

11-01

Ionic Liquid Emulsions Stabilised Solely by Nanoparticles

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When colloidal particles are partially wetted by both oil and water they adsorb very strongly to the oil-water interface and can serve as excellent emulsion stabilisers. The emulsion type, i.e. water-continuous or oil-continuous and the emulsion stability can be tuned by control of the particle surface's affinity for the two solvents which can be expressed in terms of the contact angle between the oil-water interface and the particle surface. In this presentation, we describe the formation of both simple and multiple emulsions containing an ionic liquid with either water, an oil or both stabilised solely by silica nanoparticles. We show how emulsion type and stability can be optimised and emulsion phase inversion can be effected by varying the surface coating of the silica nanoparticles. Using different combinations of mutually immiscible mixtures of water, an ionic liquid and an oil we have successfully prepared many different types of simple and multiple emulsions (e.g. "water-in-ionic liquid-in-oil") which show excellent stability. The emulsion results are correlated with liquid-liquid contact angle measurements on coated silica surfaces.

11-02

Molecularly-Engineered Nanoparticles and Assemblies for Analytical/Bioanalytical Applications

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We have been exploring a general bottom-up pathway towards processing and assembling metal and alloy nanoparticles for analytical/bioanalytical applications. This pathway entails molecularly-engineered processing of particle size, shape, composition and surface properties and molecularly-mediated assembly via fine-tunable interparticle interactions including van der Waals forces, covalent bonding, hydrogen-bonding, or ligand coordination. The advanced materials present new opportunities in a wide range of technological applications, including fuel cell catalysis, chemical or biological sensing, and medical diagnostics or treatments. The unique electronic, interparticle spacing, chemical specificity, framework binding, molecular channeling, and catalytic properties of the nanostructured materials provide fine-tunable chemical/biological sensing interfaces. Recent results of our investigations will be discussed.

11-03

Some Phase Diagrams of Fruit Acids and the Consequences in their Application for Skin Lotions

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The difference from a formulation point of view between a di-carboxylic acid and its two related hydroxy acids with one and two hydroxy groups was investigated by comparing the

structure of their emulsions with a simple non-ionic surfactant as stabilizer and the changes taking place during evaporation.

The results showed the introduction of a hydroxy group into the structures to have a radical impact on the structure of the emulsion and, especially the changes during evaporation.

An evaluation of the volume fraction of vesicles in the emulsion showed these to occupy a larger volume than is intuitively assumed.

The phase diagrams were determined of lactic and isohexanoic hydroxy- acids as well as salicylic acid with water, a nonionic surfactant and a paraffinic oil to outline the influence of the hydroxy-acids on the structure in a model for a skin lotion.

The results showed the influence of the acid to be similar to that of the oil, but that the difference in chain length between the two alpha acids had only insignificant influence. The results are discussed from two aspects; the structures involved in the lotion as applied and the action of the lotion residue on the skin after the evaporation of the water

11-04

A Novel Method for the Computer Simulation of Surfactant Self-Assembly

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With the help of increasing computational power, Molecular Dynamics (MD) and Monte Carlo (MC) simulations are very useful for investigating the microscopic features of matter and material. To investigate the molecular-level features of the surfactant solutions, several researchers have implemented the MD and MC simulations of surfactant systems. However, it is still difficult to simulate the self-assembly of surfactants using the atomistic models, because long-time simulations of the large-scale systems are required to examine the surfactant self-assembly. A common alternative is the use of coarse-grained models to mimic the oil/water/surfactant systems. The coarse-grained model simulations, however, provide only the qualitative results, which are sufficiently suggestive but are not quantitatively comparable with the experimental results.

In this talk, we present an implicit solvent model for the simulation of surfactant molecules in aqueous solutions, where no water molecules of the solvent are treated explicitly, but the effects are incorporated using the solvent-averaged interactions between the surfactant segments in water. This model has been applied to the MD simulations of (i) the self-assembly of *n*-decyltrimethylammonium chloride surfactants at different concentrations and (ii) the single micelles of different sizes. The results will be compared with those from experiments and atomistic model simulations.

11-05

Transformation of Organized Assemblies in Surfactant Solutions

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By the variation of molecular structure and physicochemical conditions, the formation and transformation of amphiphilic molecular organized assemblies such as: micelle, vesicle, were studied.

Transition of surfactant aggregates by adding non-polar organic compounds was investigated in the cationic-anionic surfactant systems. The two-phase systems were transformed into homogenous solutions with the octane addition. The results of DLS demonstrate the decrease of vesicles and the increase of spherical micelles upon octane addition. Such transformation of the surfactant aggregates was also corroborated by the results of time-resolved fluorescence quenching and viscometry.

Surfactant aggregates were also studied in the mixed systems bolaform amphiphiles and opposite charged conventional surfactant. Superior high temperature stability of vesicles was found in some mixed systems. DSC, VT-IR and Fluorescence probe results all revealed that vesicles in C₂₀Na₂/DEAB mixed systems can keep stable even at 80.

Temperature-induced micelle—vesicle transformation was also found in the mixed cationic-anionic surfactant systems. Cylindrical micelle to vesicle transition upon the increase of temperature was demonstrated in the system of SDS/DEAB. Notable transition occurred during 30-50°C and such transition was remarkably influenced by surfactant mixing molar ratio and total surfactant concentration.

11-06

Thermodynamics and Dynamics of Diblock Copolymers at Polymer/Polymer Interfaces

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The efficacy of diblock copolymers for stabilizing interfaces between immiscible polymers depends on both thermodynamic and dynamic factors. We study the equilibrium and dynamic concentration profiles of an AB diblock co-polymer (i.e., the surfactant) at an A polymer/ B polymer interface. We create thin polymer films containing two surfactant-bearing polymeric interfaces and follow the transient concentration profiles of the diblock copolymer by dynamic secondary-ion mass spectroscopy (SIMS). For well-equilibrated films, the measured concentration profiles and the adsorption isotherms are in good agreement with self-consistent field theory (SCFT), where all necessary parameters were determined independently from SANS and gel-permeation-chromatography measurements. For the nonequilibrated films, transport of the diblock copolymer depends on the two binary Fickian diffusion coefficients and on the depth of the thermodynamic potential wells that hold the surfactant molecules at the interface. Diffusion coefficients of our system were measured in independent SIMS experiments. We again find excellent agreement between the measured transport rates of the AB surfactant across the film interfaces and those calculated using a SCFT free-energy profile and diffusion in a potential field. Fascinatingly, no kinetic barriers to adsorption/desorption are found. For the first time, surfactant adsorption dynamics at a polymer/polymer interface is addressed.

11-7

The Linker Effect in Microemulsion Systems

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The surfactant-water and surfactant-oil interactions control the overall thermodynamic equilibrium of microemulsion systems. Intuitively, by enhancing these molecular interactions, more oil and water can be co-solubilized in microemulsion systems. One way to enhance these interactions is by introducing lipophilic and hydrophilic linkers in the formulation. Lipophilic linkers such as long chain alcohols (with more than eight carbons), fatty acids, and low HLB non-ionic surfactants tend to segregate near the tails of the surfactants, serving as an extension of these molecules into the oil phase. Hydrophilic linkers, on the other hand, are surfactant-like molecules with short hydrophobe (between six to nine carbons) that co-adsorb at the oil/water interface, increasing the interfacial area. The combination of lipophilic and hydrophilic linkers produce self-assembled pseudo-surfactants at the interface that produce efficient microemulsions with a wide range of oils, without using toxic medium chain alcohols, or high electrolyte concentrations. The use of linker formulations in cleaning applications, environmental remediation, and drug delivery systems will be discussed. The partition / segregation of linkers will be discussed using the “zipper” self-assembly hypothesis that has been proposed to explain the combined linker effect.

11-08

Experimental Observations of Dynamic Surface Tension at Highly Curved Microfluidic Interfaces

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In microfluidic devices, interfaces between two liquid phases are constrained by system geometry to have high curvature. Recent scaling arguments report a new timescale relevant to curved interfaces and predict a shift in the mechanism of surfactant mass transport from diffusion controlled to kinetic controlled based on geometry alone. We have developed a microtensiometer to measure the dynamic surface tension using a highly curved interface formed at the tip of a glass micropipette, immersed in a reservoir of surfactant solution. We show microtensiometer measurements for air-liquid interfaces using aqueous solutions of well characterized poly-ethoxylated surfactants. Our data indicate that the dynamic surface tension equilibrates earlier at more highly curved interfaces, validating the prediction of a shift at microfluidic length scales. Characterizing the dynamics of surfactants at microfluidic length scales will enable better control over the deformation and breakup of drops in microfluidic devices as well as a greater understanding of the role of surfactants in these dynamical processes.

11-09

Processing of Phospholipid Vesicles Using Supercritical and Compressed Fluids

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Emerging applications of supercritical fluids to bioprocessing exploit the interaction of CO₂ with phospholipid vesicles. This work examines the influence of CO₂ on the bilayer fluidity of liposomes, which are representative of model cellular membranes, at the elevated pressures (up to 13.9 MPa) associated with CO₂-based processing of liposomes and microbial sterilization. Fluidization of aqueous dipalmitoylphosphatidylcholine (DPPC) liposomes by pressurized CO₂ (present as an excess phase) was studied by steady-state fluorescence anisotropy using the membrane probe 1,6-diphenyl-1,3,5-hexatriene (DPH). Reversible, pressure-dependent fluidization of the phospholipid vesicles was observed in both the gel and fluid phase states of the DPPC bilayer (DPPC, T_m ~ 315 K). These experiments demonstrated substantial melting point depression ($\Delta T_m = -4.8$ to -18.5 K) and a large broadening of the gel-fluid phase transition region, which was interpreted using conventional theories of melting point depression. The pressure-dependent surface activity of the of aqueous DPPC liposomes at the CO₂ interface was determined using high pressure interfacial tension measurements. This technique provided complementary information on the influence of the CO₂ interface on the adsorption and disruption of phospholipids vesicles.

11-10

Synergistic Interactions Between Linear Polyethylene Oxide Surfactants and the Effect on Surface Tension, Phase Behavior and Wetting

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In this paper we report findings in synergistic interactions with respect to air-liquid interfacial tension reduction, lyotropic phase behavior and wetting. We have previously reported that combinations of 1-dodecanol with the polyethyleneglycol n-alkyl ether surfactants are able to reduce the air-liquid interfacial tension to values on the order of 20 mN/m when the total surfactant loading is on the order of 0.05% by weight. The mechanism for such significant interfacial tension reduction is not yet completely understood, but we have been able to draw correlations between the tension reduction and the presence of lyotropic phase, in the surfactant solution. In order to gain insight as to what surfactant aggregate structures exist in our mixtures, we employ cross-polarized microscopy and depolarized light scattering, where anisotropy of the aggregated structures gives rise to characteristic patterns that can be observed using a digital camera. We also report here, the ability for some of these surfactant systems to wet a model hydrophobic surface and offer possible implications that can be made about the role of the lyotropic phases and wetting. The model hydrophobic surface used is an octadecyltrichlorosilane self-assembled monolayer on bare silicon.

11-11

On the Self Assembly of Asphaltene s to Form Nanoscale Aggregates

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Asphaltenes are the n-heptane insoluble and toluene soluble fraction of petroleum fluids. This solubility definition leads to a heterodisperse mixture of molecules that contain fused aromatic rings, a significant percentage of N, S, O heteroatoms (2-10%, w/w), and an aliphatic periphery and aliphatic connectors of aromatic moieties. This unusual molecular architecture leads to the characteristic colloid-forming properties of asphaltenes: colloidal instability during pressure and temperature reductions, deposition during transportation and processing, self assembly in solution, and adsorption onto solid-liquid, liquid-liquid, and liquid-vapor interfaces. Here, we report a comprehensive study of the self assembly properties of asphaltenes, primarily as probed by small angle neutron scattering (SANS) in organic solutions of heptane, toluene, methyl naphthalene, methanol, and their mixtures. We have systematically explored the fitting of a variety of geometric form factor models to our data and concluded that an oblate cylindrical model with polydispersity in the radial dimension best fits a large dataset of independent experiments. Such a fit, which agrees well with unbiased Guinier analyses of radii of gyration and data extrapolation to obtain zero-Q scattering intensities, enables the evaluation of mean aggregate volume and moments of the aggregate volume distribution. This in turn enables a number of very important conclusions to be drawn about the physical properties of asphaltenic aggregates. First, it is clear from our analysis that asphaltenes entrain a significant fraction of solvent, as much as 50% (v/v), within the interior of the aggregates. Second, this entrained solvent appears to rapidly exchange with solvent in the bulk. Third, the apparent fractal dimension of these aggregates varies over a broad range from 2.2-3.0 and would seem to suggest that asphaltenic aggregates, at least in the nanoscale range ($1 \text{ nm} < R_g < 15 \text{ nm}$), would seem to be better characterized as globular aggregates with roughened surfaces, rather than as mass fractals as many investigators have suggested. We have also been able to probe the flocculation of nanoscale aggregates into larger microscale aggregates. Finally, we report on the interactions of these nanoscale aggregates with each other by evaluating second virial coefficients and by exploring the role of selective solvating agents, such as resins, acids, and polymeric additives.

11-12

Interfacial Alignment of Micelles in Surfactant-silica Aggregates as a General Approach to Materials with Oriented Mesopores

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When silica and a cationic surfactant are precipitated from an ethanol/water/ammonia solution, nearly monodisperse spherical particles with uniform, radially oriented channels result. This structure is ideal for catalysis, adsorption, and chromatography because it combines low tortuosity with high accessibility. We investigate the formation mechanism of this structure during precipitation of tetraethoxysilane with CTAB. Using TEM to observe samples extracted early in the process and rapidly cooled, thinned and dried, we show that

small disordered CTAB-silica aggregates initially form. These aggregate into large spheres, and then CTAB micelles elongate and orient normal to the particle interface, even in arbitrarily shaped particles. The micelles continuously rearrange normal to the particle interface even as the particles aggregate and reorganize into spheres. This alignment implies that there is no preference for polar or nonpolar parts of the silica-surfactant mesophase at the particle-solution interface. This mechanism - precipitating soft silica-organic aggregates followed by nucleation of an ordered structure - can be generalized to other surfactant-templated systems and possibly zeolites. For instance, in layered particles formed using a cationic fluorinated surfactant, the particles elongate perpendicular to the layers. This is consistent with silica-surfactant aggregates initially acting like dispersed soft liquid crystals.

11-13

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Abstract pending

11-14

The Application of Surfactant Phase Behavior in Developing Oilfield Product

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Phase behavior was very important for many areas of applications from drilling fluid to enhance oil recovery in petroleum industry. Drag reducing surfactant was developed with studying the phase behavior of the surfactants. The mixture of surfactants and co-surfactants reduce the gel phase of hexagonal liquid crystal, and make faster transition to drag reducing wormlike micelle phase during the dilution.

11-15

Origin of the Sphere-to-Rod Transition in Micellar Solutions: Specific Ion Hydration Matters

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Understanding the relationships between surfactant structure and aggregate morphology should permit “tuning” of bulk properties of soft materials, which have important applications as thickeners, drag reducers, and hard surface cleaners. Micelle formation and the transition from spherical to rodlike, wormlike and threadlike micelles depend not only on surfactant tail structure, but also surfactant headgroup structure and counterion type (e.g., Hofmeister series) and concentration. However, the balance of forces determining such transitions are not fully understood.

The chemical trapping method based on the heterolytic chemistry of arenediazonium ions is providing new information on the concentrations of weakly basic nucleophiles such as water, halide ions, alcohols and urea within the interfacial regions of association colloids. Recent results show that of the 12-n-12 2Br (n = 2-4) series of gemini surfactants, only the gemini surfactant with n = 2 shows a marked increase in interfacial Br⁻ with a concomitant decrease in interfacial water concentration with increasing surfactant concentration. Published cyro-

TEM results show that only 12-2-12 form rods under these conditions. This and other chemical trapping results support a model in which sphere-to-rod transitions are governed by specific ion dependent dehydration of interfacial head groups and counterions to form hydrated ion pairs.

11-16

Controlled Synthesis and Hierarchical Assembly of One-Dimensional Inorganic Nanostructures in Micellar Systems

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Both reverse and normal micelles are used as nanostructured media for synthesizing various one-dimensional (1D) inorganic nanostructures such as nanowires, nanobelts, and nanotubes. Unique catanionic reverse micelles formed by mixed cationic-anionic surfactants are employed for the controlled synthesis and hierarchical assembly of 1D BaXO₄ (X = Cr, Mo, W) nanostructures. The effects of various factors, such as the mixing ratio between the anionic and cationic surfactants, the temperature, and the polymeric additives, on the formation of 1D BaXO₄ nanostructures and the architectural control of their complex superstructures are examined. A plausible two-stage growth mechanism has been proposed for the formation of the penniform BaXO₄ nanowire/nanobelt superstructures. On the other hand, normal micelles of nonionic surfactants are employed for the controlled synthesis of single-crystalline nanotubes, nanowires, and nanobelts of trigonal selenium (t-Se). In particular, well-defined t-Se nanotubes are fabricated in micellar solutions of the nonionic surfactant C₁₂EO₂₃. It is revealed that the nonionic micelles play an important role in controlling the distribution and diffusion of amorphous Se in the solution and hence exert delicate control over the morphology of the 1D t-Se nanostructures. These results demonstrate the great potential of micellar systems in synthesizing and assembling 1D nanostructures in solution.

11-17

DNA-copolymer Vesicles for Gene Delivery

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We report the design, structural characterization, and transfection ability of cationic diblock copolymer vesicles loaded with cloning vector DNA. Encapsulation was achieved with a single emulsion technique. For this purpose, an aqueous plasmid solution is emulsified in an organic solvent and stabilized by an amphiphilic diblock copolymer. The neutral block forms an interfacial brush, whereas the cationic attachment complexes with DNA. A subsequent change of the quality of the organic solvent results in the collapse of the brush and the formation of a capsule. The capsules are subsequently dispersed in aqueous medium to form vesicles and stabilized with an osmotic agent in the external phase. Inside the vesicles, the plasmid is compacted in a liquid-crystalline fashion as shown by the appearance of

birefringent textures under crossed polarizers and the increase in fluorescence intensity of labeled DNA. The compaction efficiency and the size distribution of the vesicles were determined by light and scanning electron microscopy, and the integrity of the DNA after encapsulation and subsequent release was confirmed by gel electrophoresis. We demonstrate the gene transfer ability of this new model carrier system by the transfection of encapsulated pEGFP-N1 plasmid into HeLa cancer cells through the fluorescence of the expressed GFP protein.

11-18

Synthesis and Chiral discrimination of Chiral Sensor with Self-Assembled Monolayers of Functionalized *b*-Cyclodextrins

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Three chiral sensors were synthesised and studied by using a quartz crystal microbalance (QCM) coated with self-assembled mercaptyl functionalized β -cyclodextrin (β -CD) derivatives. which are (6^A- ω -mercapto-ethylureado-6^A-deoxy)heptakis(2,3-di-*O*-benzoyl)-6^B, 6^C, 6^D, 6^E, 6^F, 6^G-hexa-*O*-benzoyl-***b***-cyclodextrin (Ph- β -CDS), (6^A- ω -mercapto-hexanureado-6^A-deoxy)heptakis(2,3-di-*O*-benzoyl)-6^B, 6^C, 6^D, 6^E, 6^F, 6^G-hexa-*O*-benzoyl-***b***-cyclodextrin (Ph- β -CDM) and (6^A- ω -mercapto-undecanylureado-6^A-deoxy)heptakis(2,3-di-*O*-benzoyl)-6^B, 6^C, 6^D, 6^E, 6^F, 6^G-hexa-*O*-benzoyl-***b***-cyclodextrin (Ph- β -CDL). The preferential binding of the chiral analytes at these β -CD monolayers in comparison with that on the reference coating suggested the formation of inclusion complexes. Improved chiral discrimination was achieved by the β -CD monolayers modified QCM sensors in comparison with GC and HPLC separation performance. Furthermore on-line determination of enantiomeric composition in the samples by these QCM sensors was described. We also studied the specific host-guest interactions between enantiomeric analytes and the self-assembled ***b***-CD monolayers on QCM under gaseous atmosphere and liquid phase. Thermodynamic parameters about these chiral discriminatory processes were obtained in gas and liquid phase from the linear curves of temperature-dependant chiral discrimination factors of the three β -CD monolayers, which revealed the existence of excellent compensatory enantioselective enthalpy-entropy relationship from the linear curve of $\Delta_{R,S}\Delta H$ vs.

11-19

Droplet Breakup in Shear and Elongation Dominated Flows in Microfluidic Devices

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Microfluidic devices have recently been demonstrated as an effective platform for generating monodisperse drops and bubbles on a drop-by-drop basis. Precise control over droplet size has the potential to impact a wide range of applications from emulsification to drug delivery and lab on a chip. In this talk we compare drop formation mechanisms in microfluidic devices in which flows can be either predominantly shear flows, or predominantly elongational flows. In either case, drops of an aqueous liquid form due to viscous stresses imposed by a second oil phase. However, we show that the two different flow types lead to dramatically different

ability to control droplet sizes. We characterize the drop formation mechanism and the resulting drop size over a large number of experiments by varying capillary number, volume fraction, and viscosity ratio. We observe several distinct modes of breakup that depend on these three dimensionless parameters, as well as the flow type and microfluidic design.

11-20

Sulfolane Microemulsions as Possible Inert Reaction Media

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Very recently, it turned out that nano-structured reaction media containing highly inert solvents as tetrahydrothiophen-1,1-dioxid (sulfolane) are needed in strongly oxidizing or reductive reactions. Due to their ability of solubilizing polar and nonpolar solvents with a large nano-structured interface in particular microemulsions provide such interesting reaction media. Starting from the pseudo-ternary microemulsion H_2O -*n*-octane- $C_{12}E_4/C_{12}E_5$ (polyoxyethylene *n*-alkylether) water was successively replaced by the highly inert tetrahydrothiophen-1,1-dioxid (sulfolane). It is found that an increasing sulfolane content drives the system beyond the tricritical point. Replacing the already long chain surfactants $C_{12}E_4$ and $C_{12}E_5$ by a mixture of the really long chain surfactants $C_{18}E_6$ and $C_{18}E_8$ a sulfolane-microemulsion was prepared for the first time. In a second step the phase behavior of the hydrophilic sulfolane - *n*-octane - $C_{18}E_8$ system was tuned at constant temperature (reaction condition) by adding the hydrophobic cosurfactant 1-octanol. Thereby, the size of reverse micelles were investigated by DLS exhibiting radii varying from at least 8 nm to 20 nm.

11-21

Stabilization of Water-in-Oil Emulsions by Silica Nanoparticles and Surfactant

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Emulsions are metastable due to the excess energy associated with the large interfacial area. Electrostatic stabilization by surfactants and steric stabilization by macromolecules are quite well understood and the focus is now on solid particle- stabilized systems. Some of the unanswered issues in the area of mixed particle-surfactant systems are the following: What happens when solid nanoparticles and surface-active molecules are used in water-in-oil emulsions? Do particles or surfactant or both go to the interface or is there a preference for one to be at the interface over the other? What happens if solid particles and surfactant form complexes in bulk or at the interface? Do particles and surfactant act synergistically to enhance the long term stability of the emulsions? What are the implications of complexation on the rheology of the emulsion? In this paper, we answer these intriguing questions from systematic studies using water-in-silicone oil emulsions prepared with silica nanoparticles and a polymeric surfactant. These emulsions are characterised by light scattering, optical microscopy, freeze fracture electron microscopy and rheology.

11-22

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: airwater, 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.

11-23

Controlled Polymerization of Acrylates by Macromolecular Design via Interchange of Xanthates in Microemulsions

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The ability to produce stable latex nanoparticles of monodisperse polymer chains is desired for many applications. Reversible addition-fragmentation chain transfer (RAFT) has proven to be a successful method of controlled polymerization for many monomers and reaction conditions. However, the polymerization mechanism is not well understood. Implementing RAFT in microemulsion polymerization provides a model system in which to study the RAFT mechanism because microemulsion polymerization eliminates biradical termination by segregating the propagating polymer chains into surfactant stabilized polymer particles.

In this work we have implemented the RAFT process of Macromolecular Design via Interchange of Xanthates (MADIX) in the microemulsion polymerizations of butyl acrylate and 2-ethylhexyl acrylate. The kinetic rates, polymer molecular weights and latex particle sizes have been measured for several MADIX agent to micelle ratios at two initiator concentrations. The results of these experiments provide insight into the mechanism of RAFT polymerizations.

11-24

Ultrasound for Characterizing Soft colloids

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We present experimental data and its interpretation regarding characterization of various emulsions, mini- and micro-emulsions using ultrasound. Characterization includes droplet size distribution and ζ -potential for both, water-in-oil and oil-in-water systems. This characterization allowed us to establish a link between electric properties and evolution of these systems.

11-25

Flow-induced Phenomena in Solutions of Wormlike Micelles

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Surfactant molecules in solution can self-assemble into wormlike micelles. Micellar solutions are common in the cosmetic, detergent and food industries. Solutions of these wormlike micelles have behavior similar to that of polymers, but are also able to reversibly break and recombine. Current work probing two viscoelastic micellar solutions of identical surfactant concentration has found the concentration of incorporated salt to critically influence solution behavior. While the two samples are quite similar in viscosity across a range of shear rates, only one sample exhibits shear-induced phase separation (SIPS). The important length scales of the two micellar networks are investigated via dynamic rheology, rheo-optics and small-angle neutron scattering (SANS). The mesh size and entanglement length of the micelles that exhibit SIPS are smaller than the other sample. Therefore, the solution that phase separates under flow forms a more densely entangled network. Additional investigation into the nonlinear rheology of these samples is completed using particle tracking velocimetry (PTV) and flow-SANS in the 1-2 plane. PTV finds shear banding for the sample exhibiting SIPS while the other sample behaves like a power law fluid. The appearance and growth of the shear bands for the sample exhibiting SIPS will be explored in detail.

11-26

Effect of Oil on Emulsion Characteristics: Manipulating the Interfacial Domain

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The ternary systems (water, triton X-100 and *n*-alkane) were investigated using freeze-fracture TEM, rheology, laser diffraction particle sizing, and PFG-NMR. The stability of the oil-in-water dispersed droplet emulsions significantly increased with both the surfactant concentration and the chain length of the oil component. The PFG-NMR experiments monitored a superposition of the restricted diffusion of the oil in the droplets and free and restricted diffusion of the droplets themselves, and were correlated with the TEM images and the particle sizing data. Moreover, the present investigations were compared with earlier investigations where toluene was used as the oil. The change from the aromatic oil to an alkane-based oil dramatically changed the characteristics of the interfacial domain. The concentration range for the formation of emulsions and the variety of microstructures realized were severely restricted, but the interfacial film was much more stable leading to an extremely reduced rate of droplet coalescence. Additionally, concerning the destabilisation mechanisms, the alkane systems followed a much more complicated process compared with the toluene system. It was found that the principal destabilisation process was the same for all alkanes, whereupon the time constant of this process can be adjusted by using the appropriate chain length of the oil.

11-27

Old and New in Emulsion Science

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Abstract pending

11-28

Liquid Crystalline Silicate/Surfactant Mesophase in Nanoscale Confinement

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Cooperative assembly of silicate/surfactant replicates liquid crystalline mesophase of surfactant resulting in highly ordered mesostructures of inorganic/organic composite (e.g. cubic, hexagonal, lamellar structure). The self-assembly process can be altered readily by interfacial, geometric and other boundary conditions due to its weak non-covalent driving forces. In this presentation, we will show self-assembly behavior of liquid crystalline silicate/surfactant mesophase within nanoscale cylindrical pores of anodized alumina membranes. Morphology of the liquid crystalline silicate/surfactant composite was studied using XRD, TEM and SEM. We observed the transition from hexagonal to lamellar mesostructure of the liquid crystalline mesophase within the nanoscale confinement when surfactant concentration is increased. The hexagonal silicate/surfactant mesophase in nanoscale cylindrical pores prefers to orient along long axis of alumina pores, which is distinct from circular hexagonal mesostructure prepared by evaporation induced self-assembly process^[1]. Lamellar silicate/surfactant layers grow along curved pore wall surface resulting in oriented concentric lamellar mesophase. The corresponding mesoporous silica wires with oriented hexagonal tubular and concentric lamellar pore channels were obtained after removal of surfactants. The novel structured mesophase and corresponding mesoporous silica/alumina composite are expected in membrane based application such as separation, templating synthesis, etc. This work also will bring the insight of nanoscale confinement effect on self-assembly process.

11-29

Aggregation Phenomena on the Mixed Surfactant Systems Containing Dialkyldimethylammonium Bromide in Water. Mixed Micro-aggregates, Vesicles and Micelles

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The formation of mixed colloidal aggregates has been investigated on several ternary ionic-ionic and ionic-nonionic systems constituted by: i) a dialkyldimethylammonium bromide ($\text{di-C}_n\text{DMAB}$), double-chain cationic surfactants; ii) a ionic or nonionic single-chain surfactants, and; iii) water. The study has been carried out by means of conductivity, ζ -potential, fluorescence spectroscopy, transmission electron microscopy (TEM) and cryogenic transmission electron microscopy (cryo-TEM) experiments on the highly diluted, very diluted and moderately diluted regions. The formation of mixed micro-aggregates, prior to the appearance of mixed vesicles, has been confirmed by several of the analysed properties. The concentrations at which these mixed colloidal aggregates form, i.e. the mixed critical micro-aggregate concentration (CAC^*), the mixed critical vesicle concentration (CVC^*), and the

mixed critical micelle concentration (CMC*), have been determined from conductivity data, while the ζ -potential experiments allow for the characterization of the aggregate/solution interface. The shape and size of the micro-aggregates and vesicles have been evaluated from TEM and cryo-TEM micrographs, respectively. The interaction of TNS and PRODAN fluorophore molecules with solvent and the autoaggregates can be used to analyze the surface and the interior of the mixed aggregates formed. All these experimental evidences have been also analyzed in terms of the theoretical packing parameter, P .

11-30

Microstructure of Bicontinuous Nanoporous Materials Prepared from Methyl Methacrylate/Hydroxyethyl Methacrylate Microemulsions Formulated with Biocompatible Surfactant

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The biocompatible surfactant Ryoto Sugar L-1695 stabilizes transparent microemulsion precursors from the monomers of methyl methacrylate (MMA) and hydroxyethyl methacrylate (HEMA). Polymerized bicontinuous microemulsions showed nanoporous structure under scanning electronic microscopy (SEM). The pore size distribution of the polymeric materials was determined from freezing point depression (PFD) of water which was characterized by two different methods: differential scanning calorimeter (DSC) and pulsed gradient spin-echo (PGSE) NMR. Results from both DSC and PGSE-NMR indicated that the aqueous content in microemulsion precursor influenced the microstructure of the polymer formed whereby. Increased pore size was observed when increasing aqueous content.

11-31

The Use of Pluronic Microemulsions for Drug Detoxification: Investigation of the Interaction Mechanism by NMR Spectroscopy.

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Various Microemulsions (MEs) have been developed to address the problem of the lethal effects of overdosed drugs. Pluronic MEs efficiently abate the induced cardiotoxicity in living animals. However, the exact mechanism and important physico-chemical phenomena by which the drug binds to the ME are not clearly understood and need to be investigated on the molecular level to improve ME design and further enhance the efficacy of the ME. Pulse NMR spectroscopy is an expedient technique for elucidating the structural and dynamic interactions between drug and ME. Investigations were carried out using ¹H chemical shift, ¹³C NMR relaxation and self-diffusion measurements to determine the ME-drug interaction mechanism. Results indicate that at low concentrations molecules of the antidepressant, amitriptyline, initially bind with the hydrophobic portion of the Pluronic but bind to sodium caprylate, with increasing concentration. A steep increase in the slope of sodium caprylate

chemical shift on increasing amitriptyline concentration compared to the slope of Pluronic indicates that, in addition to the Pluronic molecules, sodium caprylate molecules in ME617 enhance the amitriptyline binding significantly. Additionally, self-diffusion studies indicate that amitriptyline binding stabilize the self-assembly structure of ME617 and show that amitriptyline preferentially binds to the Pluronic and sodium caprylate molecules than to the ethyl butyrate in the microemulsion.

11-32

CHRIS BRANCEWICZ

Abstract pending

11-33

Transition from Unilamellar to Bilamellar Vesicles Upon the Addition of an Associating Biopolymer

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The effect of adding a hydrophobically-modified chitosan to unilamellar surfactant vesicles is studied using SANS and cryo-TEM. The hydrophobes on the polymer have a tendency to become embedded in vesicle bilayers. This leads to changes in the size and ultimately in the morphology of the vesicles. At low amounts, the addition of polymer decreases the unilamellar vesicle size. At higher polymer concentrations, high-q peaks emerge in the SANS spectra which imply the co-existence of multilamellar vesicles together with the unilamellar ones. Detailed modeling of the SANS data suggests that most of the multilamellar vesicles have exactly two concentric bilayers (i.e., they are bilamellar). This intriguing prediction is confirmed by cryo-TEM images. The origin of the changes in vesicle morphology will be explored in this presentation.