impact, continuing impression, and stability of the fragrance are crucial in reinforcing this message to the consumer and the ability to predict, and control this aspect of the product is of obvious interest to the manufacturers.

In this study, end experiments were carried out to understand the effect of the formulation and methodology on the level of deposition and substantivity of a selection of fragrance materials from model shampoo formulations onto human scalp hair. The concentrations of the materials were monitored by solvent extraction of the hair and analysis by gas chromatography.

The investigation into the washing and drying protocol has suggested that once the fragrance has been deposited onto the hair during washing their subsequent evaporation is not only dependent on the volatility of the fragrance alone. Increased washing temperature was seen to increase the rate of evaporation of the fragrance, which was believed to be related to swelling of the hair at higher temperatures allowing further adsorption of the ingredients. Experimental results from rinsing experiments also suggested that once the ingredients had penetrated into the hair shaft they were less susceptible to subsequent loss by excessive rinsing. Further investigation has also begun to shed light into the role of the surfactant and the physicochemical properties of fragrance ingredients on the level of deposition onto the hair shaft.

COATINGS BY COLLOIDAL PARTICLE DEPOSITION: I. PREPARATION AND STABILIZATION OF INORGANIC COLLOIDAL PARTICLES

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Colloidal particle deposition offers several features for the preparation of coatings with embedded colloids in medicine and other technological areas. Solid inorganic and organic colloidal particles, jelly or hollow nanospheres or even liquids can be incorporated and immobilised by suitable film forming polymer dispersions. These processes have given rise to develop different preparation strategies of various inorganic and organic colloidal particles. Beyond close restrictions in the size scale of particles necessary for the formation of filled coatings, highly mineralised coatings for biomedical application (e. g. bone cement, denture or sealing) requires further dispositions. The suitability of the minerals is determined by small differences in stoichiometry, crystallinity and morphology, which could have an effect on the physical properties of the material designed in nanometer range.

In the present work we describe strategies for the preparation and stabilisation of oxide, mixed oxide and apatite particles with different shape and morphologies and analyse the effect of varying the mode of preparation. Oxide particles were prepared in polyols by hydrolysing appropriate precursor molecules [2]. Apatite powders were synthesised from CaCl₂, Na₂HPO₄ and K₂F by either precipitation from aqueous solution or from polyols, biomimetic syntheses in organic matrices and hydrothermal synthesis [3]. The concentration of the reagents, the reaction time, initial pH and ageing time were varied and finally the effect of annealing the synthetic samples were analysed. Different morphologies of mineral aggregates were obtained e.g. some agglomerates had a spicular morphology and others had spherical shape. The smallest size of primary apatite particles was about 60 nm and the largest was up to 500 µm.

Conclusively with our preparation strategies it is possible to produce various agglomerate morphologies and large series of particle sizes which provide the stock for the creation of a variety of functional coatings [4].

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LOIDAL STABILITY OF MICROGEL PARTICLES

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rogels are soft materials used for fundamental studies in Colloid Science, but also
mous interest in pharmaceutical, food and petroleum industries. Mesoscopic gels can
librium between these particles and the surrounding liquid. The result is a particle
ge: the particles swell and de-swell as an answer to changes in the ambient medium.
In particle size modify inter-particle interactions that control the suspension colloidal
this work we will present a general overview of the colloidal stability of microgel
particular, we will show results for two different microgels; a thermosensitive system
ionic microgel with pH-dependent inner and surface charges [2]. In both cases
gregation (flocculation) of the microgel particles was observed as temperature or
concentration were increased and decreased; a behaviour that arises from the soft
the particles.

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THE INFLUENCE OF CATIONICITY AND MOLECULAR WEIGHT OF POLYELECTROLYTE SLUDGE CONDITIONERS ON ACTIVATED SLUDGE DEWATERING PERFORMANCE

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Up to now, the selection of conditioning polyelectrolytes in sludge dewatering is a very
empirical procedure in which the polyelectrolyte type and application dose required are often
based on visual inspection of macroscopic floc properties. The objective of this study was to
investigate the role of polyelectrolyte chemical properties such as cationicity and molecular weight
in the flocculation and dewatering behaviour of activated sludges and to provide an easy, yet
scientifically based way to determine the polyelectrolyte type and dosing rate. A series of
experiments was performed in which wastewater treatment sludge samples were conditioned with
polymeric polyelectrolytes of varying measured cationicity [1] and molecular weight, with
different application doses. It was derived from the cake resistances, the amounts of filtrate and
CST (capillary suction time) values that an optimal dewatering performance was obtained at a
given polyelectrolyte concentration. This dose depended mainly on the nature of the
polyelectrolyte and was related to the flocculation mechanism. For medium or low molecular
weight polyelectrolytes, the optimum dose corresponded to a zero zeta potential of the flocculated
sludge particles, indicating that sludge was flocculated by the charge neutralisation mechanism.
For the ultra-high molecular weight polyelectrolytes, the optimal dose was only about half of the
required dose for medium/low polyelectrolytes. In this case, charge neutralisation was not
obtained, which suggests that the flocculation mechanism was based on bridging, whereby many
sludge particles are interconnected by a common polyelectrolyte chain [2]. This type of
polyelectrolyte flocculation is therefore much more economical, since less polyelectrolyte is
required compared to charge neutralisation.

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ING OF TEXTILE MATERIALS WITH INORGANIC-ORGANIC HYBRID POLYMERS

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creasing demands for specialised textiles, above all technical textiles as high products can be observed world-wide. Therefore intensive research work is done for methods that lead to well-aimed modification or functionalisation techniques for fibre surfaces yielding in improved or even new properties. Innovative methods for coating are the coating of fibre material with organic-inorganic hybrid polymers following process to create certain surface properties.

modern material development ceramic materials, primarily the application of thin films offer far-reaching possibilities for permanent surface modifications. In this context and on organically modified ceramics (organic-inorganic hybrid polymers) as known materials [1,2], have an immense potential for creative modifications of surface with a comparatively low technical effort at moderate temperatures.

modification of the inorganic-organic hybrid polymers with nanosized metal oxides to improvements in the scratch resistance and may increase the wear resistance of coatings. By filling sol-gel-networks with nanosized ZnO particles transparent coatings with isopropion can be created. The networks can also act as host for dyestuffs, act as barrier against aggressive atmospheres, influence the wettability or improve the ballistic fabrics[3,4].

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HIGHLY FILLED "NANO-ZIRCONIA" SCREEN PRINTING PASTES USING WATER/ALCOHOL MIXTURES AS LIQUID PHASE

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Ceramic - metal multilayer structures are common in industrial applications. However, high sintering temperatures of ceramics often limit the choice of metals in such systems. Ceramic particles exhibiting a diameter of a few nanometers ("nano-powders") promise lower sintering temperatures and thus may allow new material combinations.

A well-known way to produce such layers is screen printing. For this technique usually slurries or pastes with ceramic solid loading of 15vol% and higher are necessary. Yet van-der-Waals forces are present in such systems, making these kind of loadings extremely difficult to achieve [1]. Dispersants are used to modify the particle surface leading to a repulsion force and thus a stable suspension [2] [3]. This process is commonly characterized in a model solvent, which simplifies the analysis. However, such solvents are generally not useful for industrial production. As a new attempt, we used a alcohol/water mixture as the suspension fluid, which is suitable for screen printing pastes.

Three different dispersants (polyfunctional, trifunctional and monofunctional acids) were used to process nano-zirconia powder (primary particle size 13nm, BET-specific surface area 60m²/g). Rheology measurements were taken and correlated with AFM force-distance analysis and zeta-potential data to understand and explain the dispersing mechanisms in the chosen fluid mixture. Based on these results suspensions were prepared with particle loading above 20vol%.

Finally, structures were produced by screen printing and the influence of the sintering temperature on the microstructure was analyzed.

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PHASE TRANSITIONS IN POLYELECTROLYTE GELS

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We have studied surfactant-induced volume transitions of covalently cross-linked sodium polyacrylate microgels by means of light and fluorescence microscopy. During the transition a collapsed, surfactant rich, surface phase is formed enclosing the swollen gel core. Evidence is found for equilibrium between core and surface phase in the collapsed state of the gel, previously reported only for centimetre size gels. The kinetics of diffusion controlled gel shrinking is analysed theoretically. The model considers the transport of surfactant from bulk, through the "stagnant" liquid layer and the surface phase, to the gel core. During shrinking, the osmotic swelling of the gel is assumed to be in quasi-equilibrium with the bulk and calculated using recent time-resolved experimental shrinking curves. The result suggests that the shrinking is controlled by stagnant layer diffusion of surfactant and that the relative swelling at intermediate stages during the collapse is the same as for slab gels of the same composition. The lag time measured before shrinking starts is longer than the time expected for the surfactant concentration to exceed the critical aggregation concentration in the gels, suggesting that the gels are arrested for some time in a meta-stable state prior to "nucleation" of the surface phase.

Conditions for volume transitions and the co-existence of swollen and collapsed phases in networks is discussed in relation to the phase behaviour of mixtures of surfactants and linear polyeion, the storage of peptides and transmitters in secretory vesicles, and the release of secretory vesicle contents during exocytosis [2]. The results should be useful for the design of drug carrier systems (encapsulation, controlled release, etc.).

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REACTIONS OF IGEPAL® SURFACTANTS WITH DODEXTRIN AND A SOLUBLE β -CYCLODEXTRIN POLYMER. LIGHT SCATTERING, SIZE EXCLUSION CHROMATOGRAPHY AND NMR STUDIES

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oxyethylene nonylphenyl ethers, most frequently known as Igepal®, are non ionic which consist of a hydrophilic chain of a variable number of ethylene oxide groups linked to a hydrophobic one made of a benzene ring. These amphiphiles are surfactants, wetting agents, dispersants, stabilizers, sanitizers and defoaming agents, with applications that include agrochemical emulsifiers, industrial cleaners, textiles, paper de-inking products and detergents, as well as intermediates for the synthesis of anionic dyes.

The goal of this work is to investigate the effect on the phase behavior of some of these surfactants when an encapsulating agent with a preference for the hydrophobic part of the cyclodextrins) competes with the self-aggregation to form an inclusion complex [3]. For this purpose, we have used a series of Igepal® with 5, 9, 40, and 100 EO units (CO-890, CO-890, and CO-990, respectively), and studied its aggregation in pure water and in the presence of β -cyclodextrin (β -CD) and a β -CD polymer, by using dynamic light scattering, size exclusion chromatography and NMR methods. The hydrodynamic radii of the micelles and monomers have been measured as a function of temperature, and the hydrodynamic radii deduced. β -CD covers the hydrophobic part of the Igepal, raising the concentrations at which micellization and cloud point occur. The hydrodynamic radii of the complexes have been also calculated, and the mode of inclusion and stoichiometries of the complexes discussed according to the NMR data.

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POLYAMINOACID-BASED NANOPARTICLES FOR PROTEIN DELIVERY

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Therapeutic proteins have very short half life in vivo, necessitating frequent parenteral administrations to get efficient therapeutic effect. Moreover, after administration, the high protein concentration induce severe side effects. Flamel has developed two families of polyaminoacid-based nanoparticulate protein carriers, namely Medusa I and Medusa II, which overcome these problems by extending the duration of action of native proteins while decreasing their concentration at peak. Both solubility and stability of the proteins are improved as well.

Medusa I are self assembled nanoparticles of block copolyaminoacids of -l-leucine and sodium-l-glutamate (size between 10-100 nm). These nanoparticles have been studied and characterized by a wide array of techniques (NMR, CD, IR, Raman, RX, AFM, TEM, SAXS). Proteins such as insulin adsorb spontaneously onto the surface of these Medusa I nanoparticles. A clinical phase I trial has demonstrated that this Medusa I/insulin complexes can release insulin over more than 24 hours and is thus a promising new long acting insulin dosage form.

Medusa II is based on hydrophobically modified poly(L-sodium glutamate) chains (HMpGlu). Therapeutic proteins (interferon alpha, IL-2, EPO, ...) associate spontaneously in water to the hydrophobic domains of HMpGlu. This association leads to a dramatic increase of both the stability and the solubility of hydrophobic proteins such as IL-2. The structures of the HMpGlu suspension and the protein/polymer complex in water have been fully characterized. A particular attention has been paid to the characterization of the hydrophobic domains by fluorescence techniques (TRFQ) and molecular mobility of the protein/polymer complex by NMR and FRAP. Compared to Medusa I, Medusa II system allows higher protein loadings (up to 1 to 4 proteins per chain i.e. 100% to 400% w/w) and long time of release reaching two weeks in vivo. In vivo results after subcutaneous injections in humans and in several animals will be correlated to the discussion of the structure of the protein/polymer complex.

HEL HETEROTOPIC COLLOIDS OF PORPHYRINS TANGLED IN AMPHIPHILIC CYCLODEXTRINS: CTROSCOPY AND INTRACELLULAR DELIVERY

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entanglement process between porphyrin and some amphiphilic cyclodextrins (CD)
; occurrence of various species at different porphyrin/CD ratios have been proved by a
of UV-Vis absorption, fluorescence anisotropy, time-resolved fluorescence,
ht scattering and circular dichroism. The effect of the entanglement process on the
diameter and the vesicle surface charge have been measured, in a wide concentration
asielatic light scattering and laser Doppler electrophoresis (zeta potential analysis)
the entanglement process, increases remarkably the porphyrin solubility in water, in
ater insoluble species and promotes a transfer of free molecules from solvent into the
he case of the water soluble porphyrin. In this latter case the experimental results
the presence of porphyrins in this colloidal system promotes some structural changes
rge interaction, which are responsible for a sensitive variation of relevant parameters
les dimensions and surface potential. In the range of porphyrin/CD ratio between 1:10
orphyrin is solubilized in monomeric form ($\tau_1 = 11.5$ ns) and photosensitizes
f singlet oxygen (1O_2). At the same ratios this amphiphilic cyclodextrin is able to
yryns inside tumor cells, showing high specificity in the nuclear compartment. These
be of potential interest for the development of photodynamic therapy.

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APPLICATIONS OF TEXTILES WITH PERMANENTLY FIXED CYCLODEXTRINS

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Cyclodextrins are polysaccharides built from six to eight ($\alpha=6$, $\beta=7$, $\gamma=8$) D-glucose units
and are formed during the enzymatic degradation of starch. The molecules are torus shaped with
hydrophobic cavities. The cavity radii of this relative rigid molecules vary between 0.50 and 0.85
nm. Cyclodextrins are non-toxic and not skin sensitising. Cyclodextrin derivatives with reactive
groups e.g. the monochlorotriazinyl group are able to react with the hydroxyl groups of cellulose
fibers like reactive dyes. Permanent fixation on fibers made from polyester is only possible with
cyclodextrin derivatives with long alkyl chains or other hydrophobic groups. On polyamid fibers
cyclodextrin derivatives with sulfonic acid groups are fixed by ionic interactions with amino groups
on the polymer surface.

Textiles with permanently fixed cyclodextrins have several advantages compared with
"normal" textiles:

The fixed cyclodextrin molecules are still able to complex substances into the empty
cavities e.g. organic molecules from sweat. Therefore the possible formation of malodor by
microbiological decomposition of the organic substances is prevented.

The complexation of organic substances from sweat results in a preconcentration and
their analytical treatment becomes easier. Thus, the identification of the organic compounds from
the sweat of patients enables new ways in medical diagnostics.

On the other hand the cavities of the cyclodextrins can be filled with perfumes, cosmetic
compounds or even pharmaceutical active substances. All these substances are set free by wearing
of the textiles. Perfumes evaporate due to their high vapor pressure. Other substances remain on
the surface of the skin or will even penetrate into the skin. In this way the treatment of extensive
skin diseases is simplified.

PHARMACEUTICAL ASPECTS OF DISPERSED TROPIC LIQUID CRYSTALLINE DRUG DELIVERY VEHICLES

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Effective solutions for increased bioavailability of orally administered biomolecular drugs are a major challenge of modern pharmaceutical science. The versatility in particle-size, morphology and composition of dispersed lyotropic liquid crystalline (e.g. Cubosome® and nB®) systems make these attractive candidates for tackling the specific problems associated with e.g. oral delivery of peptides and proteins [1]. In particular enabling survival in the environment of the intestine and possibly mediating penetration of the epithelial barrier.

For insulin, the mitigation of these obstacles has been shown possible by using a novel delivery system [2]. Here we discuss the design of disperse lyotropic liquid crystalline systems for oral drug delivery and relate performance criteria to basic physicochemical parameters including phase behavior, polymorphism, peptide binding, colloidal stability, and lipid metabolism.

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THE VESOSOME: A NEW EXTENDED RELEASE DRUG DELIVERY SYSTEM

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An efficient drug delivery system should increase the stability of drugs in vivo, improve their bioavailability while reducing their toxicity, and provide a controlled drug release at a specific site. For systemic delivery, the sizes should also remain in the colloidal range. Accordingly, such designs use submicron sized hydrogels, biocompatible polymer microspheres, microemulsions, or liposomes for example. The potential of liposomes as drug delivery carriers has been recognized long ago, however this system also has strong limitations, mainly in that it relies on a single membrane to optimize the features of an efficient drug delivery vehicle.

Inspired by the higher level of intracellular division of labor in eukaryotic cells vs. prokaryotic cells, we developed the concept of bilayer-encapsulated vesicles, to yield a very versatile drug delivery system. We produce lipid based multicompartamental structures (called Vesosomes) via a combination of simple self- and directed assembly steps. In addition to vesicles of various compositions, using this technology we can encapsulate, within a lipid bilayer, potentially any colloidal suspension.

In the bloodstream, drug release is not only intrinsic to the carrier – as would be in saline liposomes, although they have long circulation times, the encapsulated drug leaks rather fast while the membrane interacts with the surrounding medium. In the vesicles within a vesicle system that we developed, the external membrane sets an additional physical barrier, and protects the drug loaded vesicles from direct degradation. Our working hypothesis is that the membranes have to be compromised in sequence to release the encapsulated material. Here we compare the release of model compounds from liposomes and Vesosomes (liposomes within a liposome) in a model medium containing phospholipase A2, and study to which extent the presence of the outside bilayer delays the enzymatic hydrolysis of the internal vesicles, leading to release of their contents.

ALA AND ALA-ESTER PENETRATION THROUGH PORCINE EAR SKIN - IONTOPHORESIS AND PASSIVE DIFFUSION

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The iontophoretic and passive penetration of the HCl salts of 5-aminolevulinic acid (its methyl-, hexyl-, and octyl-esters through porcine ear skin were studied. ALA and its esters are used for the treatment of basal cell carcinoma with photodynamic therapy. The idea behind the therapy is to deliver high amounts of ALA in the tumor area. After chemical steps, a light sensitive molecule, protoporphyrin IX (PpIX), is produced. Irradiation with red light gives rise to oxygen radicals which destruct the tumor cells. We have earlier investigated the flux of ALA obtained from a lipid sponge phase of monolein, propylene glycol and water (buffer). All three components are known to transport of drugs through skin and one aim of that study was to investigate possible effects. The sponge phase, consisting of one congruent lipid bilayer in a sea of solvent mixed at roughly equal amounts of the three components and should, due to its structure, be able to function also with iontophoresis, a method in which a current drug through skin.

Our results show that the sponge phase gives rise to ALA fluxes several times higher than obtained from buffer and buffer/propylene glycol solutions, respectively. With no applied, i. e. allowing for passive diffusion only, no detectable amounts of ALA were in the receptor chamber after 10 hours. This is not unexpected since the load of ALA in the sponge phase was only 15 mM (<0.3 % w/w), and the drug was in its charged HCl form.

In this study we will present skin fluxes, obtained with iontophoresis and passive diffusion of methyl-, hexyl-, and octyl-ALA in the sponge phase. Of special interest is the influence of the more lipophilic ester drugs with the sponge structure, and the influence it may have on skin penetration.

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INTERACTIONS BETWEEN POLAR AND AMPHIPHILIC POLYMERS AND LIQUID CRYSTALLINE PHASES

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Over the years a large variety of monolein (MO)-water based systems have been studied with an emphasis on the cubic liquid crystalline phases and on dispersions of these phases (cubosomes). The particular properties of monolein-water based cubic phases including the bicontinuous structure, high internal surface area, adhesive property, and low cost raw material, make them desirable for consumer product and pharmaceutical industry applications. Unfortunately, however, the cubic liquid crystalline phase is too viscous to be utilized generally and large efforts are made to develop stable cubic dispersions. Interestingly, the lifetime of cubosomes has been found to increase in the presence of an amphiphilic block-copolymer (poloxamer). This discovery has led to an increased interest in monolein-polymer-water systems. We have studied the interactions between the lipid monolein and the hydrophobically modified polymer ethyl hydroxyethyl cellulose (HMEHEC) by following the phase behaviour, macroscopic appearance, and microstructure of the aqueous system over a wide concentration range. By combining different techniques, it was found that the ternary MO-HMEHEC-H₂O system exhibits a large variety of aggregate structures including the cubic particles and vesicles that form spontaneously at very high water content and cubic, lamellar, and hexagonal liquid crystalline phases at different compositions. The formation, stability, and size distribution of cubic lipid particles will be discussed in relation to the phase behaviour. Since the steric stabilized cubosomes exist at low polymer/lipid ratio as well as at high polymer/lipid ratio, the application areas of these cubic lipid particles span over a wide range. Cryo-TEM (cryogenic transmission electron microscopy) and light microscopy were employed in the studies of the dispersed phases and SAXD (small angle X-ray diffraction), polarising microscopy and NMR techniques in the studies of the liquid crystalline phases.

SED GRADIENT SPIN ECHO NMR AND DYNAMIC LIGHT SCATTERING STUDIES OF A DIMERIC SURFACTANT WITH β AND γ -CYCLODEXTRINS

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meric or oligomeric (Gemini) surfactants consist of two hydrophobic chains linked at head groups by a spacer. These amphiphiles are known to exhibit unusual properties CMC, high surface activity, dramatic improvement of the solubilization,...) when with the equivalent single chain surfactants [1-3]. However, these properties can be then an encapsulating agent with a preference for the hydrophobic part of the surfactant (ins) competes with the self-aggregation to form an inclusion complex [4]. This work we have synthesized the bis-(dodecyl)dimethylammonium bromide) (GEM1), and studied its aggregation in the presence of β and γ -cyclodextrin (β and γ -nic strengths and temperatures by PGSE-NMR and dynamic light scattering. The behavior of the collective diffusion and self-diffusion coefficients has been discussed. The data, fitted by applying an action mass model, allows to obtain the CMC, the number and the hydrodynamic radii of the monomers and micelles. The presence of β -CD or γ -CD, a shift of the CMC is observed, according to the stoichiometries of the complexes. Thus, β -CD yields a 1:1 complex, whereas γ -CD mixture of 1:1 and 2:1 stoichiometries (two CD units per surfactant). The diffusion of the complexes, as calculated by using DOSY methods, have been compared to ed by QELS. Molecular Mechanics (MM), together with ROESY experiments, give information about modes and structure of the complexes.

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GRAVITATIONAL STABILISATION OF AQUEOUS SUSPENSIONS BY MICROFLUIDIZATION

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During the last decade, the formulation of active compounds has become increasingly important in pesticide, pharmaceutical, food and cosmetic product development. Hereby, both chemical and physical aspects have to be considered. As far as the latter are concerned, particle size have received much interest, *ia* because it can have an effect on the solubility and hence on the bioavailability and activity of the active compounds. Two alternative approaches for particle size reduction have been described: in the production of DissoCubes[®], high-pressure homogenization is used, whereas NanoCrystals[®] are obtained by pearl milling.

In this contribution, the capabilities of microfluidization to produce colloidal suspensions of a model drug compound were investigated. It will be shown that nanosuspensions may be obtained by a proper choice of microfluidisation time and intensity, provided that the temperature is properly controlled.

Besides the operational instrumental aspects, the choice of additives is equally important. First of all, a stabilizer is required in order to prevent extensive flocculation by hydrophobic interactions that leads to excessive visco-elasticity. Experimental results indicated that the amount of surfactant required to prevent severe aggregation must be about 5% of the amount of active ingredient. In addition, a thickener is needed to prevent the formation of caking during long-term stability. The effect of both formulation aids on the microfluidisation treatment was investigated by particle sizing using both laser diffraction and TOT-measurements.

In order to assess the sedimentation properties of the newly developed microfluidized nanosuspensions, the concentration of the active ingredient was determined as a function of time and depth in sedimentation columns upon 1000-fold dilution of the drug product.

The results indicate that a proper selection of instrumental and formulation parameters enables the development of a drug formulation that is suitable for drinking water application.

INTERFACIAL CHEMISTRY IN AQUEOUS TIN-(S)PHOSPHONATE / HYDROXYAPATITE SYSTEMS

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Organic phosphonates (organic compounds with a P-C-P bond) are widely used in the treatment of various bone disorders [1]. Metal-ligand complexes with a radioisotope of a phosphonate or phosphonates as the ligands, administered intravenously, have been used for many years to relieve pain from bone metastases. The role of these complexes is to deliver a (palliative) therapeutic dose of radiation to such a tumour without affecting the surrounding healthy tissue [2]. The success of bone-seeking (radio)metal-(bis)phosphonates mainly depends on their interaction with the mineral phase of bone. The work described here deals with the interfacial transfer of the (radio)metal-(bis)phosphonate complexes and/or their subsequent fixation to hydroxyapatite; a model for bone and its metastases. In our experiments with Sn(II)-hydroxy ethylidene-1,1-diphosphonate (HEDDP) - labelled complexes, the ^{119m}Sn-ions (including ^{119m}Sn-ions) are actually reacting with the complex but the tin-ions (including ^{119m}Sn-ions) are actually reacting with the free binding sites exposed to the solution at the solid / liquid interface [3]. However, similar experiments (with ¹⁵³Sm-labelled Sm(III)-bisphosphonates) other authors have reported that the whole metal-bisphosphonate complex and not only its metal ion component is attached to hydroxyapatite [4,5]. Obviously a new, holistic approach is required to elucidate the interfacial chemistry of this theoretically important and biologically important tin-bisphosphonate / hydroxyapatite and other similar systems. This is the central feature of the present paper.

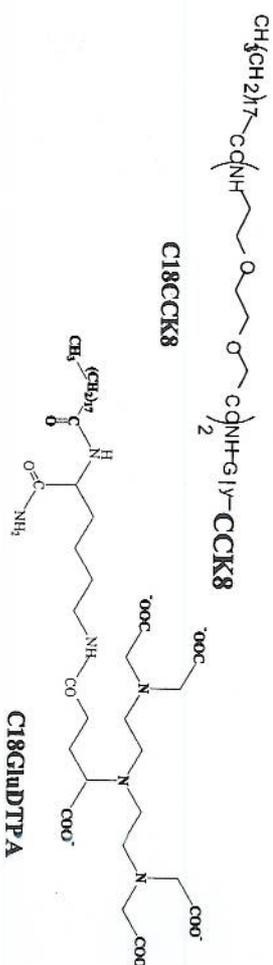
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MIXED MICELLE AGGREGATES CONTAINING BIO-ACTIVE PEPTIDES AND CHELATING AGENTS FOR METAL COMPLEXES

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There is an increasing interest in developing new molecules able to target metal ions on specific receptors for diagnostic applications by Nuclear Medicine (NM) or Magnetic Resonance Imaging (MRI). In recent years micelles formed by monomeric amphiphilic Gd chelates were prepared with the aim of obtaining contrast agents for Magnetic Resonance Imaging (MRI). Our goal is focused on obtaining micelles able to target G-protein coupled receptors (GPCR) overexpressed by cancer cells, by using bioactive peptides. Such systems could be basically formed by three compounds: a surfactant, a bio-specific probe capable to recognize tumor cells, and a bi-functional chelate containing a stable metal that allow highlighting tumor tissues. In our first attempt the mixed micelles are based on the cholecystokinin peptide CCK8 (bio-specific probe) that displays high affinity for the two cholecystokinin receptors and a claw molecule able to complex an appropriate metal (contrast agent): ¹¹¹In(III) for NM application or Gd(III) for MRI. Both these molecules contain a hydrophobic chain which allows them forming mixed micelles leaving the hydrophilic head of the molecules in the outer shell of the aggregates, available for the appropriate task. Addition of a non-ionic surfactant to this system could result in an increase of the micelle stability. In the current report we present a physical-chemistry characterization of pure and mixed micelles formed in the different systems. In particular surface tension, fluorescence quenching, intra-diffusion coefficients, EPR measurements were performed on the binary C18CCK8-water, C18GluDTPA-water system and on the corresponding ternary system in the presence and absence of non-ionic surfactant.



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IN THE MECHANISM OF DRUG RELEASE FROM THERMOSENSITIVE LIPOSOMES

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desired property of drug carrying liposomes intended for cancer treatment is a fast and drug release at the tumour site. One idea is to use liposomes with a transition temperature, T_m , of about 40°C and specifically heat the tumor area to achieve hyperthermia and drug release.

liposomes containing thermosensitive liposomes encapsulating the anticancer drug doxorubicin, have shown to be more efficient than other thermosensitive liposomes in a human xenograft mouse model [1]. The increased efficacy is due to a very rapid release that results in a high local drug level.

In this study we investigated the drug release mechanism of lysolipid containing and thermosensitive liposomes by studying the morphological features before and after drug release. Cryo-TEM revealed that bilayer discs and open liposomes formed in both cases upon cycling through T_m . Importantly the presence of lysolipid in the membrane facilitates disc formation substantially. Non-thermosensitive liposomes did, on the other hand, not form discs after cycling.

A possible mechanism for the disc formation is the accumulation of micelle forming lipids such as lysolipids and PEG-molecules, at grain boundaries and other packing defects in the membrane. When the temperature is increased the defects pre-melt before T_m and the PEG-lipids and lysolipids adapt a micellar conformation, which enables them to dissociate or liposome openings to form. This would explain the burst-like release of drug material observed at temperatures just below T_m . Other studies indicate that discs are more easily formed after prolonged storage of the thermosensitive liposomes. This could be due to lipid hydrolysis and/or diffusion of drug and PEG-lipids to the defects and grain boundaries.

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4. New Methods of Investigation:

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

*

THERMOPHORESIS IN COLLOIDAL SUSPENSIONS AND MACROMOLECULAR SOLUTIONS

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Thermophoresis, consisting in the drift of dispersed particles due to a thermal gradient, is the analogous in macromolecular solutions or colloidal suspensions of the Soret effect (thermal diffusion) in simple fluid mixtures [1]. Recent experiments on DNA solutions have shown that polymer thermophoresis may lead amplification up to a thousand fold of the local macromolecular concentration [2]. Yet, thermophoresis still lacks any microscopic picture: for instance, in most cases disperse particles migrate to the cold, displaying a 'thermophobic' behavior. However, examples of 'thermophilic' motion (diffusion to the hot side), missing so far any explanation, have frequently been reported. By measuring the Soret coefficient S_r of SDS solutions, we have recently investigated charge contributions to thermal diffusion, showing that electrostatic interactions play a crucial role in thermophoresis [3]. In the single-particle regime, S_r grows as the square of the Debye-Hückel length. Yet, collective effects yield a fully reversed situation even at very low c . Single particle behavior and collective contributions can be understood in terms of a 'microscopic thermocapillary effect', originally proposed by Ruckenstein [4], relating thermophoresis to particle-solvent interfacial tension gradients. This approach, suggesting thermophoresis as a probe of particle-solvent interactions, can be generalized to other disperse systems showing different particle solvation. We shall discuss optical methods allowing for fast and accurate measurements of particle thermophoresis [5], and we shall present results relative to other complex fluids and disperse systems, ranging from proteins near crystallization [6] to flexible polyelectrolytes, mixed ionic-nonionic micelles, and polystyrene latex particles, showing that the Soret coefficient can be carefully tuned in amplitude and even its sign by controlling solvent-particle interactions.

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HIBITION OF HYDROPHOBIC ASSOCIATIONS BY ODEXTRINS AS A TOOL TO STUDY CROSS-LINKING MECHANISMS OF HYDROPHOBICALLY MODIFIED POLYMERS

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The thickening effect of a hydrophobically modified polymer (HMP) in an aqueous solution is dependent on intermolecular hydrophobic associations, and if the polymer concentration is significantly above the overlap concentration also on chain entanglements. In this work we have added different cyclodextrins (CD) in order to decouple hydrophobic polymer associations via inclusion complex formation with the polymer hydrophobic groups. The HMP was either a long chain polyethylene glycol with hydrophobic groups at both ends (PEG) or an ethyl (hydroxyl ethyl) cellulose with hydrophobic groups attached along the chain (HEEC). The effects of adding CD to the aqueous polymer solutions were studied by dynamic light scattering (DLS) and NMR-diffusometry measurements.

For both polymer systems addition of CD resulted in reduced viscosity, η . This is referred to as the effect of the polymer network when hydrophobic associations are disrupted due to the formation of inclusion complexes between the hydrophobic groups of HMP and CD since a hydrophobic group cannot take part in the network formation.

As CD the viscosity became virtually the same as in a solution of first decreased strongly, provided complex formation was not hindered. This suggests that virtually all hydrophobic links, originating from the hydrophobic modification process could be deactivated. For HMP-PEG the viscosity reduction due to CD addition was even more dramatic. A reduction of a small fraction (10% or below) of the total amount of polymer hydrophobic tails led to a level almost corresponding to that of the unmodified parent polymer. The suggested mechanism is that initially CD mainly reduces probability for hydrophobic associations between different clusters of polymer micelles, whereas at higher CD concentrations inter-association of individual clusters into separate HMP-PEG molecules, decorated with CD, is important.

STUDY OF HETEROGENEOUS SUSPENSIONS: A NEW QUANTITATIVE APPROACH BY COUPLING LASER GRANULOMETRY AND UV-SPECTROPHOTOMETRY

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As it is well known, suspension are commonly used in many industrial fields such as pharmaceutical industry, food industry, materials, waste and water treatments...

In this work, studied suspensions are mixtures of heterogeneous compounds differing from chemical nature and size (ie mineral particles, organic fibers, soluble or adsorbed substances).

The aim of this work is to propose a complementary approach for the characterisation of heterogeneous suspensions using two optical methods: UV spectrophotometry and Laser granulometry [1]. The complementary nature of both techniques is based on a complementary scale of analysis which allows identification and quantification of each component in a very large size distribution to be performed [2, 3]. This can be achieved from molecular substances, colloids to millimetric particles. This coupling can be applied in order to select and optimize industrial processes as well as separation treatments (filtration, flotation, hydraulic sizing...).

Moreover, this experimental approach allows to investigate suspension stability by detecting mass transfer phenomena (such as dissolution, agglomeration, adsorption...) which are basic for understanding the dynamic of complex systems.

First of all, this methodology has been developed on model mixtures and has allowed identification and quantification of different kind of components (Kaolin, carbonate, latex, optical whitener...) in mixture to be performed. Then applications to real industrial suspensions coming from papermaking processes are presented.

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OR4/4

NEW COLLOIDAL-BASED METHOD TO STUDY MOLECULAR RECOGNITION

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We use magnetic colloids in order to study molecular recognition and, more generally, processes at the colloidal scale. We study both molecular bridging between colloidal a weak polyelectrolyte and specific antigen/antibody molecular recognition. We have an optical method to measure directly the colloidal force profile as a function of the between two magnetic beads. Magnetic colloids effectively form chains of equidistant n submitted to an external magnetic field. When the magnetic field is turned off, the disperse instantaneously by Brownian motion whereas they remain in permanent chains if chemical, or biospecific links form between the beads. We also follow the kinetics of of permanent magnetic chains by optical imaging and by anisotropic static light he beads is due to bridging by polyacrylic acid and are now being applied to antibody molecular recognition. The strategy thus consists in grafting antibodies to the beads and following the kinetics of formation of molecular links between the beads sence of antigens. These measurements should allow us to obtain both the activation d the characteristic frequency of the recognition between the antibody and the antigen as are also at the origin of a new method to improve the sensibility of biomedical assays based on colloidal agglutination.

OR4/5

NEAR FIELD SCATTERING

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We will present a series of novel, unconventional optical techniques that are capable of performing both static and dynamic measurements of low and ultra-low scattered light, and are therefore of potential interest for colloid physics and complex fluids in general. They are based on the statistical analysis of the scattered intensity in the near field of the scattered light (NFS). At variance with the classical methods, the NFS techniques are extremely simple to set up, the requirements on alignment and mechanical stability being very relaxed. The scattered intensity from a low power He-Ne laser is collected by means of a CCD camera, and in the homodyne method the transmitted beam is blocked, while in the heterodyne version (HNFS) the transmitted beam is allowed to fall onto the CCD together with the (weak) scattered light. The intensity distribution is then the result of the interference between the scattered light and the strong (local oscillator) transmitted beam. The HNFS is therefore a self-referencing method, and therefore it allows the determination of absolute scattering cross sections. Also static stray light contributions can be rigorously subtracted from the data, without the necessity of blank measurements. While HNFS proves to be quite superior to the Homodyne NFS, we will show that at extremely low scattering angle, the HNFS gradually merges into the Shadowgraph method. Accordingly, the data analysis becomes rather involved, because of the multi zero Shadowgraph instrumental function. Finally, we will show a newer version of the heterodyne method that compensates for the Shadowgraph instrumental function and that allows to push the technique to arbitrarily small scattering angles with a perfectly flat instrumental function.

OR4/6

IS A SUBLAYER CONTRIBUTING TO THE SURFACE TENSION?

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Absorption layer of soluble surfactant exhibit certain puzzling peculiarities such as the observed linear decrease of the surface tension in dependence of the logarithm of the bulk concentration. According to Gibbs this means that the surface excess remains despite the fact that the surface tension drops significantly. This apparent paradox may be a contribution of the sublayer to the surface tension. In this contribution we address it by a novel experiment which combines the nonlinear optical technique Surface Harmonic Generation, SHG with the technique of the oscillating bubble. The technique of the bubble generates a non-equilibrium state by a periodic compression and expansion in a very well defined fashion. The design of our chamber gives access to the times t to 1 ms and the chosen geometry suppresses Marangoni flow. The state of this bubble has been investigated by SHG. SHG is a surface specific nonlinear optical technique which is sensitive to the adsorbed species. The combination yields the molecular exchange rates and relates them to the surface tension.

OR4/7

DIRECT MEASUREMENT OF THE PREVAILING ION DISTRIBUTION AT CHARGED INTERFACES

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The distribution of ions close to a charged wall is a classical problem in colloidal physics. The traditional approach consists in a mean field analysis of the counterion distribution leading to the Poisson-Boltzmann theory. Recently this field has attracted renewed attention with several theoretical papers addressing effects beyond the mean field level such as fluctuations or the discreteness of charges. These papers reveal certain new features which are not captured in the mean field picture. In this contribution we demonstrate that Ellipsometry allows a direct determination of the prevailing ion distribution. A simple analytical expression is derived which can be used to retrieve the number of ions within the Stern-layer. This formalism is applied to the experimental data gained on aqueous alkyl pyridinium bromide solutions. The analysis of the experimental ellipsometric isotherm provides evidence for the existence of an ion condensation just before the cmc. The derived formalism relates the ellipsometric signal to the surface charge and promises great potential in order to discard or proof the recently introduced concept of fluctuation driven ion condensation.

REAL-TIME WAVELET-TRANSFORM SPECTRUM ANALYZER. APPLICATIONS TO DYNAMIC LIGHT SCATTERING

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We describe a wavelet transform spectrum analyzer (WTSA) operating in real time in the range 3×10^{-5} - 1.3×10^5 Hz. The WTSA has been built on a low-cost digital signal board running at 150MHz. The WTSA has been tested by performing Dynamic Light Scattering measurements on colloidal suspensions. The wavelet decomposition of the signal allows the processing of signal characterized by a broad range of timescales and represents the useful correlation functions when $\alpha > 1$. We present experimental results of the number of particles in a dilute colloidal suspension with a wide beam illumination, characterized by a spectrum with exponent $3/2$. We compare the experimental results with those obtained from a traditional multi-tau correlator.

SUPERCRITICAL WATER AS A MEDIUM FOR COLLOID SCIENCE

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Usefulness of supercritical water (SCW) as a reaction medium for the destruction of hazardous waste has been realized in the last two decades, and properties and reactions in SCW have been actively studied. In supercritical state ($T_c = 374$ °C, $P_c = 22.1$ MPa), water behaves remarkably differently from water at ambient conditions. For example, the static dielectric constant decreases down to 6 at 400 °C and 30 MPa, which is comparable to that of organic solvents.

SCW is also an interesting medium for colloid science in two aspects. First, the solvent properties of SCW can be manipulated continuously over wide range by temperature and pressure. Thus, in SCW, interparticle interactions such as van der Waals or electrostatic interactions can be controlled through the medium properties by changing temperature and pressure. Secondly, intense density fluctuation is present in the vicinity of the critical point. The water molecules move cooperatively in the density fluctuation, and such cooperativity would alter the motion of the dispersed particles from Brownian to non-Brownian. The interparticle interactions would also be affected by the fluctuation, leading to change of colloidal stability.

Experimental study on the colloidal dispersions in SCW requires special instrument with a high temperature and pressure cell that can hold hot and compressed aqueous fluids while providing optical access to the sample for the measurements. Also, attention should be paid to the chemical stability of the colloidal particles used.

In this paper, optical microscope and dynamic light scattering systems, both of which allow measurements in SCW, will be described [1, 2]. Experimental results obtained for several colloidal dispersions will also be presented.

This study is carried out as a part of "Ground-based Research Announcement for Space Utilization" promoted by Japan Space Forum. Financial support from The Kao Foundation for Art and Sciences is acknowledged.

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ETICS OF MICELLAR GROWTH: TIME-RESOLVED NS STUDY OF THE LECTHIN-BILE SALT SYSTEM

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queous mixtures of lecithin and bile salt form spherical micelles at high concentrations. In this work, these micelles grow into elongated, worm-like micelles. We studied the kinetics of this growth using time-resolved small-angle neutron scattering combined with a home-built pump-probe device. This allows us to follow the micellar growth with high temporal resolution on the most molecular length scales.

SIZE FRACTIONATION IN PHASE-SEPARATED FERROFLUID STUDIED BY ATR-IR

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Using a vertically oriented attenuated-total-internal reflection (ATR) prism, the concentrations of coexisting colloidal phases can be determined *in situ* by infrared spectroscopy (IR) [1]. The possibilities of the method are illustrated with a phase-separated ferrofluid consisting of toluene, free PDMS polymer molecules, and highly polydisperse magnetic nanoparticles stabilized by a surface layer of oleic acid. Phase separation occurs in this system due to the depletion interaction [2].

The contributions of PDMS, magnetic, and oleic acid to the infrared absorbance spectrum are easily separated from each other and are simply linear with the concentrations. Starting out with a highly concentrated phase-separated ferrofluid, a phase diagram giving the colloid and polymer concentrations above which phase separation occurs is obtained in a few dilution steps. The absence of a carbonyl absorbance peak indicates that all the oleic acid molecules are adsorbed to magnetic particles. The relatively large amount of oleic acid in the top phase therefore reveals that the magnetic particles are smaller than in the bottom phase. This is confirmed by TEM analysis of about 10 000 particles per phase: the particle size distributions are different from that of the oil-phase system obtained after sufficient dilution, in accordance with theory [3,4].

The results demonstrate that height-resolved ATR-IR can be used to determine the concentrations of different chemical components in coexisting colloidal phases. Presumably, the method could be applied to a wide range of systems, even highly turbid or opaque ones, judging from the fact that our ferrofluids look black to the naked eye.

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OTHER STUDIES OF PERFORATED BILAYERS IN LEUCOSYSTEMS OF LIPIDS AND SURFACTANTS

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ryo-Transmission Electron Microscopy is a method allowing visualisation of many of the structures that form by self-assembly of amphiphilic molecules in aqueous systems. The distinctive feature of the method is that the objects are examined without dehydration. This is achieved by capturing the structures in very thin aqueous films that are gently vitrified and examined in the microscope at liquid nitrogen temperature. Objects range from 5 to 500nm are well suited for the method. In cryoTEM investigations vesicles were found [1], an observation that triggered extensive studies of the nature and formation of such structures. In systems comprising bilayers build by a polar lipid where surfactant is added on addition of an ionic surfactant the question arises whether the holes formed are enriched in the surfactant. Some experiments will be discussed in which a surfactant electrode was used to determine the isotherm of surfactant adsorption onto the bilayers. This indicates that the pores form in a cooperative process similar to micelle formation, and that the rims of the pores are covered by a ring-formed half-cylindrical micelle, and a surfactant.

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FOAMS AS VIEWED BY SMALL ANGLE NEUTRON SCATTERING

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We report, for the first time, on Small Angle Neutron Scattering measurements obtained in situ on three-dimensional aqueous foams stabilized by sodium dodecyl sulfate. Isotropic as well as anisotropic scattering data has been collected for two kinds of foams: wet foams in the steady state regime of constant gas bubbling and dry foams under free draining conditions. Reliable scattering spectra were obtained within a few minutes, even for very dry foams. All spectra have a basic $I(q) \sim q^{-4}$ behavior on which a foam specific structure is superposed. The q^{-4} decrease at low q can be interpreted in terms of a Porod law from which the average bubble size is determined for both wet and dry foams. For wet foams, the intensity is modulated at high q by the structural organization of the surfactants in the liquid fraction of the foam (micelles). Remarkably, for dry foams only, structure also appears at intermediate q , corresponding to the film thickness. This signal. Anisotropic measurements on dry foams reveal spikes in the 2D scattering data, suggesting an interpretation in terms of the reflection of the incident beam on the film surfaces. The isotropic scattering data may also be interpreted in terms of reflectivity instead of Porod scattering. Our experiments show the feasibility of scattering measurements as a means to obtain rapid information of average, global foam properties from the film to the bubble scale. The method is also suited as a tool for studying cooperative effects in foams.

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INVESTIGATION OF MICELLIZED RADICAL PAIRS STIMULATED NUCLEAR POLARIZATION (SNP)

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This report contains the investigations of radical pairs (RPs) in micelles by novel indirect magnetic resonance - Stimulated Nuclear Polarization (SNP) and CIDNP with fast External Magnetic Field (SEMF). In the SNP technique, the resonant microwave the rate of singlet - triplet conversion within RPs and thereby alters the measured of nuclear spins in diamagnetic reaction products. The SNP spectra essentially EPR spectra of RPs; therefore they are more sensitive to the effects of the exchange and spin-selective decay on the intersystem crossing within the micellised RPs as the CIDEP technique, which mostly reflects the contribution of free radicals. Besides, it serve as a very informative probe of the micelle properties. It has been demonstrated that the Stimulated Nuclear Polarization (SNP) spectra of MRPs are sensitive to the frequency of the radicals, which depends on the micelle size and intramicellar rate the temperature change and salt additions alter the micelle size and viscosity and affect the reencounter frequency, the shape of the SNP spectra is expected to exhibit a temperature and salt additions dependence. The influence of temperature and salt on SNP spectra and kinetics have been investigated experimentally. From the of the experimental data with the model calculations the influence of the temperature of correlation time of translational diffusion of radicals is the same as the temperature of rotational correlation time. Theoretical and experimental SNP investigations of micellized radical pairs are presented. It has been shown that SNP spectra of radical pairs very sensitive to the mechanism of the electron relaxation.

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5. Inorganic Colloids:

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

FRAGMENTED STRUCTURE OF ADSORBED LAYER OF NON IONIC SURFACTANT ON COLLOIDAL SILICA

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The structure of the adsorbed layer of a non-ionic surfactant on small colloidal silica beads in water at high pH is investigated by SANS. Experiments of fluorescence decay on porous silica [1], neutron reflectivity on wafers [2] and SANS on colloids [3] suggest a fragmented structure in some case, like e.g. at high pH. To our knowledge, no direct evidence (besides the decrease of the average layer density) of lateral structures has ever been reported.

Here, measurement which unambiguously rule out all continuous layer models will be presented [4]. First, the adsorption isotherm was constructed by centrifugation and subsequent spectroscopic determination of the concentration of non-adsorbed surfactant in the supernatant. Secondly, the shape of the surfactant-silica complexes was measured by Small Angle Neutron Scattering in dilute solutions. External contrast variation was used to enhance scattering from the silica and the surfactant, respectively. Finally, a model of decorated silica beads has been developed. It will be shown to agree quite nicely with the experimentally observed intensities.

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ERVATION OF EQUILIBRIUM, NANOMETER SIZED CLUSTERS OF SILVER IODIDE IN AQUEOUS SOLUTIONS

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thermodynamically stable clusters containing up to ten or more silver iodide pairs have
been observed in aqueous electrolyte solutions using ultra centrifugation and cryo electron
microscopy. These clusters are in equilibrium with an excess phase of solid AgI. We measured the
distribution of the clusters by their size dependent shift of the excitation peak at visible
light and show that their weight is determined by their interfacial free energy. We argue
that the equilibrium cluster distributions, but with varying widths, must be present in all
systems in contact with electrolytes that contain adsorbing potential determining ions.

SURFACE-CAPPED MOLYBDENUM SULPHIDE NANOPARTICLES: SYNTHESIS, PROPERTIES AND APPLICATION

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Sulfur containing molybdenum complexes (dithiophosphates, dithiocarbamates) are
widely used as friction modifying and antioxidant additives to hydrocarbon-based lubricants [1]. It
was shown that antifriction properties of molybdenum complexes provide with the formation of
MoS₂ layers on the friction surfaces as a result of Mo compounds decomposition *in situ* at high
temperature [2]. However, the synthesis of molybdenum containing complexes is usually
complicated and expensive.

Recent achievements in nanochemistry [3] supply the possibility to synthesize
molybdenum trisulphide nanoparticles, which may be used as additives for lubricants. In this work
we proposed the method of surface capping with specific surfactant-type compounds, which
chemically interact and/or adsorb strongly on molybdenum trisulphide nanoparticles as well as
contain long hydrocarbon chains to provide solubility in hydrocarbon media.

By this means two pathways of synthesis nanosized molybdenum trisulphide were realized.
The first one represents classical route for inorganic nanoparticles and includes controlled stepwise
oxygen-sulfur substitution in water-soluble molybdate salts located in aqueous core of reverse
microemulsion followed by separation of nanosized MoS₂ and their treatment by surface-capping
compounds. The second method comprises a decomposition of thiomolybdate salts in an organic
hot matrix in the presence of surface-capping compounds. Solubility of synthesized MoS₂
nanoparticles strongly depends on the nature of surface-capping agent.

Nano-scale parameters of synthesized particles were characterized using SAXS and AFM
techniques. The average dimension was shown to be in the range 2.5-3.0 nm, while size
distribution of nanosystems highly depends on synthesis route.

Nanosized MoS₂ revealed excellent antifriction properties especially at increased
temperature and critical load in comparison with traditional Mo additives.

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ANOPOROUS INTERFACIAL LAYER INDUCED BY WATER DEGRADATION OF GLASS MONOLITHS

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The surface of glass monoliths can be altered by water. Leaching of some specific Na, B, part of Si, ... from the matrix results in the formation of a *surface altered layer*. Ion of water in the solid body is an interfacial phenomenon, which is present any time terrils are in contact with water or atmospheric humidity. It is most often undesirable glass windows from cathedrals, glasses in washing machines, nuclear waste storage), but ating glass fibers are accidentally inhaled one desires a rapid dissolution by the lung's ical serum.

The existence or not of these protective properties is not well understood and it is related *roporous structure* of the altered layer. Since a few years the different teams present in ct have started a long term study to understand the relation between the oxides on of glasses [1], the morphology of their altered layers and the protective properties.

Results will be presented on model glass powders containing only sodium, boron, silicon ent amounts of zirconium ($\text{SiO}_2/\text{B}_2\text{O}_3/\text{Na}_2\text{O}/\text{ZrO}_2 = (70/15/15/0-10)$). Using SAXS at the as been demonstrated that the specific porous surface and volume by are linearly linked centration of leached silicon. The presence in the composition of insoluble elements such um stops the shrinkage of the grains during alteration and decreases the average pore ng the layers more protective.

In the case of smooth monoliths (classical use of glasses) Grazing-Incidence-SAXS ts were performed at the ESRF at different incidence angles. As the layers are a few ick, a methodology to extract the diffuse signal at the absolute scale was established. In c the grain studies, it allows to demonstrate that there is no gradient of porosity lar to the interface in the case of the mentioned simplified glasses. The results will be in the framework Monte-Carlo simulation model recently published [2].

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PREPARATION OF GIBBSITE PARTICLES: CONTROL OF SIZE AND COATING WITH SILICA

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Gibbsite is the main component of the aluminum ore bauxite and in that capacity it is studied extensively [1]. At the Van 't Hoff Laboratory, plate-like gibbsite particles are used as model colloids for liquid crystal transition studies [2,3]. Plate-like gibbsite particles, synthesized by hydrolysis of aluminum alkoxides, have a diameter of 150-200 nm, a thickness of 10 nm, and a polydispersity of 2.5-30%.

In this work, a method to grow gibbsite with a diameter up to 400 nm and a polydispersity as low as 12% (figure 1^b) will be presented. The adjustable size and the lower polydispersity of the particles open new opportunities for liquid crystal studies, in particular the columnar phase.

Mixtures of particles of different size and shape also offer opportunities to observe new phases. To explore the possibility of mixtures of gibbsite with silica spheres, we coated gibbsite with silica successfully (figure 1^c). Two methods are explored: via a poly(vinyl pyrrolidone) coating and the three-step method, known from boehmite [4].

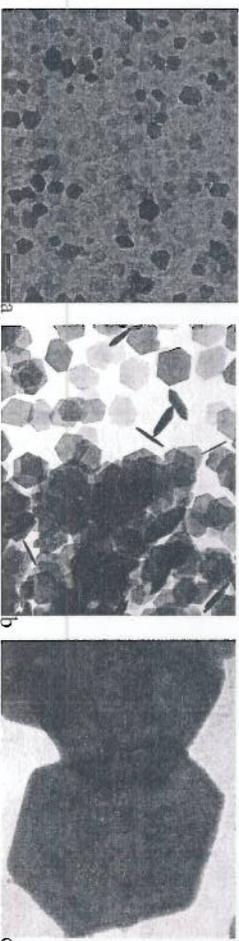


Fig. 1, a gibbsite particles 150 nm, scalebar 500 nm, b gibbsite after 3 growing steps, 390 nm, same magnification as a, c silica coated gibbsite (10 times larger magnification)

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OWNIAN RELAXATION OF MAGNETIC COLLOIDS

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Magnetic fluids are colloidal suspensions of magnetic nanoparticles in liquid carrier. We varied CoFe_2O_4 nanoparticles by controlled precipitation. The particles were coated and in glycerin/water mixtures of different composition.

The diameter of the primary particles was determined using X-ray diffraction with a typical Bragg reflection line shape. The hydrodynamic diameter was determined by light scattering. The magnetization curves exhibit a typical Langevin behavior.

The dynamic magnetic susceptibility was measured in the frequency range between 10 Hz and 10 kHz. It reveals a typical Debye behavior superimposed with a particle size distribution. On the other hand we could calculate the relaxation time from the loss peak of the susceptibility and on the other hand we were able to evaluate the distribution of the hydrodynamic diameters. This last result is in good agreement with the light scattering data.

Increasing viscosity of the magnetic colloid decreases the relaxation time of the magnetic susceptibility. This proves the Brownian relaxation mechanism of CoFe_2O_4 [1].

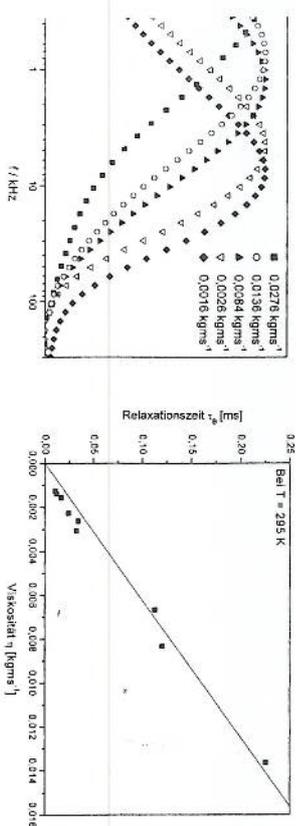


Figure 1: Imaginary part of the magnetic susceptibility of CoFe_2O_4 with different ratio of water. Right: Relaxation time vs. viscosity.

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GIANT COLLOIDAL CRYSTALS

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Giant colloidal crystals have been formed, for the first time by the author (1992), for the diluted and exhaustively deionized colloidal suspensions [1]. Crystal size is largest at the sphere concentration slightly higher than the critical concentration of melting (ca. 0.0002 in volume fraction) and decreases sharply as the sphere concentration increases. The lattice structure of the giant colloidal crystals is investigated using the reflection spectroscopy. The lattice spacing decreases as sphere concentration increases, and agrees with the calculation value from the sphere concentration and sphere diameter. The colloidal crystallization takes place by the Brownian movement of colloidal spheres and the purely electrostatic inter-sphere repulsion never attraction). Blinking phenomenon of the crystals, where the meta-stable crystals move by the Brownian motion, has been observed. Crystallization kinetics is studied intensively by the time-resolved reflection spectroscopy and the dynamic light-scattering techniques. Crystal growth processes are quite similar to those of other crystal systems, where the inter-particle interaction is attraction. Importance of the dynamic phase transition has been clarified. Microgravity experiments for the colloidal crystallization have been investigated in detail. Structural relaxation time, melting temperature, critical sphere concentration of melting, elastic modulus, viscosity, visco-elasticity and other physico-chemical properties have been studied in detail. Electro-optic effects of colloidal crystals are clarified. Phase difference, second-order and the higher-order harmonics, synchronous oscillation and the existence of the characteristic frequencies are clarified [2-5]. Dissipative structural patterns formed in the course of drying the colloidal crystals on a cover glass have been observed. Broad ring, spoke-like and ring-like patterns are formed in macroscopic scale, whereas fractal patterns are formed in microscopic scale.

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COLLOID PARTICLE DEPOSITION AT HETEROGENEOUS SURFACES

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reversible adsorption (deposition) of colloid particles at heterogeneous surfaces was theoretically and experimentally. The substrate surfaces of a desired heterogeneity were covered by uniform surfaces by coupling sites of controlled concentration and sizes of particle deposition kinetics on surfaces produced in this way were carried out to Monte-Carlo-RSA (random sequential adsorption) model discussed in Refs. [1-2]. In addition, also the jamming coverage and monolayer structure was quantitatively evaluated by simulation. The interesting case of multilayer adsorption, which were formed by deposition of oppositely charged particles, was also studied theoretically. Results from simulations were used for interpretation of experimental data obtained for negatively polystyrene latex colloids of micrometer size range. Model surfaces of controlled heterogeneity used in these studies were mica sheets covered by positively charged latex of various sizes. Deposition kinetics of latex was studied as a function of the heterogeneity degree and particle size ratio of particles. Particle distributions over surfaces and coverage were quantitatively evaluated using the direct microscope observation techniques. Two types of cells were used in this studies: the diffusion cell and the impinging-jet cell enabling one to measure the liquid convection on kinetics of particle deposition and the monolayer structure. Using the impinging-jet cell, the jamming coverage of colloid particles at heterogeneous surfaces was measured for the first time in the literature. Structural aspects of particle monolayers also were quantitatively evaluated via the pair correlation function. These experimental data confirmed, in accordance with theoretical predictions, the two main features of particle deposition on heterogeneous surfaces: (i) the deposition rate attained the maximum values for heterogeneity degree as small as a few percent and (ii) the site multiplicity effect exerted a pronounced effect on the structure of deposited particles, making it possible to produce particle clusters of targeted composition.

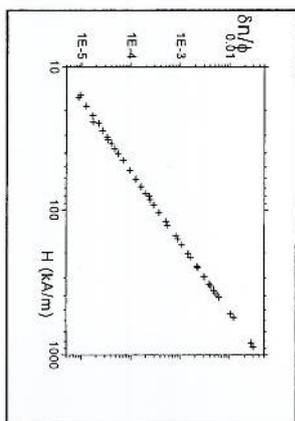
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NANOSIZED NICKEL HYDROXIDE DISPERSION

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Colloidal dispersion of platelets can self assemble into birefringent phases even at low concentrations. This phase behaviour has been probed with electrostatically dispersed clays [1,2] or sterically stabilised oxide platelets [3,4]. In this work, we present results obtained with electrostatically stabilised hexagonal platelets of β -Ni(OH)₂ dispersed in aqueous medium. Nickel (hydr)oxide compounds present a wide interest in technical and industrial applications. It is known to be an active material in electrochemical cycling occurring in Ni-Cd, Ni-H₂, or NiMH_x batteries. In a previous work, we have investigated the effect of experimental conditions of the synthesis on the particle size. Depending on the nature and the concentration of the base used in the precipitation medium, the large crystalline diameter of the platelets can vary from 20 nm up to 90 nm [5]. Particles, used in this work, have been prepared by precipitation of Ni(NO₃)₂ salt in an ammonium hydroxide solution ([Base]/[Ni] = 4) in order to obtain particles with diameter around 80 nm. Then citrate ions are used to disperse the particles. A surface complexation occurs and the unbound carboxylate functions of the adsorbed citrate induced negative surface charge, electrostatic repulsion between the particles are achieved. Concentrated dispersions are obtained by osmotic compression. The organisation of the platelets and the optical properties of the dispersion are studied as a function of the volume fraction (ϕ) at different ionic strengths (I). The colloidal structure has been probed by SAXS. A sol-gel phase transition is observed for a volume fraction which depends on the ionic strength. Gel samples ($\phi = 7.3\%$) exhibit spontaneous birefringence when they are observed between crossed polarizers. The liquid dispersions exhibit a magneto-induced birefringence which is negative. For weak concentrations, this birefringence is proportional to the volume fraction and to the square of the magnetic field H with a Kerr constant equal to $4 \cdot 10^{-8} \phi$ (kA/m)² (Fig. 1).



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BALANCE AND LASER-OPTICAL INVESTIGATIONS ON SILICA NANOPARTICULATE FILMS FORMED AT WATER-AIR INTERFACE

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Monolayers of Stöber silica nanoparticles at water-air interface have been studied in a
balance.

Brewster angle microscopy, scanning angle reflectometry and atomic force microscopy
are used to investigate the effects of the particle size and hydrophobicity on the immersion
of individual particles and the structure of the nanoparticulate film.

The particle-particle interactions have been derived from the surface pressure – area
isotherms. The interactions are employed in a molecular dynamics computer simulation that
allows to investigate the structure formation during compression.

The main results will be presented.

CLOSED PORE FORMATION IN NANOPOROUS STRUCTURE OF SILICA TEMPLATED FROM BLOCK COPOLYMER MICELLES

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Nanoporous silicas with different pore structures were prepared by sol-gel process using
pluronic P123 as the template. The closed pores were shown to be formed in the nanoporous silica
templated by triblock copolymers by evaluating the apparent mass density measured by helium
pycnometry. The rate of drying was shown to be quite responsible for the finally templated
nanoporous structure of the silica. The more rapid drying is more preferable for replicating the
mutually isolated pluronic micelles which results in the closed pores in the nanoporous silica,
whereas the more moderate drying leads to the formation of the ordered liquid crystalline structure
which gives rise to open pores. The closed pores were considered to be formed immediately after
the silica sol was rapidly dried and immobilized in the silica matrix due to the instant removal of
the solvent at higher temperature. This rapid drying method is expected to be a practically useful
pathway to nanoporous silica templated from pluronic molecular aggregates with superior
mechanical or electrical properties.

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INTEGRALED SYNTHESIS OF GOLD NANOPARTICLES INTO ONION-TYPE MULTILAMELLAR VESICLES, COUPLING BETWEEN PARTICLES AND LAMELLAR PHASE EVIDENCED BY CRYO-TEM

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Synthesizing inorganic particles within constrained domains such as microemulsions, vesicles, lamellar lyotropic liquid crystals and liposomes is explored to control particle shapes taking benefit of matrix confinement. These organic-inorganic materials can be used to specific properties. For instance, there is a strong interest in synthesizing gold particles in lipid systems for biological applications. Indeed, gold particles, as electron-dense metal, are used as probes to trace liposomes-cell interactions. The *in situ* growth of gold nanoparticles reported for small unilamellar[1,2] or multilamellar vesicles[3]. Here, gold nanoparticles are synthesized without adding any external reducing agent into onion-type multilamellar vesicles. Usually, gold nanoparticles formation is asserted by conventional electron microscopy[1-3]. However, the above technique requires vesicles drying and staining to enhance contrast. Such pretreatment leads to formation of electron-dense aggregates (artifacts) that are mistaken for metallic nanoparticles[1,3].

In this paper, we use cryogenic temperature-transmission electron microscopy (cryo-TEM) to show embedding of nanoparticles synthesized in between lipidic lamellae. We reveal the coupling between the particles shape and the structure of the templating lamellar phase. We also show the simple mechanism of particles growth within multilamellar vesicles based on cryo-TEM observations.

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6. Interfacial Chemistry:

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

HYDROPHOBICALLY MODIFIED PROTEINS AT INTERFACES

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The ability of proteins for adsorption at interfaces of various types as well as the ability to pass across biomembranes in many vital biological processes depend considerably on the hydrophobicity of their molecules. Within certain limits it is possible to increase the hydrophobicity of the protein molecules by covalent attachment of alkyl chains.

We prepared the hydrophobized forms of a number of proteins (human IgG, horse radish peroxidase, glucose oxidase, gelatin, α -lactalbumin) by covalent attachment of alkyl chains to the lysine amino groups of their molecules by reaction with *N*-hydroxysuccinimide esters containing caprylic, lauric or palmitic chains. The changes in the protein hydrophobicity were estimated with a fluorescent probe, 8-anilino-1-naphthalenesulfonate, which binds to hydrophobic sites of protein molecules, and the position of the fluorescence band as well as the quantum yield of emission strongly depends on the polarity of microenvironment.

Hydrophobized proteins were found to possess enhanced surface activity at the air/water interface and displace preadsorbed native proteins from the interface. In addition, hydrophobized proteins display enhanced ability to penetrate into lipid monolayers spread at the air/water interface as compared with the native proteins.

In general, increase in the protein hydrophobicity results in an increase in the affinity for hydrophobic solid supports (polystyrene, silica coated by phosphatidyl choline or cholesterol monolayers) and in formation of more compact surface layers.

In order to evaluate the nature of interactions, which control the adsorption of proteins at solids, we evaluated the calorimetric parameters of the adsorption of the native and hydrophobized human IgG onto silica. It was found that adsorption of all forms of IgG is endothermic, that is the process is entropy driven. Both structural changes in the protein molecules and dehydration of their hydrophobic sites may contribute to the positive entropy of adsorption.

The adsorption isotherms, reversibility of adsorption and contributions of various interactions into adsorption of proteins are discussed.

AMPHIPHILIC BLOCK COPOLYMER MICELLES IN LAR AND AQUEOUS MEDIA. EXPERIMENTAL STUDY AND COMPUTER SIMULATIONS

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Block copolymers containing a long hydrophobic block, e.g., polystyrene (PS) and a long ionic block, e.g., poly(methacrylic acid), PMA are insoluble in water. However, micellar micelles with hydrophobic cores and water-soluble shells may be prepared by dissolution of samples in a mixed common solvent and by dialysis in aqueous media. micelles are usually kinetically frozen in water and properties of micellar solutions are studied by the polyelectrolyte behavior of micellar shells. [1]

Recently we studied (i) self-assembly of nanoparticles formed by PS-PMA with triblock modified PMA blocks. A multidisciplinary study, both experimental (SLS, fluorescence, NMR, AFM, electrochemical techniques, FCS) [2] and theoretical (MC and MD) yielded conclusive results on the behavior of modified micellar systems. The non-polar ends of hydrophilic PMA blocks try to avoid the aqueous medium and bury in the shell of the nonpolar PS core forcing the PMA chains to loop back. The formation of loops is usually unfavorable and the distribution of hydrophobic tags in the shell is a result of the entropic interplay. Further we studied (ii) the formation of three layer "onion" micelles lyrene-block-poly(2-vinylpyridine)-block-poly(ethylene oxide), PS-PVP-PEO in aqueous media. Their cores are formed by PS. Since the protonated PVPH⁺ is soluble in acid media and the unprotonated PVP is insoluble in basic media, the micelles may be reversibly transferred from the core/shell micelles to the state of "onion" micelles and back by simple alkalimetric or titration.

In this communication, we present new results on (i) hydrophobically modified PS-PMA systems and (ii) PS-PVP-PEO micelles, which we compare with micelles formed in the presence of PS-PVP and PVP-PEO. [4]

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DNA COMPACTION ON DIFFERENT SURFACES BY CATIONIC SURFACTANT

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Complexes between DNA and cationic surfactants, the so-called lipoplexes, are thought to be useful as potential vectors for gene transfection. Among the factors that control DNA compaction upon interaction with cationic surfactants in the bulk are the nature of both the DNA [1] and the surfactant [2]. In vivo, the complexes will encounter different types of interfaces in the blood stream (walls of protein vessels, blood cells, proteins, etc.) before being thoroughly delivered. Interactions with such interfaces are likely to occur and therefore influence the uptake behavior of the lipoplexes. Hence, the interfacial behavior of lipoplexes will partly determine how efficiently DNA is delivered to the target cells. We have studied the adsorption behavior of DNA and DNA-cationic surfactant complexes on different surfaces by means of ellipsometry [3,4] and dynamic light scattering. Emphasis has been placed on the DNA molecular weight as well as its conformation (single and double stranded). Both hydrophobic and hydrophilic surfaces have been used. On hydrophobic surfaces, cetyltrimethylammonium bromide (CTAB) induces partially irreversible compaction of DNA adsorbed layers. Additionally, there is a synergistic increase in the adsorbed amount when both CTAB and DNA are present as compared to the surface excess concentration of either of the individual components [3]. On negatively charged surfaces, cationic surfactant addition induces adsorption of DNA-CTAB complexes despite the fact that surfactant free-DNA does not adsorb at all [4]. The DNA molecular weight and conformation have a large effect on the surfactant-free DNA adsorption behavior but not on the mixed DNA-CTAB adsorption behavior on hydrophobic surfaces [3]. The adsorption of DNA and DNA-CTAB complexes on polystyrene particles has been studied by means of dynamic light scattering. Consistent results have been found between the two techniques used.

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WALL INDUCED MOBILITY-INCREASE UPON DENSIFICATION IN A COLLOIDAL MODEL SYSTEM

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Concentrated suspensions of colloidal hard spheres near a hard wall were studied in real time by means of time-resolved fluorescence confocal scanning microscopy. Both structure and dynamics of these systems differ dramatically from their bulk analogues (i.e., far away from a wall). In particular, systems that are a glass (a solid phase without long-range positional order) in bulk show significant hexagonal order at a wall. The amount of hexagonal order depends on the (k) volume fraction of the system. It will be shown how the (heterogeneous) dynamics of these systems is coupled to structural order and how this can result in an increase of displacements and diffusion in a certain density-range.

NANO-ENGINEERED MICROCAPSULES AS STIMULI-RESPONSIVE SENSORS AND MICROREACTORS

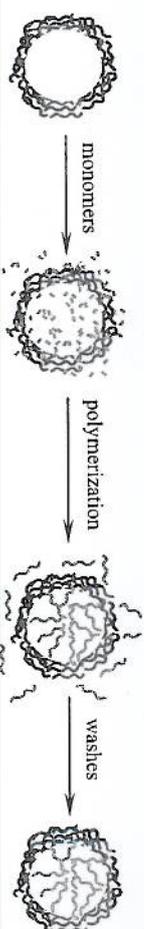
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Multilayered polyelectrolyte microcapsules are in great interest due to their possible use as microcontainers. Recently, they have been used for the synthesis of inorganic particles in their restricted volume [1].

Here we present the results about capsules loaded with polymers and their potential use as stimuli-sensors and microreactors. The microcapsules were prepared by alternative adsorption of oppositely charged polyelectrolytes on the surface of colloidal templates. The colloidal core was then decomposed at conditions where the polyelectrolyte multilayers are stable, leaving a hollow polyelectrolyte capsule. The polyelectrolytes used are water-soluble; we usually used the sodium salt of styrene poly(sulfonate) (PSS) and the poly(allylamine) hydrochloride (PAH). Basically, small solutes such as ions or dye molecules can readily penetrate polyelectrolyte multilayers, while large molecules cannot. This property was used to encapsulate polymers inside the capsules by synthesis from suitable polymerizable monomers [2].

Synthesized polymers were chosen depending on their stimuli-responsive properties: metal complexants for reversible complex formation in the presence of metal ions, acid or basic



polymers for their pH-responsive properties, gelling polymer such as poly-NIPAM for its thermo-responsive properties. These loaded capsules would be therefore used as stimuli-sensors. Such encapsulated polymers could also act as adsorbents for substrates or as substrates themselves, and will be used for chemical reactions inside the capsules that will thus be employed as microreactors.

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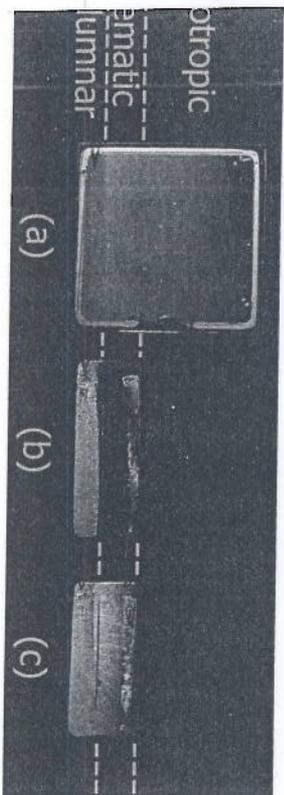
LIQUID CRYSTALLINE PHASE TRANSITIONS IN SUSPENSIONS OF CHARGED COLLOIDAL PLATELETS

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In 1938, Langmuir [1] reported on a bentonite clay suspension that separated into an isotropic (I) and a birefringent nematic (N) phase. Although many experiments have been performed on clay suspensions, macroscopic I-N phase separation has never again been observed. However, it was impeded by gelation. Here, we report on a suspension of charged colloidal platelets that not only exhibits the I-N phase transition, but also shows the nematic-ar (N-C) transition.

In addition to the shape dependent thermodynamic driving force it appears that the effect of gravity is important. The phase behaviour, which initially is only a matter of thermodynamics, is affected markedly in a gravitational field. For example, a biphasic (I-N) suspension becomes uniphase (I-N-C) after several months, see the figure. This effect is well described by a simple compression model. Our observations demonstrate that gravity can induce novel and interesting phase behaviour in colloidal systems of platelike particles.



Our sample was initially biphasic (I-N) but became triphasic (I-N-C) after 6 months due to gravity. (a) depicts the sample at ordinary illumination, (b) and (c) show the sample after 6 months. In (b) and (c), the sample is slightly tilted to reveal the homeotropic orientation of the platelets.

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THERMODYNAMICS, KINETICS AND DILATIONAL RHEOLOGY OF INTERFACIAL LAYERS

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A comprehensive description of surfactant adsorption layers at liquid interfaces comprises the thermodynamics, the formation process and the behaviour at external perturbations. Over the recent years the understanding of equilibrium adsorption layers has been strongly improved [1]. The physical concepts of orientational changes or formation of aggregates of adsorbed surfactants have been successfully elaborated and applied to experimental data.

Each thermodynamic model has a specific impact on the adsorption kinetics as well as on the two-dimensional rheology. It has been shown that molecular processes in adsorption layers like reorientation of 2D-aggregation can change the rate of adsorption remarkably. These effects also change the dynamic surface elasticity and viscosity of adsorption layers [2]. In addition, a new phenomenon has been taken into consideration that is essential in understanding the dilational rheology of surfactant layers, its two-dimensional compressibility [3]. This effect has large impact on the viscoelasticity of an adsorption layer while the equation of state does not change very much as compared to negligible compressibility. Experimental data are presented to support the developed theoretical models.

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BLE SURFACTANT-FREE OIL-IN-WATER EMULSIONS

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It has long been known that an oil surface develops a negative charge in contact with from the pH dependence of the electrophoretic mobility it has been assumed that the charge from adsorption of hydroxide ions at the surface, but this has been difficult to prove on emulsions.[1] The large surface area created in concentrated emulsions eliminates the of trace contamination and amplifies the pH change caused by the adsorption of the ions at the surface. We have measured simultaneously the pH and the droplet size of 2.0% hexadecane-in-water emulsions by electroacoustics as emulsification progressed.[2] demonstrate quantitatively that the dissociation of water produces hydroxide ions which the oil droplets in surfactant-free emulsification.

A coarse emulsion of 2 vol% hexadecane in water at pH 9 (NaOH) in the absence of any it or other electrolyte was continuously passed through a four-stage piston homogeniser flow-through cell of a prototype AcoustoSizer-II[3] under an inert atmosphere of N₂ while roeacoustic dynamic mobility spectrum and the pH and conductivity were simultaneously d. The pH tended to drop as emulsification occurred but was maintained at pH 9.0 by addition of NaOH solution. The uptake of hydroxide was linearly dependent on the of the surface area of the emulsion, which was calculated from the droplet diameter which d from >2 μ m to about 500 nm, as determined from the dynamic mobility spectrum. At the on of the process the surface charge was calculated from the hydroxide consumption to be μ C/cm².

These surfactant-free emulsions are remarkably stable in low salt solutions. Droplets of diameter formed at pH 10 in 1 mM NaCl solution could be reversibly titrated to pH 5 a their zeta potential from -40 to -20 mV. Comparison of dielectric response and ousities measurements on the 5 vol% emulsions in 0.5 mM NaCl indicates a small amount ntl layer conduction in the NaOH double layer. Addition of 1-2 mM SDS produces a large in stagnant layer conduction to the levels observed in emulsions prepared in SDS

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idal Dynamics Pty Ltd, Warwick, RI, USA and Sydney, Australia

NANOBUBBLES AND ACID-BASE INTERACTIONS

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It has been shown recently that nanosized bubbles very probably exist on surfaces with low surface energy [1]. These so called nanobubbles give rise to a long-range hydrophobic attraction [2] that often causes adsorption of hydrophobic colloids on hydrophobic surfaces. Nanobubbles influence e.g. fouling under process conditions, where hydrophobic surfaces are used, and hydrophobic contaminants occur in water. Results the experiments, in which the effects of nanobubbles were determined with QCM-D and contact angle measurements, are presented. Hydrophobic polystyrene, teflon and gradient surfaces from silica, on which the surface energy increased linearly, were used as model surfaces. The measurements were made both in normal and in helium atmosphere with and without degassed water. The role of hard and soft Lewis acidity and basicity on the formation of nanobubbles is discussed.

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LF-ALIGNMENT OF IRON PARTICLES IN A LIQUID CRYSTAL INDUCED BY THE INTERACTIONS AT INTERFACE

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To obtain highly organized structures, which can be modulated by the application of an magnetic field, we want to align iron particles (typically of micrometer size) in a nematic liquid crystal (NLC). When the NLC molecules are strongly and perpendicularly anchored at the surface of a spherical particle, this one acts like a radial hedgehog carrying a topological charge of ± 1 . This topological charge is fixed into a uniformly aligned nematic matrix and to ensure the boundary conditions at the interface a total topological charge of zero, the particle must nucleate a further defect in its environment. For large particles and sufficiently strong anchoring, the dipole is the configuration $[1]$. This topological dipole is formed by one spherical particle and its companion al defect, called hyperbolic hedgehog, arises from the minimization of the elastic energy and allows the nematic director to be aligned along the horizontal axis far from the particle. As the electric dipoles, the dipoles arising from the elastic deformation of the NLC tend to the dipolar attraction $[2]$. The condition of dipolar attraction is: $WR/K \gg 1$ (equation where R is the radius of the particle, K an intrinsic elastic constant of the NLC and W the anchoring energy).

The first part of this study consists in creating a strong and homeotropic (ie uniaxial) anchoring of the NLC molecules on the surface of the iron particles. We have at the iron surface treated with long molecules derived of silanes induces a sufficiently strong anchoring of the nematogens to permit the self-alignment of these particles. In these linear conditions the presence of the companion defect prevent the contact between neighbouring particles. The distance of the companion defect is fixed by the parameters of the equation (1) and can be modulated by an external magnetic field. Our aim is, in a second part, to appreciate the influence of an magnetic field on this structures.

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EFFECT OF SURFACTANT HLB ON NANO-EMULSION FORMATION

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Nano-emulsions are a class of emulsions with uniform and small droplet size (typically in the range 20-200 nm) that are attracting increasing attention for their applications in pharmaceutical, cosmetic, chemical, etc. fields. Although there have been numerous studies on basic aspects of nano-emulsions, the mechanisms leading to their formation and stability are not fully understood yet. It is well known that when using dispersion emulsification methods, the higher the energy input the lower the droplet size. However, nano-emulsions can be also produced by means of condensation or low-energy emulsification methods. Indeed, O/W nano-emulsions with droplet diameter as low as 50 nm were obtained by the PIT (Phase Inversion Temperature) emulsification method in the water/C₁₂E₄/hexadecane system at 20 wt% oil concentration and oil-surfactant weight ratios lower than 85/15 $[1]$. As a part of a study on the mechanisms of nano-emulsion formation, the aims of this work were to find out the relation between surfactant HLB number and nano-emulsion droplet size and stability. The HLB number was varied mixing two polyoxyethylene-type nonionic surfactants and emulsification was carried out by fast cooling of the samples from their corresponding PIT to 25°C. Nano-emulsion stability was assessed by measuring droplet size as a function of time. It was found, as expected, that as surfactant HLB number increases, the PIT also increases. The interfacial tensions at 25°C should be higher the higher the PIT of the system. Therefore, an increase in droplet size was expected with the increase in surfactant HLB. However, similar droplet sizes were obtained for a wide range of HLB numbers, an indication that equilibrium interfacial tension is not the only critical factor for nano-emulsion formation. Moreover, nano-emulsion stability could not be fully explained by the Ostwald ripening mechanism. These results have been interpreted by considering the type of phases involved in nano-emulsion formation.

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MONODISPERSE SURFACE MICELLES OF SEMIFLUORINATED ALKANES IN LANGMUIR MONOLAYERS

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formation of surface micelles was observed by atomic force microscopy (AFM) and X-ray diffraction in Langmuir monolayers of semifluorinated alkanes $C_nF_{2n+1}C_mH_{2m+1}$ (FnHm $n = 6, 8, 10; m = 14, 16, 18, 20$) that had been transferred onto silicon wafers. These micelles are monodisperse. The hydrogenated segments of FnHm molecules are directed to the substrate, while the fluorinated segments are pointing outwards toward air. We note that the size of these micelles is controlled by the density mismatch between the hydrogenated and fluorinated segments of the FnHm molecules. A disk-like shape is observed on the basis of electron density calculations. These results offer new perspectives for the elaboration of nanopatterned surfaces with a tunable periodicity.

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MODELLING OF POLYAMPHOLYTE DIBLOCK BRUSHES

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Polyampholyte brushes at a spherical interface immersed in an aqueous solution have been studied by use of Monte Carlo simulations and a mean-field lattice theory. The studied brushes are block copolymers of two oppositely charged blocks. Two types of diblock brushes are considered; one type contains short and long blocks, and another one consists on two blocks of equal length. Influence of chain grafting density is also studied. It was found that the structure of the polymer brushes is strongly dependent on the relative charge of the blocks, chain composition and grafting density; at certain conditions a coexistence of coiled and stretched chains is observed. Most of the results obtained by the two different theoretical approaches are in good agreement.

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NONLOCAL VISCOELASTICITY OF POLYMER FILMS AT THE LIQUID - GAS INTERFACE

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The dilational dynamic surface elasticity plays an important role in the stability of foams and emulsions. On the other hand, measurements of the dynamic surface elasticity in a broad frequency range allow studying the kinetics of relaxation processes in surface films. It is rather difficult to measure the dynamic elasticity of adsorbed polymer films has not been investigated in a way until recently. In this paper we present the results of application of three different methods of the relaxation spectrometry of the liquid surface layer to adsorbed and spread surface films of various polymers. The methods of longitudinal and transverse surface waves and also the barrier method have been applied to spread films of polyethylene oxide (PEO) and films of PEO, polyvinylpyrrolidone, polyethyleneglycol (PEG). The frequency of the surface wave perturbations changed from 0.01 up to 520 Hz. The viscoelastic behavior of polymer films is found to be different from the surface viscoelasticity of solutions of conventional low-molecular weight surfactants. First, the modulus of the dynamic surface elasticity was rather low (less than 1 N/m) and thus approximately one order of magnitude lower than the corresponding modulus of conventional surfactants. Second, while the surface elasticity of surfactant solutions usually increases with concentration, the elasticity of polymer films decreases with the monomer concentration. Third, the imaginary part of the dynamic surface elasticity is usually less than the real part with the exception of the low concentration range where the surface elasticity can be determined. The obtained concentration dependences of the surface elasticity can be explained by means of the dynamic model of the polymer solution surface layer. The main relaxation processes consist in the monomer exchange between different regions of the surface layer. The work was supported by the Russian Foundation of Fundamental Research (3-32366).

7. Biocolloids & Biomaterials:

*Chemistry and Physics of biological colloids, design of
biocolloids, biomimetic materials*

INTERACTIONS BETWEEN BSA LAYERS ADSORBED ON DIFFERENT SUBSTRATES MEASURED WITH AN ATOMIC FORCE MICROSCOPE

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The participation in a lot of very important biological processes and the application in a great number of industrial, pharmaceutical and environmental techniques have converted proteins in very interesting systems. Many works have been devoted to the study of these important molecules. To interpret correctly the behaviour of proteins is necessary a complete knowledge of the interactions between them. The electrostatic repulsion and the van der Waals attraction play an important role in the stability of proteins and colloidal systems in general, and they are taken into account in the classical DLVO theory. But in proteins other repulsive force of very short range has been observed, which is able to prevent the aggregation even though the electrostatic repulsion is negligible. It is thought that these forces, which can not be explained by the DLVO theory, are due to the arrangement of the water molecules around the hydrophilic surface of the protein; that is why they are known as hydration forces. These special forces have also been observed in other systems of hydrophilic nature [1].

By the aid of an atomic force microscope (AFM) and the colloid probe technique, the interaction forces between BSA layers adsorbed on different substrates (silica and polystyrene) have been measured directly as a function of pH and salt concentration (NaCl and CaCl₂). Electrostatic and steric forces dominate the interactions at low salt concentrations. At high salt concentrations, when electrostatic interactions are screened, a very strange behaviour is found as a function of pH. The behaviour around the i.e.p. of the protein is also very striking: the interaction is attractive at low salt concentration, but it is repulsive at high salt concentration. These results could be explained if the presence of hydration forces is assumed. The influence of the substrate nature (hydrophilic in the case of silica and hydrophobic in the case of polystyrene) on the conformation of the adsorbed BSA and interactions between layers of these protein can also be observed.

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INVOUS PHASE TRANSITION IN GANGLIOSIDE GM3 DISPERSED BILAYERS

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Small Angle (SAXS) and Wide Angle (WAXS) X-ray Scattering experiments were performed on ganglioside GM3 bilayers dispersed in bulk solution, in a wide range of concentration (0.1-15%) and temperature (15-60°C). Density measurements were also performed as a function of temperature. GM3 is a glycosphingolipid, with a sugar headgroup and a long hydrophobic tail, the ceramide. SAXS experiments evidenced peculiarities in the section profile of the bilayer at low temperatures, as previously found also for GM3 at low concentration, 0.1% [1]. Both WAXS and densitometry revealed the presence of a phase transition extending over a wide temperature range, 25-60°C, to be compared to the one occurring in diacylglycerol lipids attributed to the highly cooperative order-disorder transition of the hydrophobic chains. The experimental results indicate that, rather, a glass transition is likely to take place in GM3 bilayers, with the sugar headgroups playing a role in the hydrophobic chains from assuming the mutual position needed to form the ordered lipid bilayer. Sugar headgroups of gangliosides are known to display preferential interactions with water conformers, driving to cooperative surface behaviors, presumably triggered by enthalpic interactions, that couple to the hydrophobic ones [2]. These findings are particularly relevant as gangliosides, naturally present in the outer leaflet of plasma membranes, are known to be involved in lipid driven microdomains (sphingolipid enriched domains, SED) together with a number of selected lipids and proteins involved in important biological functions. Nevertheless, the role is known on the physical basis of SED formation and on their structural properties. The segregation process of sphingolipids and diacylglycerol packing properties could well be at the origin of the segregation process of sphingolipids. Interestingly, recently a glass transition has been reported to occur in sphingomyelin monolayers and ceramides have been found to assume different behaviors from those of common diacylglycerols. Both systems have the same chemical part of GM3, and both peculiar behaviors have been tentatively attributed to differences occurring at the level of the hydrophobic-hydrophilic interface. 

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NOVEL SOLID SURFACES FOR PLANAR SUPPORTED LIPID BILAYERS

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The lipid bilayer is the central structural feature of all cell membranes. Many proteins are associated with or inserted into these bilayer structures. An important feature of natural membranes is that they are fluid, that is many of the components within or associated with membranes can diffuse in two dimensions [1]. This is essential for the formation of functional biological assemblies and for a dynamic response to various stimuli. Supported lipid bilayers are unique, self-assembling, two dimensional fluid systems. Supported membranes can be formed by spontaneous fusion of lipid bilayer vesicles with an appropriate hydrophilic surface such as glass and few hydrophilic self-assembled substrates described below. Supported bilayers are separated from the solid substrate by a thin (~7-15Å), lubricating film of water, and they retain many of the properties of free membranes including lateral fluidity. The fluidity is long-range, with mobile components of both leaflets of the bilayer freely diffusing over the entire surface of the substrate. Bilayers on solid supports were originally developed for studies of interactions between living cells where they have proven highly useful [2-3], the planar geometry is ideal for imaging and quantification using microscopy and a variety of surface-sensitive techniques. Many functions and reactions in biological membranes depend on the lateral mobility of lipids, lipids with specialized head groups, and membrane associated or anchored peptides and proteins. Incorporation of these components in supported bilayers will be considered successful if they retain their structure, capacity to assemble, and activity, and display a mobility that is similar to that of the same molecule/structure in free vesicles or on cell surfaces. Despite extensive efforts in many labs, only limited success has been reported in demonstrating mobility and function for membrane anchored or integral membrane proteins. For example, with the bilayer directly supported on glass, membrane spanning integral membrane proteins interact strongly with the solid support [4]. More subtle effects such as a loss of membrane flexibility can affect the stability, functionality, and mobility of membrane-associated biomolecules, such as ion channels. We have shown that potassium channels can be incorporated and kept stable and functional in a mobile (supported) lipid-mixture bilayer. The surface sensitive techniques we mainly used to investigate these properties are: Electrochemistry, QCM (Quartz Crystal Microbalance), FRAP (Fluorescence Recovery After Photo Bleaching) and X-ray scattering.

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STRUCTURE AND INTERACTIONS IN DILUTE AND CONCENTRATED PROTEIN SOLUTIONS

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We have studied the structural and dynamic properties of concentrated protein solutions as well as their dominating interaction forces, aggregation phenomena and phase transitions such as liquid-liquid phase separation and crystal and glass formation. Here we report on small angle X-ray scattering (SAXS) and light scattering investigation of the static and dynamic structure of concentrated solutions where we vary the interaction potential from purely hard sphere to soft sphere plus a short range attraction. Such a short range attraction leads to an interesting phase behavior with the possibility of a liquid-gas coexistence curve that is very different from the liquid-liquid coexistence curve of a simple fluid. We will discuss the experimental data will be compared with results from computer (MC) simulations. We will also discuss the experimental findings in view of biologically and physiologically important processes such as cataract formation in eye lenses and protein crystallization.

THERMODYNAMICS OF DNA-LIPID HYDRATION

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In this presentation we will show our recent studies on the thermodynamics of hydration of stoichiometric complexes of DNA with cationic lipids [1].

In most cases where DNA functions in the intracellular environment it interacts strongly with oppositely charged proteins with only a limited number of water molecules, per base pair, directly participating in the formation of the complex structure. In the DNA-lipid complexes we have a similar tight interaction between DNA and an oppositely charged species, while the system is simple enough to lend itself to a detailed thermodynamic characterization.

Both lamellar and hexagonal structures were found for stoichiometric aggregates of DNA and different lipids. In nearly all structural studies one has considered systems in equilibrium with a bulk aqueous solution of low osmotic pressure and the extent, as well as the role of the hydration, has not been an issue.

We have used a microcalorimetric vapor sorption technique developed by Wadsö and Markova that makes it possible to simultaneously measure both the partial molar free energy and the partial molar enthalpy of the water at non-saturated conditions [2].

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LYSIN FORMATION DURING THE DISSOLUTION OF LIPID LAMELLAR PHASE

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After contact with water, lipid lamellar phases can show spectacular instabilities: multi-tubules, so-called myelins, grow from the L_{α}^d /water interface into the water. We have recently investigated the growth of these myelins as well as changes in the lamellar phase structure using cryo-electron microscopy, direct observation and time- and space-resolved small-angle X-ray scattering. This provides detailed quantitative information on the dynamics of myelin growth, the swelling of water as well as the swelling and textural changes of the lamellar phase. Based on these observations a semi-quantitative model for myelin growth is proposed.

METASTABILITY AND SUPERSATURATION IN LYSOZYME CRYSTALLIZATION

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Nucleation of protein crystals takes place only for supersaturation values, with respect to the equilibrium solubility concentration, which are far larger than what is commonly found for solutions of simple molecules. This puzzling behavior is very probably related to the peculiar potential of the mean force between protein monomers, containing a very short range attractive contribution. Besides, protein equilibrium solubility display a strong temperature dependence, which cannot be easily framed within a simple Debye-Hückel approach to interparticle interactions.

In this work, we show that nucleation kinetics in lysozyme solutions allows to introduce a rather well defined 'metastability limit' c^* , which we have studied, for different temperatures, as a function of the solution ionic strength I . We observe that c^* scales with electrolyte concentration as a power law, with an exponent which does not depend on temperature and pH. The ratio between c^* and the solubility concentration increases with I . A different scaling behavior of c^* is observed when polymers, instead of simple electrolytes, are used as precipitating agent, and the metastability ratio remains constant when polymer concentration is increased.

The ionic strength dependence of the supersaturation ratio can be partly explained with the help of a model for protein interaction near crystallization recently proposed [1,2]. Conversely, temperature effects call for a more detailed scrutiny the hydrophobic contribution to protein salting-out effects.

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CIPITATION OF DNA BY CATIONIC SURFACTANTS, DIFFERENCES BETWEEN SINGLE- AND DOUBLE-STRANDED DNA

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It is known that DNA-cationic surfactant systems associatively phase separate with the formation of a precipitate. This is an important feature for the purification and counting of nucleic acids, for example.

In this work the phase behaviour of DNA and the cationic surfactant trimethylammonium bromide, DTAB, was studied as a function of salt, NaBr, and urea. The boundary of the two-phase region of the phase maps was evaluated by titrimetry. Melting temperature curves of DNA solutions at different salt concentrations were obtained, and the state of the DNA molecules was checked by circular dichroism.

It was found that the phase behaviour of DNA-DTAB is dependent on the ternary composition of the DNA molecule. Single-stranded DNA, probably due to its higher flexibility and hydrophobic parts, precipitates earlier with the addition of the positive surfactant than the double-stranded molecules. This can be very interesting for applications like purification, since it allows an easy separation of single and double-stranded DNA molecules.

BIOMATERIALS IN MICROCHANNEL MIXING DEVICES MANUFACTURED BY SOFT LITHOGRAPHY TECHNIQUES

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Handling and manipulation of extremely small volumes are important issues whenever biomaterials are used, which are often hard to isolate in larger amounts. The usage of microfluidic devices does not only allow to analyze small volume fractions but also gives access to faster observation and improved characterization. We are manufacturing microchannel systems such as crossed single channels, parallel aligned straight channels and curved channels with variable radii for the manipulation of biomaterials. In a crossed-channels device the laminar flow gives access to diffusional mixing experiments by hydrodynamical focusing of a center stream by two side streams. Due to a resulting steady-state flow profile the time evolution of the mixing reaction can be observed with fluorescence microscopy, Raman microscopy, and small angle x-ray scattering by varying the observation position along the stream. Our studies on biomaterials are focused on the DNA condensation induced by multivalent cations of different shape and size.

DNA AS A LINKER BETWEEN COLLOIDS

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Magnetic particles form reversible chains under magnetic field, due to field induced. When the field is removed, particles re-disperse by Brownian motion. However, in the presence of specific biomolecules, links may appear between adjacent particles and magnetic chains persist. We thus grafted streptavidin on 200 nm-sized magnetic beads and used 5', 5'-double-stranded DNA to form permanent and flexible chains. We were able to form linear assemblies with DNA of different lengths and to study both the formation and the disassembly of these objects. The kinetics of formation of molecular links between the beads was assured by direct imaging of the chains and by small-angle static light diffusion. Once these links were formed, the properties of the molecular link were studied with the so-called magnetic force technique [1]. Under a given magnetic field, equilibrium occurs between the attractive force due to the field and the repulsive colloidal forces. By analyzing the light diffracted by the chains, the colloidal repulsive force can be determined in the presence of DNA as a function of the distance between the beads and of the length of the DNA used. In parallel, we also studied the flexibility of the permanent chains as a function of the DNA length using an imaging technique developed by Goubault *et al.* [2]. Finally, we were able to synthesize well controlled colloidal assemblies with DNA as a linker and determined the influence of DNA length on the physical properties of these assemblies.

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MIXED MICELLE FORMATION OF SODIUM CHOLATE
CONJUGATES AND PHOSPHATIDYL-CHOLINE,
AND SOLUBILIZATION OF CHOLESTEROL INTO THE
MIXED MICELLES

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Micellization of sodium glycocholate (NaGC) and sodium taurocholate (NaTC) was studied for the critical micelle concentration (CMC) at various NaCl concentrations by pyrene fluorescence and light scattering, and the degree of counterion binding to micelle was calculated using the Cortin-Harkins plot. The aggregation number of NaGC (8.7) and NaTC (6.0) micelles was determined by static light scattering. Solubilization of phosphatidylcholine (PC) to the above micelles was then studied at different temperatures by an enzymatic method and by transmittance of the suspension system. The average mole ratio (PC / bile salt) decreased with increasing bile salt concentration above the CMC. Hydrodynamic diameters (d_h) of PC-saturated NaGC and NaTC aggregates were measured by dynamic light scattering as a function of bile salt concentration at 308.2 K. Change of the d_h values with increasing bile salt concentration indicated shape transition from vesicle (d_h : 150 nm) to micelle (d_h : 10 nm). The maximum additive concentrations of cholesterol into the aqueous micellar solutions of NaGC and NaTC were spectrophotometrically determined using enzymatic analysis. The cholesterol solubility increased in the order of NaTC < NaGC at the same concentration. Thermodynamic analysis was made for the solubilization.

**NANO-SIZED SELF-ASSEMBLED LIQUIDS FOR IMPROVED
SOLUBILIZATION****N. Garti***Casali Institute of Applied Chemistry, School of Applied Science, The Hebrew University,
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In our recent studies we have found a unique mixture of water, special food-grade oil, mixture of food-grade surfactants, cosolvent (polyol) and coemulsifiers that can self-assemble to form new nanosized modified microemulsions of U-type, totally dilutable with aqueous phase. The "concentrate" is capable of solubilizing nutraceuticals that are poorly soluble in water or oil phase at ca 15-20 folds over their solubility capacity. Nutraceuticals such as lycopene, lutein, CoQ10, phyosterols, etc. have been solubilized.

We have used advanced techniques such as SAXS, SANS, SD-NMR, QELS to evaluate the microstructures in the absence and in the presence of the guest molecules.

The presentation will bring data on the solubilization of the nutraceuticals, their chemical protection against oxidation, and their improved bioavailability. Effects of guest molecules and microemulsions ingredients on the microstructure transitions and reactivity will be discussed.

CHANGES ON THE PHYSICO-CHEMICAL SURFACE
PROPERTIES AND ADHESION BEHAVIOUR OF
PROCOCCUS FAECALIS BY THE ADDITION OF SERUM
OR URINE TO THE GROWTH MEDIUM

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Enterococcus faecalis is a bacteria which has been widely recognized as a pathogen in the tract [1]. Also, in the last years, nosocomial infections such as endocarditis are sometimes by this microorganism. These infections are most of the times originated from the adhesion to the surface of a indwelling human device, process starting with the physico-chemical ion between bacteria and substrata [2].

In this context, this work analyses the physico-chemical surfaces properties of *E. faecalis* 29212 grown in a standard culture medium without and with serum or urine. Contact angles e liquids, surface tension determinations and zeta potential measurements are the analytical s employed. In addition to the physico-chemical surface characterization, the adhesion of glass was studied in a parallel plate flow chamber. These data were related with the ons of the adhesion obtained through the interaction free energy as proposed by van Oss et al.

Water contact angles present serum-grown cells as the most hydrophobic organisms, with a favorable negative interaction free energy and the highest adhesion to In the other hand, urine-grown cells and control cells (grown without serum or urine) show hydrophobic behavior, also reflected in the nearly equal values of the interaction free and initial adhesion rates to glass.

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OIL ENTERING A PROTEIN-COVERED WATER SURFACE:
THE EFFECT OF PROTEIN HARDNESS ON A
STRETCHING-INDUCED WETTING TRANSITION

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Various slightly polar oils (ϕ) can completely wet a water(w)-air(a) interface: their spreading parameter $S = \gamma_{wa} - (\gamma_{wo} + \gamma_{oa})$ where γ_{ij} is an interfacial tension, is positive. This implies an oil droplet, when it enters the water-air interface will spread completely to a continuous thin film. However, when the surface is covered with a monolayer of surface-active molecules, γ_{wa} is smaller and spreading may be suppressed. We report here experiments in which emulsion droplets of oil are brought in close vicinity of a water-air surface on which a 'Langmuir-film' of protein is spread. These various proteins used (β -casein, β -lactoglobulin and glycinn) all initially exert surface pressures of about 25 mN/m which is enough to suppress any spreading.

Stretching of the surface increases γ_{wa} and thus lowers S . As soon as the condition $S = 0$ for a wetting transition is reached the oil droplets massively insert into the surface, forming a wetting film. Hence, we are dealing here with a stretching-induced wetting transition. The way this transition occurs depends dramatically on the mechanical properties of the protein film. For β -casein, which forms a liquid-like film, the transition occurs smoothly through nucleation of (oil-wet) holes which grow in a gradual manner. For β -lactoglobulin, which forms somewhat elastic films, insertion happens very suddenly, together with pronounced rupture of the protein film. For glycinn, which is the 'hardest' protein of the three, the transition is accompanied by a most dramatic fracture event in which the protein film explodes into many small fragments.

MACROSCOPIC PROPERTIES AND MICROSCOPIC STRUCTURE OF ORGANOGELS: SENSITIVITY TO CHEMICAL MODIFICATIONS AND POLAR ADDITIVES

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Organogels can be formed by a large variety of different low molecular weight gelators able to gel organic solvents even at very low concentrations of 0.1-1 wt%. In our work we employed 12-Hydroxy stearic acid (HSA) as a basic gelator molecule and studied also modified variations of it as well as the influence of polar or semipolar additives on the gelation process in various different organic solvents, such as dodecane, paraffin oil, triglycerides, almitate and silicone oils. The macroscopic gel properties were characterised by means of rheology experiments, differential scanning calorimetry (DSC), and optical microscopy. The microstructure of the samples was studied by means of small-angle neutron scattering (SANS), wide-angle x-ray scattering (WAXS) and freeze-fracture microscopy.

In these experiments it has been observed that addition of polar additives such as alcohols to suppress the gelation process. However, this effect depends strongly on the chain length of the alcohol employed being significantly more effective for short chain alcohols (e.g. ethanol) than for longer chain alcohols (e.g. hexanol, geraniol), where correlations between local structure of the microfibrils and the rheological properties are observed. HSA gels that are chemically modified at the acid group show a gelation behaviour that strongly depends on their chemical modification. Finally also mixtures of HSA and stearic acid were studied with respect to their gelation properties in various organic solvents. The presence of stearic acid increases the ability for microfibril formation and thereby reduces the elastic modulus of the gels

THE INTERACTION OF *ESCHERICHIA COLI* MEMBRANE PHOSPHOLIPIDS WITH THE NONIONIC SURFACTANT OCTAOXYETHYLENE-DECYL ETHER (C₁₀EO₈) AND THYMOL

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Polyoxyethylene nonionic surfactants [C_nH_{2n+1}(OCH₂CH₂)_mOH, C_nEO_m] are generally regarded as mild, having little biological activity. However, some derivatives capable of delivering good hard surface detergency have unexpected biocide activity, which is enhanced by the presence of small alcohol or phenol "coactives". [1] We have investigated the possible molecular mechanisms involved in this biocide activity by examining the influence of a representative surfactant, octaoxyethylene-decyl ether (C₁₀EO₈), and thymol (2-hydroxy-1-isopropyl-4-methylbenzene), on the mesophase behaviour of *Escherichia coli* lipids. Previous work has given an excellent account of the lipid composition, including alkyl chain distributions. [2] Both the whole cell lipid extract and the (major) phosphatidyl ethanolamine fraction have been examined using polarizing optical microscopy and NMR spectroscopy, over a range of concentrations and temperatures. For the latter technique we have examined the ²H spectra of samples prepared with ²H₂O, and ²H spectra of samples containing added lauric acid-d₃ as a probe. Our results show clearly that dispersions of the lipid extracts in water at ambient temperatures form a heterogeneous mesophase system, probably consisting of two lamellar (L_α) phases. In addition, at low temperature the lipids form a gel (L_β) phase, whilst at high temperatures a reversed hexagonal phase appears. In the presence of the nonionic surfactant and thymol only a single lamellar phase is formed. The implications of these results for the structure of intact *E. coli* membranes and for the likely biocide molecular mechanism will be discussed.

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CRYO-TEM INVESTIGATION OF MILK FAT GLOBULE MEMBRANE STRUCTURES OF CREAM

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Milk fat globule membrane (MFGM) lipids in milk have an emulsifying role in milk and are therefore important in the stability of milk products. The main membrane lipids in milk are the monoglyceric phosphatidylcholine, phosphatidylethanolamine, sphingomyelin and the anionic phosphatidylinositol and phosphatidylserine. Depending on composition and temperature the MFGM shows different phase behaviour [1].

In this study milk fat globule membrane lipids are isolated from cream (40% fat). The MFGM is investigated with Cryo-TEM, which is a powerful tool for investigating membrane structures. The MFGM fraction is also characterised using X-ray diffraction and DSC. The MFGM structures are characterised using gel electrophoresis. The structures are compared between samples from different processed cream. The structures are related to a model milk membrane [2].

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AGGREGATION OF FLAVAN-3-OLS IN MODEL WINE SOLUTIONS: EFFECT OF WINE POLYSACCHARIDES, ETHANOL CONTENT AND IONIC STRENGTH

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Polyphenolic compounds are widely present in many beverages and are of primary importance for both stability and organoleptic properties. Condensed tannins made of flavan-3-ol units are found in e.g. cider, wine, tea... Due to their molecular structure, they have a tendency to form colloidal particles in hydro-alcoholic solutions [1]. Tannins are also known for their ability to complex with proteins (gelatin added during fining treatment, salivary proteins...). This is of primary importance for both technological and organoleptic aspects (astringency). Several studies have been conducted on tannins-proteins interactions, mainly by NMR, microcalorimetry, turbidimetry and more recently dynamic light scattering [2]. However, less has been done on polysaccharides-polyphenols interactions [3]. Yet, polysaccharides, naturally present in wine, can interact with tannins and modify polyphenols-proteins interactions. It is thus of importance to further investigate this point.

We studied, mainly by means of dynamic light scattering, the influence of different wine polysaccharides fractions (RG-II, mannoproteins...) on the formation of commercial flavan-3-ols and grape seed procyanidins colloidal particles in model wine solutions (typically aqueous solutions containing 12% of ethanol, with pH adjusted to 3.4 with tartaric acid). Polysaccharides did not prevent polyphenols from forming colloidal particles, but in some cases they prevented the particle growth (mannoproteins), whereas in other cases aggregation was enhanced. The effect of the medium (ethanol content, ionic strength...) was also investigated.

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INSERTION OF LAPONITE CLAY PARTICLES IN SURFACTANT LAMELLAR PHASES

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The stability of suspension and microstructure result from the interplay of attractive and repulsive forces between colloids. A small variation in the intermolecular force may induce a re-orientation in the system, for instance phase separation or phase transition. That explains the complexity of the phase diagrams but also the difficulty of mixing different colloids. In this study we study the possibility of mixing organic and inorganic colloids. We used Laponite, a synthetic clay, made of monodisperse disks of 30 nm diameter and 1 nm thickness which particles are considered as colloidal model. We worked in parallel with three surfactant systems: an anionic (AOT), a cationic one (DDAB) and a non-ionic one (C₁₂E₅) to modulate the molecular weight and put in evidence the role of electrostatic or steric repulsion. Phase diagrams have been determined optically and the structures have been determined by small angle neutron and x-ray scattering (SANS and SAXS) experiments. At low surfactant concentration, surfactant is adsorbed on the particles. Isotherms combined with SANS under contrast match conditions allowed to determine the average thickness of the adsorbed surfactant layer. An AOT bilayer surrounds the edges and an almost complete bilayer of DDAB or C₁₂E₅ is formed on the basal faces [1]. In the monophasic lamellar domain, the particles stay between the membranes, when the water content is larger than the particle thickness. In the biphasic domain dense clay aggregates are in equilibrium with a lamellar phase containing few amounts of particles. They enter the AOT phase when the water thickness is smaller than 8 Å [2]. From the phase diagram and interaction energy, three conditions of stability emerge:

- an osmotic one : the osmotic lamellar pressure is higher or equal to the colloidal one.
- an energetic one : the interaction energy between a particle and the surfactant bilayer is higher than the particle energy in aqueous suspension.
- an entropic one : particles should not inhibit the stabilising fluctuations of the lamellar phase.

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ABOUT *IN VIVO* LUMINESCENCE OF THE AROMA OF FRUITS AT THEIR SURFACE

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An unusual luminescence from above the surface of a number of common fruits has been observed *in vivo* upon optical excitation [1,2]. Although molecular luminescence, arising from proteins, chlorophyll and other fluorophores, is common in many biological materials, and this is the region where some chlorophyll fluorescence may be expected, we believe this emission to have a different origin. It was suggested that this luminescence could be attributed to the gaseous atmosphere of native organic volatiles emitted from the surface of fruits, such as alcohols, aldehydes and esters [1]. However, this is not simply molecular luminescence of the volatile molecules: in our experiments, the light excitation energies (1.9-4.9 eV) are too low to transform them into excited electronic states by a single-photon process. We feel, from both theoretical and experimental analysis of this effect that it arises from emission involving vibrational overtones of species present in the fruit's vapour. Treating the overtone spectra in more detail, these are likely to be associated with the highest energy vibrational modes, such as CH and OH stretches. Our calculations show that the temperature of these vibronic modes about 1300-1400 K can be sufficient to sustain luminescence from thermally excited vibrational overtones with the intensity and spectral location similar to experimental spectra. Organic volatiles are seen to luminescence effectively when escaping through the skin of fruit (such as through a porous membrane). The role of this membrane has been examined by laser fluorimetry in model experiments for the free expansion of a vapour of a volatile compound through a nozzle. Our results demonstrate that the natural *in vivo* processes of escaping of aroma volatiles through the skin of fruit are similar to a distinct nonequilibrium process of an expansion of a vapour through a nozzle. This can provide a new insight into the current vision of surface respiration of fruits, which makes such remote detection a very generic approach and potentially an extremely powerful tool for the *in vivo* investigation not only of plants, but also animals and humans and, therefore, in biomedical applications.

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ONSET OF COHESION IN CEMENT PASTE

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It is generally agreed that cohesion of cement paste occurs through the formation of a network of nanoparticles of a calcium-silicate-hydrate (CSH). However, the mechanism by which particles develop the cohesion has not been established. In this work we calculate the forces between CSH nanoparticles immersed in an ionic solution that is typical of early cement paste. We find, during the hydration of cement powder, the interparticle forces become strongly attractive due to correlations of calcium counterions. This effect is general, and it will cause the attractions in any dispersion where the surface charge density and counterion concentration are high, especially so in presence of multivalent counterions.

LIQUID-LIQUID PHASE SEPARATION OF A SURFACTANT-SOLUBILIZED MEMBRANE PROTEIN

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Stable solutions of membrane proteins can be obtained only by exploiting the solubilizing properties of specific detergents used for extracting proteins from the supporting cell membrane [1]. Therefore, surfactant self-assembly phenomena unavoidably coexist with, and strongly influence, membrane-protein solution behavior. The Reaction Center (RC) is a 100 kDa bacterial pigment-protein complex, which spans the intracytoplasmic membrane and accomplishes the primary events of energy transduction by promoting photoinduced charge separation across the membrane [2]. RC, which was the first membrane protein to be crystallized, can be extracted from bacterial membranes by using lauryldimethylamino-N-oxide (LDAO), a surfactant acting as a very efficient solubiliser. We shall show that ionization of LDAO, tuned by the solution pH, induces strong cooperative electrostatic effects between surfactant and protein leading, in a narrow pH range, to phase-segregation of the mixture into mesoscopic 'droplets', with a typical size of the order of a few μm and a relatively narrow size distribution [3]. After a moderate initial growth, droplets persist in a quasi-stationary state for very long time, with little further ripening or coalescence. It is therefore tempting to describe this liquid-liquid phase separation as a kind of 'spontaneous emulsification'. At variance with what is found for most aggregation phenomena in complex fluids, phase segregation of RC/LDAO complexes is fully hindered by screening of the electrostatic interactions with the addition of salt. We also observed noticeable effects of the phase segregation process on RC photochemistry, concerning both the absorption spectrum and electron-transfer kinetics, suggesting that RC photo-cycle depends on its aggregation state.

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