

13-1

### **The Role of Phase Science in Colloid Science**

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Those systems of historic interest in the development of colloid science do *not* display discontinuous changes of state over the range of temperatures studied, and the solvent is not incorporated into the dispersed phase. The dispersed phases of water-insoluble surfactants, however, *do* incorporate solvent water – lots of it. They also undergo discontinuous phase changes near ambient temperatures. The incorporation of solvent has a profound effect on the ratio of coexisting phases, and all those properties associated with phase ratios. Incorporation as crystal hydrates may introduce complex and interesting colloid chemistry when these are heated past peritectic temperatures.

In biological cell membranes, temperature changes which pass the chain melting temperature should affect not only the membrane structure, but also its water composition. Such changes are predicted to affect the water content of the cytoplasm, and thereby *the thermodynamic activity of every water-soluble component in the cytoplasm*. The impact of these changes has been neglected, but may extend far beyond the structural perturbations that have been the focus of interest to date.

13-2

### **What's New with The Gibbs Adsorption Equation?**

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The Gibbs adsorption equation and some of its implications will be recalled. What had for a quarter century been thought to be the analog of the Gibbs adsorption equation for the line of three-phase contact was recently discovered to be incorrect. A brief account of that problem, and of the related question of how adsorptions at the line of three-phase contact behave as a transition to complete wetting is approached, will be presented.

13-3

### **Some Applications of Surfactant Phase Diagrams**

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A series of examples are presented for which the phase diagrams of the systems were either necessary or helpful to solve problems within emulsions, microemulsions and foams.

The examples vary from the stability of foams from non-polar solvents to formulation of microemulsions to the action of hydrotropes to the structural changes in simple emulsions during evaporation. Finally the advantage of applying analytical geometry to such systems is exemplified.

13-4

**“Stained Glasses”, Thin Liquid Films and Lamellar Liquid Crystals**

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Foam films drawn from aqueous solutions of sodium naphthenates and Aerosol OT, at concentrations close to or just above the lamellar liquid crystal (LLC) phase boundary, contain domains of uniform color (thus of uniform thickness) with sharp boundaries, resembling 'stained glasses'. To be colored, the domains must be thicker than half of the visible light wavelength. Analysis of Newton rings shows that these domains exist well above 1  $\mu\text{m}$  thickness. To have a uniform thickness, the domains must contain hundreds of ordered layers of molecular dimension. Statistical mechanical considerations for hard spheres (which represent micelles) predict the existence of only a few such layers. It is thus likely that Wasan and Nikolov's model of film stratification, based on parallel layers of ordered micelles, describes film structure at moderate surfactant concentrations. At high concentrations however, LLC-like organization is likely responsible for film stratification, in agreement with pioneering works of Stig Friberg.

13-5

**Emulsion Structure and Stability: Role of Depletion and Structural Forces**

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In this paper, we will review the recent work performed in our laboratory in the areas of structure and stability of emulsions and foams. We will particularly highlight the role of long-range oscillatory forces, including attractive depletion and structural, in controlling dispersion stability. We have developed a novel hybrid surface force apparatus referred to as the capillary force balance in conjunction with a differential interference microscopy method to investigate surfactant micelle or nanoparticle structuring phenomenon inside thinning liquid films confined between droplets or foam bubbles in concentrated colloidal dispersions. In addition, we have used a nondestructive Kossel diffraction technique to obtain the structure factors, and the advanced optical imaging method to obtain the emulsion radial distribution function to determine the effective inter-droplet interactions. We have used these techniques to investigate the effects of surfactant type (i.e., water soluble and oil soluble), proteins, gums, fat substitute, temperature and shear rate on emulsion structure and stability. We have carried out theoretical calculations using the Ornstein-Zernike equation of statistical mechanics and Monte Carlo simulations to elucidate the role of long-range oscillatory forces in concentrated dispersions, and showed that the experimental results are consistent with theoretical simulations.

13-6

**Phase Diagrams of Ternary Lipid Bilayer Mixtures Containing Cholesterol**

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Determination of the phase diagram for a 3-component bilayer mixture of lipids requires use of several different methods in order to resolve ambiguities in the phase boundaries. We employed fluorescence spectroscopy and microscopy, ESR spectroscopy, x-ray and neutron diffraction, and light scattering. Mixtures containing cholesterol that model the outer leaflet of animal cell membranes show rich phase behavior. DSPC/DOPC/cholesterol (distearoyl-PC/dioleoyl-PC/cholesterol) is one such mixture, with a large region of macroscopic separation of  $L_2 + L_0$  phases. In contrast, DPPC/DLPC/chol (dipalmitoyl-PC/dilauroyl-PC/cholesterol) shows a much smaller region of separation of  $L_2 + L_0$  phases, and the phases are “nanoscopic”. Sphingomyelin/DOPC/chol shows “nanoscopic” coexistence of  $L_2 + L_2$  phases, but macroscopic separation of  $L_2 + L_0$  phases.

13-7

### **Phase Behavior and Structure in Mixtures of Surfactants and Hydrotropes**

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Hydrotropes are amphiphilic molecules with hydrophobic portions too small to form micelles. Hydrotropes bind strongly to the surface of micelles and can facilitate the formation of interesting microstructures such as elongated micelles and vesicles. We have investigated the formation and polymerization of worm-like micelles and vesicles made of polymerizable surfactants. The use of water-soluble di-azo free radical initiators for these studies led to the discovery of the spontaneous formation of vesicles from simply mixing the initiator with surfactant alone, without polymerization. The characterization of these mixtures indicated that initiators behave as hydrotropes. Basic amino acids have similar molecular functionality and show a similar hydrotropic behavior, including the formation of gels. This work reveals the power of hydrotropic molecules in driving structural changes in surfactant solutions.

13-8

### **A New Approach to Dilute and Concentrated Lamellar Phases in Phase Diagrams of Nonionic Surfactants**

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The present contribution is about new results on two peculiar features in connection with the lamellar phases ( $L_2$ ) in binary aqueous solutions of nonionic surfactants. The first striking feature is the formation of highly dilute  $L_2$  phases down to 1 wt.-% of surfactant, which has been observed for a small number of nonionic surfactants which are all of the alkyl polyglycol ether ( $C_iE_j$ ) type. So far, in binary  $H_2O - C_iE_j$  systems either the absence or the presence of a dilute  $L_2$  phase has been reported. In the latter case, the dilute and the concentrated  $L_2$  phase are always connected continuously. However, for one particular silane surfactant, namely  $(CH_3)_3Si(CH_2)_6(OCH_2CH_2)_5OCH_3$ , two disconnected  $L_2$  phases were observed. Systematic investigations of the phase behaviour of the binary system  $H_2O - C_{10}E_4$  as well as of the pseudobinary systems  $H_2O - C_{10}E_4/C_{10}E_5$  enabled us to answer adequately the following questions: (a) Is the disconnected  $L_2$  phase a peculiarity of the silane surfactant or a general feature of nonionic surfactants? (b) Are there any structural differences between the connected

and the disconnected  $L_2$  phases? (c) What is the process which leads to the disconnection of the  $L_2$  phase?

13-9

### **Spontaneous Emulsification and its Relationship to Phase Behavior: Review and Recent Developments**

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The relationship of spontaneous emulsification to phase behavior is reviewed with emphasis on results obtained in recent years. Several studies have provided insight on the mechanism of self-emulsification of oils to form oil-in-water emulsions consisting of small droplets. In particular, diffusion and/or chemical reaction can cause changes in composition and hence in spontaneous curvature of surfactant films, which promote inversion from an oil-continuous to a water-continuous microemulsion. Since the latter is not able to solubilize all of the oil present, local supersaturation and subsequent nucleation of oil droplets occurs. Under suitable conditions the lamellar liquid crystalline phase is formed during the inversion process and coats the small droplets, thereby hindering coalescence and reducing the surfactant concentration required to form small droplets. Self-emulsification can also occur without large changes in spontaneous curvature when the surfactant films are initially near the balanced state of zero spontaneous curvature. Formation of the lamellar phase during this process appears to be essential for obtaining small droplets. "Nanoemulsions" with drop sizes of order 100 nm or less have been produced by self-emulsification processes which involve spontaneous emulsification accompanied by gentle stirring. When polymer is dissolved in the droplets, removal of the solvent yields small polymer nanoparticles, which are of interest in applications such as drug delivery. The results of these studies demonstrate that knowledge of equilibrium phase behavior is important in choosing suitable systems and conditions for self-emulsification.

13-10

### **Water-in-Crude Oil Emulsions – Stability Mechanisms and Environmental Aspects**

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The keynote lecture is going to view the chemistry of heavy crude oil components and their interaction forms. After this the formation, stabilization and destabilization of water-in-crude oil emulsions is viewed. The stabilizing role of the heavy components in the crude oil is discussed together with ageing effects.

Particle-stabilization is viewed from three different aspects. The impact of the association of asphaltenes to form organic nanoparticles is well-known from previous studies. In addition the role of inorganic fines and small metalnaphthenate particles is discussed. Inorganic fines, mostly oxides from the formation, will have a natural tendency to accumulate at w/o interfaces depending on their contact angle. However, what is highly changing the behaviour of these fines is the adsorption of components from the crude oil onto their surface. These components are mainly resins and asphaltenes. Another route to form fines is the reaction between organic

naphthenic acids and divalent cations. It is shown by means of dynamic interfacial tensions that reactions over w/o interfaces are important in this respect.

It becomes more and more important to understand the underlying stabilization mechanisms of the dispersed material due to the tougher regulations on discharges by the state authorities. Normally the discharges include emulsions (o/w), dispersed particles (with and without coating) and dissolved components. However, since the dissolved components will include both naphthenic acids and polar components the possibility of finding dispersed lyotropic liquid crystals should be profound. In this study we report for the first time on the results from phase diagram studies based on model components representing naphthenic acids and polar phenols in water.

13-11

### **The Role of Colloid Science and Electrokinetics in Oil Sands Processing**

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Canadian bitumen recovery from oil sands will continue to increase in the next decades. The present oil sands development in Alberta is on a massive scale. The three existing open-pit oil sand plants in Alberta produce about 700,000 barrels of bitumen a day. Increased bitumen production requires development of new technologies and improvement of existing ones. As well, it requires increasing skilled engineers to handle the increased production levels.

The presentation deals with research efforts at the University of Alberta that seek a better understanding of bitumen recovery from oil sands. A summary will be presented on the use of the state of the art techniques to probe the interfacial properties of hydrocarbon-water interfaces to elucidate the mechanisms of air-bitumen attachment, bitumen-solids separation and stabilization of water-in-oil emulsions. Among the techniques to be discussed are: Atomic Force Microscope, zeta potential distribution measurements and Langmuir-Blodgett trough.

13-12

### **Relations Between the Molecular and Nanocolloidal Structure of Asphaltenes**

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The science of asphaltenes, the most aromatic fraction of crude oil, has advanced significantly in recent years. Asphaltene molecular weight has recently been elucidated after decades of controversy; time resolved fluorescence depolarization results yielded critical results. Asphaltene molecular architecture has also largely been resolved; x-ray Raman spectroscopy delineated fused aromatic ring geometry. These findings will be reviewed. The Critical Nanoaggregate Concentration (CNAC) of asphaltenes has also recently been delineated for example by high-Q ultrasonic spectroscopy; a decade of literature was misinterpreted (Professor Friberg played a central role in correcting the problem). The governing physics of nanoaggregate formation is evident in asphaltene molecular structure; function follows structure. These precepts which are largely 'freshman chemistry' are shown essentially to define the identity of asphaltenes.

13-13

### **Liquid Crystallinity and Emulsion Formation in Ternary Oil-Water-Acid/Soap Systems Comprised of Model Naphthenic Acids and Their Mixtures with Asphaltenes from Petroleum Fluids**

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In an effort to better understand the role of naphthenic acids and soaps in stabilizing water-in-oil emulsions, we conducted a study of emulsion type and stability in model ternary systems comprised of oil, water, and aromatic and alicyclic ringed acids as functions of pH and acid/soap concentration. The acids selected for study were b-cholanic acid, deoxycholic acid, heptyl benzoic acid and pentane cyclohexanoic acid. The pH of the aqueous phase was systematically varied from 5-13 and the concentration of acid/soap was varied from 0.5-10% (w/w). All of these model systems clearly indicated a transition from oil-in-water emulsions at low pH, to water-in-oil emulsions at higher pH (which varied with the architecture of the hydrophobic group on the acid). At sufficiently high pH, some of the systems reverted back to o/w emulsions. These results are consistent with the interfacial film of acid/soap molecules adopting a lamellar structure when the balance among effective head group size due to electrostatic repulsion and the steric repulsion of cyclic hydrophobic moieties confers a molecular packing parameter close to unity on the system. Under these conditions of balance, there is clear evidence from optical polarizing microscopy that the interfacial films are liquid crystalline. This appears to be a universal phenomenon with monomerically pure acid/soaps. We have also explored the interaction of asphaltenes and model naphthenic acid/soaps as a function of aqueous phase pH and concentration of acid/soap. Under appropriate conditions of pH and using model naphthenic acids with appropriate hydrophobic groups, the presence of the acid/soap can dramatically destabilize w/o emulsion, even at extremely low concentrations (0.05% (w/w)). Interestingly, when the hydrophobic moiety of the acid is sufficiently aromatic or fused ringed aromatic, the addition of the acid/soap can dramatically *stabilize* w/o asphaltene emulsions. The results suggest judicious ways of minimizing w/o emulsion challenges during the production and refining of petroleum fluids.

13-14

### **Studies on Properties of Interfacial Active Fractions from Crude and Its Effect on Stability of Crude Emulsions**

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The influence of indigenous interfacial active fractions from crude on the interfacial property between water and crude and its effect on stability of crude emulsions was studied.

It was found that the fatty acid and carboxyl acids in the fractions of asphaltene from Gudong 1#, Gudong 4# crude and of resin from Daqing crude are responsible for decreasing the interfacial tension between the crude oils and water. These acids have smaller relatively molecule mass, more branch chain more oxygen but they were not able to stabilize emulsion formed by model oil and water. It was the acids with larger relatively molecule mass are responsible for stabilizing the emulsions. For model oil and alkali solution system the soap formed by fast reaction of the

acid, ester with smaller relatively molecule mass and alkali is responsible for decreasing the interfacial tension between crude oil and water. The soap formed by slow reaction of the acid, ester with larger relatively molecule mass and alkali is responsible for stabilizing crude oil emulsions.

13-15

### **Phase Equilibria and Separation of Amphiphilic Extractives from Wood**

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Phase equilibria, particle size and kinetics of phase separation in aqueous sodium alkanoate/sodium rosinic acid systems containing solubilizers representative of water-insoluble compounds in wood (sterols, long-chain alkanols) was investigated by light transmission and backscattering measurements using TurbiScan analyzers. Solution conditions corresponded to those obtained during cooking and washing of softwood pulp ("black liquor") and separation of crude tall oil. Creaming rates of the lyotropic phases were highly dependent on the ratio alkanoate/rosinic and the amount of solubilizer. Two-phase regions were found in which lamellar phase was in equilibrium with very dilute solutions, and separation was very efficient. This was utilized to develop method of improving the separation of soaps from dilute systems by addition of non-polar solubilizers. The method was applied successfully, in laboratory scale and mill trials, to the separation of soaps by adding non-polar solubilizers isolated from wood. The amounts of residual dissolved alkanoates and resinates could be reduced by 70-80 %, depending on the amount of "auxiliary" solubilizer added.

13-16

### **Building an Institute to Serve Industry with Innovations from Surface Chemistry Research**

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The Institute for Surface Chemistry (Ytkemiska Institutet, or YKI for short) was created to promote research in interfacial science that had relevance to industry. YKI started as a laboratory under the auspices of the Royal Swedish Academy of Engineering Science on the campus of the Royal Institute of Technology (KTH) in Stockholm. It drew strength from strong departments of physical chemistry at KTH, Lund, Uppsala, and Chalmers. Stig Friberg led YKI from its inception as a free-standing institute in 1969 until he left for the University of Missouri at Rolla in 1976. During his time as president he drove the reduction of surface chemistry theory to practice. By providing value to industry he was able to build a membership of 45 companies in the Association for Surface Chemistry Research, later to become the majority owners of YKI. Stig's ability to interpret phase diagrams as an aid in formulation was a significant contribution to YKI's growing rapport with its industrial client base.

Today, YKI remains strongly linked to academe in Sweden with doctoral students inscribed in all of the above-mentioned universities, but it can count active working relations with 100 universities and institutes around the world. More than half of the articles produced by the YKI staff are coauthored by scientists from these universities and institutes. This open innovation

model has helped to attract 70 international member companies covering ten industrial sectors to the Association for Surface Chemistry Research. The flow of ideas from this network of research partners and further development at YKI provides technology platforms on which are built consortium projects for industry. For example, cooperative work with Swedish and American universities on the creation of nanostructured materials from self assembly has been a fountainhead for delivery and release projects in a broad range of applications such as biocides in paint, drug delivery, fragrance release, sensor encapsulation, and even a new class of pigments from dyes dissolved in inorganic matrices. Similarly, innovation in surfactant chemistry has led to many industrial projects such as triggered foam or emulsion breaking, particle stabilized emulsions, surfactants that totally biodegrade, and surfactants with antibacterial and antifungal attributes. The institute that Stig Friberg started is now a company that is positioned to do well in the increasingly knowledge-based economy in which it operates.

13-17

### **Crystal Comets: Dewetting during Emulsion Droplet Crystallization**

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Liquid oil emulsion droplets can violently dewet their own solid crystals during crystallization as a result of surfactant adsorption. The crystal shape formed is a function of the relative rates of dewetting and crystallization as controlled by surfactant adsorption, cooling rate, and lipid purity. For negligible dewetting rates, crystals nucleate and grow within the droplet. At similar crystallization and dewetting rates, the droplet is propelled around the continuous phase on a crystalline “comet tail” much larger than the original droplet. Rapid dewetting causes the ejection of small discrete crystals across the droplet’s oil-water interface. It is shown that the crystallization behavior can be controlled by tuning the molecular packing geometry of the surfactant.

13-18

### **Dispersions of Glyceryl Monooleate with PEO-Copolymers Bearing Lipid-Mimetic Hydrophobic Blocks in Water.**

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Stable dispersions of the cubic phase of glyceryl monooleate (GMO) in water were first obtained by K. Larsson and suggested to require the presence of a three phase area, involving the lamellar phase in addition to the cubic and water. Using suitable stabilizing agents such as poloxamers, it was later shown that stable cubic particles can be obtained also within the two phase area. Furthermore, GMO and sodium cholate form a L<sub>3</sub> phase in brine; dilution of this phase in excess brine results in coexisting L<sub>3</sub> and cubic particles with some stability.

We have prepared copolymers with PEO as hydrophilic block and blocks containing two to eight dodecyl chains as hydrophobic anchors, in both di- and triblock versions. Dispersing a polymer-GMO mixture in glycerol, and adding this dispersion to excess water, results in the formation of small particles with a broad variation of morphologies depending on the amount and type of

copolymer. The particles have been studied by cryoTEM imaging, and their morphologies will be rationalised from packing and phase behavior.

13-19

#### **Worm-like Micelles and Microemulsions**

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Wormlike micelles form visco-elastic solutions in which long-flexible micelles are entangled. CTAB is a well-known cationic surfactant, which produces such a visco-elastic system in the presence of some inorganic and/or organic salts. Wormlike micelles are also produced by combining hydrophilic surfactant with cosurfactant in ionic and nonionic surfactant systems. Upon addition of oil to the viscoelastic systems, the considerable reduction in viscosity takes place in some oil systems whereas it is also possible to maintain the viscosity in other oil systems. These systems are also able to call microemulsions. Phase behavior of wormlike micelles and their microemulsions in the mixed surfactant systems will be reported as well as their visco-elastic behavior and structures.

13-20

#### **Friberg Correlations in Oil Recovery**

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In the presence of liquid crystal phase (LC-phase), the stability of emulsions increases dramatically. Consequently, the phase behavior of oil/organic-solvent/water systems has an effect on the efficiency of separation of emulsified water. Since LC-phase was identified in bitumen/toluene/water system under alkaline conditions, the phase behavior of sodium-naphthenates/organic-solvents/water was investigated in detail revealing the presence of lamellar LC, microemulsion and high viscosity gel phases. In this system the emulsion stability has a strong correlation with the phase behavior. The LC-phase is located between the dispersed aqueous droplets and organic medium.

In crude oil systems having low surfactant concentration, the volume of the interfacial LC-phase becomes so small that it cannot be identified easily by polarization microscopy. For this case quartz crystal microbalance (QCM) and electroacoustic spectroscopy (EAS) were introduced for the characterization of the adsorbed surface-active materials at the oil-water interface in bitumen-toluene systems. EAS revealed a time dependent relaxation of the surface charge of water-in-oil emulsions. Depending on the bitumen concentration, two distinct adsorption regimes were discovered by QCM. The threshold concentration between these adsorption regimes is in agreement with the critical bitumen concentration corresponding to the rigid-to-flexible transition of the o/w interface.

13-21

#### **Phase Behaviour in Confinement Studied with a Surface Force Apparatus**

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The free energy of a surface has a major influence on phase behaviour in systems where the area-to-volume ratio is large. These include finely dispersed solids and liquids as well as substances confined to meso- and microporous solids. In a surface force apparatus mica surfaces at or close to contact form a single model pore in which surface energy effects on phase behaviour may be conveniently studied. Capillary condensation of liquid from undersaturated vapour is the most familiar example of a surface-induced shift of bulk phase behaviour. I will describe experimental studies of capillary condensation and related phenomena such as melting-point depression in a pore, direct condensation of solid from vapour and capillary evaporation.

13-22

### **A Magneto-Optical Apparatus for Boundary Localization of Ternary Phase Diagrams**

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Knowledge of the phase diagram of any complex fluid, either colloidal dispersions, surfactant solutions, polymers or lipids, is the first step needed for efficient formulation in industry or to investigate molecular interaction.

An optical apparatus designed for the mapping of binary or ternary phase diagrams will be described. A polychromatic polarized light illuminates a sample and the rotation of its polarization is measured with a spectrometer for various magnetic fields. The measured parameters are the natural and magnetic rotatory power of the sample which allows the concentration retrieval of every compound to be done. Results show that the apparatus is suitable for correct positioning of single phase boundary on the ternary water - n-dodecyl- $\beta$ -D-maltoside - sodium chloride system.

13-23

### **Design of Experiments Approach for Decontamination Formulation Development**

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The goal of Sensitive Equipment Decontamination is to decontaminate small equipment items that would be readily damaged by traditional decontamination methods. Typical items that fall into this category are night vision goggles, handheld radios, and laser range finders. Because even the smallest damage to the items could potentially disable them, the decontaminant must be compatible with a wide range of materials consist of a variety of polymers, delicate metals, and advanced coating systems. Material compatibility requirements preclude using highly reactive decontaminants, thereby limiting the ability to conduct *in situ* agent destruction. Therefore, the decontamination must rely on agent removal from the surface, followed by subsequent removal of the agent from the spent decontaminant in order to recycle the solution in a closed-loop manner.

A formulation approach for selecting and/or developing a new solvent for the sensitive equipment decontamination is presented. One of the key features to this approach is the use of Design of Experiments to allow multiple combinations of modifications to be measured in a cost-effective and timely manner.

13-24

### **Surface Chemical Aspects of Treatments with Dental Implants**

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Reviews of factors influencing the outcome of restorative treatments with dental implants have demonstrated that lack of proper control of implant surface chemistry is one of the most likely reasons for the frequent reported failures of such treatments prior to the introduction of so-called osseointegrated Ti-implants in the 1980-ies. Thus, with earlier implant systems surface contamination was often present as the results of poor mechanical finishing and/or sterilization procedures. Such contamination prevents the establishment of initial key contacts between living cells and the actual implant surface. On a long term basis this led to the formation of connective tissue capsules around implants in stead of direct implant-bone contacts that now are known to be essential for successful long term functional control of implant loading and prevention of implant-tissue infections.

This paper present an overview of these problems as well as recent data supporting the view that the establishment of undisturbed, initial contacts between living cells and implant materials with defined surface chemical characteristics is an absolute prerequisite for long term clinical success with modern dental implant systems. It will also point on certain surface chemical problems associated with the efficacy of *in situ* hygiene procedures for patients wearing dental implants.

13-25

### **Nanolithography – The Art of Patterning at Colloidal Dimensions**

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The semiconductor industry is on the threshold of producing integrated circuits that will operate at 45-nm design rules. While these design rules rival the dimensions of self-assembled amphiphilic colloids, the super-submicron circuit features in these devices will be created using ‘top-down’ optical lithographic and subtractive etching processes that have dominated semiconductor production for more than 30 years. The demise of optical lithography has been predicted many times, but in spite of many naysayers, it continues to find new life through technological advances in light sources, optics, photoresist chemistry, and modes of processing. This presentation will recount how these advances have collectively allowed optical lithography to remain the patterning method of choice for 45-nm integrated circuit features. It will at the same time offer concepts for combining advanced optical lithography and molecular self-assembly techniques to create scalable processes for forming complex nanostructures.

13-26

### **Studies on the Stability of the Choramphenicol in the Microemulsion-based Ocular Drug Delivery Systems**

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Two microemulsion systems which were composed of Span20+Tween20+ isopropyl palmitate+H<sub>2</sub>O and Span20/80+Tween20/80+ n-butanol+ H<sub>2</sub>O+ isopropyl palmitate /isopropyl myristate were investigated as potential drug delivery systems for eye drops. Effects of choramphenicol, normal saline, sodium hyaluronate and various oils on the phase behavior were studied. The phase transition was investigated using the electrical conductivity measurements. The choramphenicol is used to treat the eye diseases such as trachoma and keratitis. However, this drug in the common eye drops hydrolyzes very easily. The main product of the hydrolysis is glycol. Here, the choramphenicol was trapped into the oil-in-water microemulsions, its stability was investigated by HPLC assays in the accelerated experiments of three months. The location of the choramphenicol molecules in the microemulsion formulations was determined by means of <sup>1</sup>H NMR spectroscopy and dynamic light scattering (DLS). The results of HPLC revealed that the content of the glycols in the microemulsion formulation was much lower than that in the commercial eye drops at the end of the accelerated experiments. It implied that the stability of the choramphenicol in the microemulsion formulations is increased remarkably. The results of NMR and DLS confirmed that the choramphenicol molecules should be trapped into the hydrophilic shell of the microemulsion drops, which were composed of many oxyethylene groups. It was this reason that enabled the choramphenicol molecules in the microemulsions to be screened from the bulk water and its stability to be increased remarkably.

13-27

### **Application of Phase Studies for the Formulation of High Ionic Strength Antiperspirant Products**

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Antiperspirant products are a very large personal care category, 90% of the American population use antiperspirants every day. The products on the markets are in different forms, such as solid sticks, soft solids, gels, sprays, aerosols, creams and roll-ons. From a colloid chemistry point of view, formulations can be emulsions, microemulsions, co-solvent systems or solid particle suspensions with or without structurants or polymers.

Aluminum salts are the main active ingredients in antiperspirant formulations. When a high salt concentration is involved in making a formulation, the phase behavior of the systems is highly impacted. In this presentation, we will introduce basic knowledge concerning antiperspirant products and how to use phase studies to reach desirable formulation for consumer products.

13-28

### **Salicylic Acid Vesicle Solutions, Emulsions and their Combinations .**

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The phase diagrams were determined of salicylic acid as beta hydroxy acid and to be compared with series of hydroxy acids such as lactic acid, isohexanoic hydroxy acid and some water soluble acids such as malic, tartaric and citric acid. The acids were combined with water, a nonionic surfactant and a paraffinic oil to outline the influence of the hydroxyl acids on the structure in a model for a skin lotion. The colloidal structures of beta carboxylic acid topical formulations were determined and the changes during evaporation after applications were estimated from phase diagrams.

The results showed that; the influence of the acid to be similar to that of the oil, but that the difference in chain length between the alpha acids had only insignificant influence, the significant difference between salicylic acid on one hand and three water soluble acids; malic, tartaric and citric acid, on the other, the water soluble acids showed an increase in the acid concentration in the water to levels that must be considered definitely harmful, while salicylic acid showed no increase in concentration in the individual phases.

13-29

#### **Theoretical Study on Synergisms of Surfactant Mixtures**

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By appointing the ideal mixture system of surfactants as the standard of comparison, synergisms in surface tension reduction efficiency and in mixed micelle formation of binary surfactant mixtures in aqueous solution have been redefined. The conditions and the corresponding optimum point values of these two kinds of synergism also have been deduced on the bases of the regular solution theory and the ideal solution theory. The conclusions have enlarged reasonably the scope of synergism theory proposed by Rosen and his coworkers.

13-30

#### **Colloid and Surface Science in Consumer Product Development**

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Colloid and surface science plays a key role in product development at many Consumer Products companies. This talk will focus on the consumer products designed for the automotive aftermarket: lubricants, chemicals, and appearance products. These products have evolved dramatically due to empirical and scientific advances in the field. Lubricants today are engine tested under conditions where suspended soot and particulates may exceed 8 % by weight. Appearance products, such as car wash, automotive waxes, tire shines and wheel cleaners, etc., have benefited from an array of advances in detergency, emulsion and microemulsion technology, and colloidal dispersion technology. Automotive chemicals, e.g. fuel system cleaners, have benefited from new detergent technology as well. The impact of colloid and surface science on these consumer products is explained, pointing out some of the key advances.

13-31

## **X-ray Studies of Mixed Surfactant Ordering and Phases at the Water-Oil Interface**

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X-ray reflectivity is used to study ordering on the Angstrom scale of a monolayer of surfactants self-assembled at the liquid-liquid interface between bulk water and hexane. This technique determines the electron density as a function of depth through the interface. Studies of the interface between water and single surfactant hexane solutions of either  $\text{CH}_3(\text{CH}_2)_{19}\text{OH}$  or  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$  demonstrate the liquid order of the hydrocarbon monolayer or the solid order of the fluorocarbon layer, as well as phase changes with temperature. Interfacial tension and x-ray studies of the interface between water and mixed solutions of these surfactants in hexane determine the phase diagram, and the molecular ordering of the phases, as a function of temperature for four different surfactant compositions. An unusual feature is the phase change from a liquid to a solid monolayer that occurs with increasing temperature. A simple model predicts the interfacial coverage as a function of temperature for the mixed surfactant system from the behavior of the single surfactant systems.

13-32

## **Monolayer Phase Morphology Induced by Bulk Flow**

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Effects of bulk flow on Langmuir monolayers are examined in open flow systems (rectangular cavities and cylinders) driven by the motion of the floor. The air/water interface covered by an insoluble monolayer (vitamin K1) is studied using a Brewster angle microscope (BAM) system that utilizes a pulsed laser to image the coexisting phase domains on the fast-moving surface. The flow field is measured using a digital particle image velocimetry system. A range of flow conditions is considered where the Reynolds number is large (large flow inertia) yet the flow is essentially two-dimensional (planar or axisymmetric). Macroscale flows can induce various mesoscale phase behaviors, such as fragmentation of phase domains. Recent results from this and other groups show that coexisting phase domains, observed over a wide range of monolayer states, have profound effects on the (macroscopic) response of monolayers to flow. We examine the effects of shearing and dilating flows on the coexisting phase domains with the aid of numerical results obtained using the Navier-Stokes equations with Boussinesq-Scriven surface model. We show that the response of coexisting phases to flow and the resulting morphological transitions from one phase to another needs to be accounted for when interfacial hydrodynamics drives the system far from equilibrium.

13-33

### **Mixed Cationic and Glycoside Surfactants: Investigation of Ternary Phase Diagram and Predictive Mesoporous Materials Synthesis**

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Mixed surfactant systems have the potential to impart controlled combinations of functionality and pore structure in mesoporous ceramics. In this instance, we combine a functional glycoside surfactant with a cationic surfactant that more readily forms liquid crystalline mesophases. The phase diagram for the ternary system CTAB/H<sub>2</sub>O/n-Octyl $\beta$ -D-glucopyranoside (C<sub>8</sub>G<sub>1</sub>) at 50 °C is investigated using polarized optical microscopy. At this temperature, the binary C<sub>8</sub>G<sub>1</sub>/H<sub>2</sub>O system forms micellar solutions up to over >70 wt% C<sub>8</sub>G<sub>1</sub>, and there is no hexagonal phase. With the addition of CTAB, we identify a large area of hexagonal phase, as well as cubic, lamellar and solid surfactant phases. The ternary phase diagram is used to predict the synthesis of thick mesoporous silica films via a direct liquid crystal templating technique. By changing the relative concentrations of mixed surfactants as well as inorganic precursor species, mesoporous silica films can be synthesized with variable glycoside content, and with 2D hexagonal, cubic and lamellar structures. The domains over which different pore structures are prepared correspond well with those of the analogous mesophases in the ternary phase diagram if the hydrophilic inorganic species is assumed to act as an equivalent volume of water.

13-34

### **Nano-Emulsion Formation by Low-Energy Emulsification Methods and Phase Behavior**

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Emulsions with droplet size in the nanometer scale (typically in the range 20-200 nm) are known as nano-emulsions, miniemulsions, submicron emulsions, etc. Due to the extremely small droplet size, nano-emulsions appear transparent or translucent to the naked eye (resembling microemulsions) and possess stability against sedimentation or creaming. These properties make nano-emulsions of interest for fundamental studies and for practical applications. In this communication, our recent work on the formation of nano-emulsions in water/polyethoxylated nonionic surfactant/oil systems by low-energy emulsification methods will be reported. O/W nano-emulsions with droplet sizes as low as 20 nm and high kinetic stability have been obtained either by the PIT method or at constant temperature (by changing the composition). It has been inferred from phase behavior studies that a requirement for the formation of minimum droplet size is to achieve a complete solubilization of the oil phase in a bicontinuous microemulsion, independent of whether the initial phase equilibrium is single or multiphase.