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MICROSTRUCTURE STUDIES IN SURFACTANT SYSTEMS

BY

VIVEK AGARWAL

A DISSERTATION SUBMITTED IN THE PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

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2004

DOCTOR OF PHILOSOPHY DISSERTATION

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ABSTRACT

Microstructures in two mixed surfactants systems that show novel transformations as a function of composition and temperature have been explored. Indirect imaging methods like Small Angle Neutron Scattering (SANS) along with direct imaging methods like Cryogenic Transmission Electron Microscopy (Cryo-TEM) and recently developed Freeze Fracture Direct Imaging (FFDI) have been used extensively to characterize and identify the changes in the microstructures in the mixed surfactant systems as a function of composition, temperature and external force fields.

As water is added to a solution of an anionic surfactant, AOT (2 ethylhexyl sodium sulfosuccinate) and a zwitterionic surfactant, lecithin (phosphatidylcholine) in isooctane, the microstructure evolves from a water-in-oil microemulsion to a bicontinuous highly viscous gel phase. SANS experiments show that the gel consists of highly ordered aqueous and organic nanochannels. Depending upon the composition and temperature these ordered phases display either hexagonal or lamellar symmetries. FFDI has been used extensively to image the hexagonal and lamellar microstructures of the gel phase and shows that the structures at high water contents are multilamellar vesicles, and not planar sheets.

It has also been observed that the application of shear orients the cylinders in the hexagonal phase in the direction of flow and reduces the inter-cylinder spacing. The lamellar polycrystalline phase does not show any preferential alignment after

application of shear, confirming that this phase consists of multilamellar vesicles. When the mixed phase (hexagonal + lamellar) is subjected to shear, the hexagonal component aligns, while the lamellar portion remains unaffected. When an aligned hexagonal phase is heated past the hexagonal to lamellar phase transition temperature, cylinders merge in the (1, 0) direction to form planar sheets parallel to the walls of a Couette cell.

Cryogenic-TEM has been used extensively to map the transformation of cetyl trimethyl ammonium bromide (CTAB) micelles to elongated micelles, vesicles and tubules and double layered vesicle structures as a range of phenolic derivatives are doped into the system. The addition of hydrotopes as well as more insoluble dopants to micelles to drive structural transitions represents an interesting approach to controlling functionality in complex fluids.

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I would like to dedicate this work to my parents for the unparalleled love and support they provided me all life long. Their love is precious to me.

I am extremely indebted to my advisor, Professor Arijit Bose, who encouraged me, guided me and supported me at every single step of my research. I learned a whole lot from him. He is the best.

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I would like to thank my colleague Mohit Singh, for being such an excellent team member, and fellow graduate students in the Chemical Engineering Department at URI.

Last, but not the least, I would like to thank Meredith Leach, Patti Corriea and Erica Conca for their valuable assistance in my stay at URI.

PREFACE

This thesis is written in manuscript form. Chapter I has already been published in *Langmuir*. This work involves the use of Freeze Fracture Direct Imaging (FFDI) as an emerging direct imaging tool to reveal microstructures, especially in highly viscous and organic rich self assembled surfactant systems.

Chapter II has been submitted to *Langmuir*. It reveals the effects of shear on the microstructures of an AOT/Lecithin/Water/Isooctane mixed surfactant system. Small Angle Neutron Scattering (SANS) has been used to analyze the changes in microstructure with the shear. The microstructural behavior is in accordance with the findings in Chapter I.

Chapter III has been prepared for submission to *Langmuir*. It reports the structural evolution of the microstructure formed in the aqueous solution of cetyl trimethyl ammonium bromide (CTAB) with the addition of various organic dopants. Cryogenic transmission electron microscopy (Cryo-TEM) has been used to capture these structural changes.

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INTRODUCTION

Self Assembly

Self assembly is a natural phenomenon, which produces well defined exquisite hierarchical structures via assembling small fundamental components¹. Self assembly of simple components into complex structures and systems is also seen as a natural order and is ubiquitous throughout nature. Formation of the beautiful snowflakes from the random aggregation of water molecules to the creation of a living organism, all demonstrate the power of self assembly at its best. In other words self assembly can be defined as the organization of materials through noncovalent interactions (hydrogen bonding, Van der Waal's, electrostatic etc.) with no external intervention.

Self Assembly in Surfactant Systems

A surfactant is an amphiphilic molecule. It has a hydrocarbon tail and a polar head group. The tail likes the company of organics while the head group has an affinity towards water. When surfactant is present in solution, above a certain concentration called critical micelle concentration (CMC), it self assembles into variety of structures such as micelles, bilayers, vesicles, liquid crystals and emulsions². It self assembles such that the hydrophilic part, i.e. the head group, resides in the aqueous environment and the hydrophobic part is protected from the aqueous environment³. The shape of these structures depends primarily on the architecture of the surfactant molecule⁴, the concentration of the surfactant molecule⁵ (should be above CMC) as well as on the solution environment that includes the solvent properties, temperature, pressure,

external force fields (e.g. shear) and the presence of interacting species and their concentrations ⁶.

In dilute solutions of surfactants the architecture of the surfactant molecule governs the packing of the surfactant molecules in the micellar structure. Based on the surfactant packing parameter, $P \approx V/a_0 \times l_c$ (where 'V' is the volume occupied by the hydrocarbon tail, 'a₀' is the area occupied by the head group and 'l_c' is the length of the hydrocarbon tail), surfactant molecules aggregate differently to produce efficient packing (Figure 1) ³. As the concentration increases entropic factors also start playing a role other than the energetic factors (packing considerations). At high concentrations of surfactant both the entropic and enthalpic factors decides the final morphology of the micellar structure. The best example of this is the aqueous solution of a cationic surfactant cetyl trimethyl ammonium bromide (CTAB) ⁷. The micellar structure evolves from globular micelles, at low concentration of CTAB in water, to worm-like micelles to hexagonal liquid crystals to cubic phases to lamellar structures with the increase in surfactant concentration (Figure 2).

The presence of an additional surface active agent (surfactant, cosurfactant, hydrotope etc.) imparts an additional degree of complexity in surfactant systems. Mixed amphiphile systems (including surfactant-surfactant, surfactant-cosurfactant, surfactant-hydrotope etc.) are fascinating from a scientific standpoint because of the complex way they associate into supramolecular, nanoscale and self assembled structures. They are technically important because they provide an additional

compositional degree of freedom which tailors microdomain properties just by simple variation in composition. This dissertation investigates various characterization techniques to characterize microstructures in mixed surfactant systems.

Microstructure Analysis in Surfactant Systems

Currently surfactant self assembly has become an extensively used technique to develop materials with nanometer dimensions, reticulated structures, and varied morphologies most typically through some form of templating effects. The templating effect offered by the surfactant aggregates has been a proven tool for material synthesis⁸. Mesoporous zeolites⁹, porous polymers¹⁰, biomimetic ceramics¹¹ and a range of other inorganic structures with different architecture can be synthesized within these templated systems¹². The various classes for templating have been classified as synergistic, transcriptive and reconstructive^{13,14}.

The detailed understanding of the underlying microstructure in surfactant solutions and their relation to the macroscopic properties is of utmost importance for using them as templates for guiding nanomaterial synthesis as well as for their scientific and industrial applications. There are two groups of techniques popular in the research world for characterizing microstructures in surfactant systems. One group of techniques is known as indirect imaging techniques and the other direct imaging techniques.

Indirect Imaging

Various scattering and spectroscopy techniques like light, X-ray and neutron scattering, NMR spectroscopy, fluorescence quenching, flow birefringence, and rheological techniques have been used very efficiently to uncover microstructures in surfactant systems¹⁵⁻²¹. However, most of these techniques require predetermined models for data interpretation and thus the structural information provided is model dependent and the interpretation of the experimental data is not unique to the microstructure^{22,23}. The most popular and most commonly used are the scattering techniques. Small Angle Neutron Scattering (SANS) has been emerged as the potential imaging technique to analyze the length scales (few angstroms to several nanometers) involved with the surfactant microstructures.

A scattering technique involves the generation of the scattering data for a given sample irradiated by a certain radiation (light, x-ray or neutron). The scattering data is then processed and fitted to various theoretically-known scattering models of common structures. The best fit gives the best possible understanding of the microstructure. The approach requires the knowledge of predetermined models and thus the structural information provided is model dependent and most importantly not unique to the real microstructure (as various predetermined model may fit the experimental scattering data very closely). Additionally the information provided is averaged over all sample volumes therefore microstructural defects are invisible and it becomes extremely difficult to study complex coexisting microstructures of different shape and size. Despite all that, SANS has been used widely to uncover microstructures in surfactant

systems through out the research community. The relatively easy sample preparation method which avoids any kinds of artifacts (shearing of the microstructure, concentration changes etc.) associated with other popular techniques and the unique ability of looking, selectively, at various parts of the samples using contrast variation are the two most important reasons behind the popularity of SANS among researchers all around the research community.^{24, 25} Contrast variation in SANS is achieved by selectively replacing a hydrogen atom (low scattering power) with a deuterium atom (high scattering power), also known as isotopic labeling, at various parts of the sample.

Direct Imaging

As the name suggests it obviously avoids the model dependent approach used in the indirect imaging techniques as the microstructures can be seen directly. However, the sample preparation is difficult and the presence of artifacts is a major issue.

But, once these experimental difficulties are resolved, the information presents the microstructure and all its manifestations in the most direct (real space with least interpretation) and easily accessible way possible.

Electron microscopy, due to the length scales involved with surfactant aggregates, has been used widely to directly visualize the microstructures in surfactant systems. As the surfactant solutions are mostly liquid, they can not sustain the high vacuum of the electron microscope because of evaporation. To overcome the high vacuum of the electron microscope and to arrest the supra molecular motion, the liquid sample is

vitrified (rapid cooling to avoid crystal formation) to very low temperatures (close to $-170\text{ }^{\circ}\text{C}$) and maintained at that temperature during imaging²⁶.

The most popular and well established direct imaging technique, undoubtedly, is the Cryogenic Transmission Electron Microscopy (Cryo-TEM) technique²⁶. The technique involves the preparation of a thin film of the sample on the specially prepared perforated TEM grid²⁶. The objective of a thin film is to ensure the fast freezing of the sample during the vitrification process and also to provide enough transmission of electrons during imaging but not thin enough to influence the microstructure due to confinement. For high cooling rates, film thickness of 200 nm is the optimum²⁷. The thinning of the sample is done by putting a drop of sample on the TEM grid and then the excess sample is removed using a blotting paper. Blotting ensures the formation of thin liquid film (100 nm thick, due to the surface tension) over the grid holes. The sample containing grid is then plunged into a liquid ethane bath, slush cooled by liquid nitrogen, for vitrification of the sample film. The vitrified sample containing grid is then stored under liquid nitrogen and imaged at $-170\text{ }^{\circ}\text{C}$ and under the high vacuum of the electron microscope. The process of blotting the excess sample works very well with the low viscosity systems but fails miserably for high viscosity systems²⁸. Blotting also impacts the original microstructure due to inevitable concentration change during blotting (the amount of solvent and the dispersed phase absorbed by the blotting paper are not the same). Size segregation and shearing of internal microstructure during the blotting process also impact the original microstructure²⁹. Direct contact with the cryogen, for rapid freezing, in Cryo-TEM is

also not favorable for organic rich samples as the liquid cryogen, ethane, is known to dissolve the organics in the sample and thus impact the microstructure²⁶.

A Freeze Fracture Direct Imaging (FFDI) technique has been developed and demonstrated as a complimentary technique to Cryo-TEM for imaging highly viscous and organic rich samples. The first chapter of this dissertation demonstrates the successful use of FFDI in obtaining direct images of a highly viscous mixed surfactant system which is not at all possible with Cryo-TEM. The FFDI technique also involves the thinning of the sample on the perforated TEM grid but in this case the thinning process is done by physical squeezing of the sample on the perforated TEM grid between two copper planchettes (a modified version of well known sandwich method)^{30,31}. This avoids the above mentioned artifacts caused by the blotting process. The sandwich assembly (sample grid enclosed in copper planchettes) is then brought into direct contact with liquid cryogen (ethane) for rapid freezing (therefore avoids the dissolution of organics from the sample) and dismantled by pulling apart the copper planchettes (helps in further thinning of the sample by fracturing the sample between the copper planchette and the TEM grid) under liquid cryogen. The TEM grid, with fractured sample, is then recovered and stored under liquid nitrogen for direct visualization using TEM.

Mixed Surfactant Systems Used in This Study

AOT + Lecithin Surfactant System

The first system used in this study is the quaternary system comprised of water, isooctane, an anionic surfactant, 2 ethylhexyl sodium sulfosuccinate (AOT) and a zwitterionic surfactant, phosphatidylcholine (lecithin). As water is added incrementally to a 0.82M solution of AOT and 0.4M solution of lecithin in isooctane, the microstructure evolves from a water-in-oil microemulsion to a bicontinuous gel phase. The viscosity increases rapidly by six orders of magnitude and a rigid gel forms at a sharply defined water/surfactant (AOT) mole ratio (W_0) as illustrated in Figure 3.³² The electrical conductivity also increases with the increase in water content indicating the presence of a percolation threshold at the critical water content ($W_0 \sim 50$ in this case).³² Beyond this critical water content the gel phase can be considered a bicontinuous system where both oil and water nano channels are separated by the surfactant layer at the interface. The high viscosity of the gel phase makes these nano channels spatially immobilized. The gel mesophase has approximately equal volume fractions of the aqueous and organic phases and it can sustain up to 70% (by volume) water without phase separation. Previous SANS results show that the gel phase consists of highly ordered aqueous and organic nanochannels. Depending upon the composition and temperature, these ordered phases display either hexagonal or lamellar symmetries (Figure 4)³³.

Direct evidence of the gel microstructure would complement the previous SANS experimental results and provide a better understanding of the gel microstructure. The

first manuscript of this dissertation reports the direct imaging results of the gel microstructure. A new visualization technique, called Freeze Fracture Direct Imaging (FFDI), suitable for artifact-free transmission electron microscopy of highly viscous soft colloidal materials, has been adapted and used to image the hexagonal and lamellar microstructures of the gel phase. FFDI shows that the structures at high water content are multilamellar vesicles, and not planar sheets. SANS could not differentiate between planar lamellar sheets and multilamellar vesicular structure. It has been shown that the Freeze fracture direct imaging technique expands the range of cryo-transmission microscopy to highly viscous, high organic content systems that typically have been difficult to visualize.

In the second manuscript of this dissertation shear behavior of these highly viscous gel systems is reported. SANS has been used to analyze the changes in the gel microstructure during the shear. It is realized that the application of shear orients the aqueous cylinders in the hexagonal phase in the direction of flow and reduces the inter-cylinder spacing. The lamellar polycrystalline phase, on the other hand, is unperturbed and does not show any preferential alignment after application of shear. This confirms that the lamellar crystalline phase consists of multilamellar vesicles and not planar lamellar sheets. Shearing the mixed phase (hexagonal + lamellar) reveals that the hexagonal component aligns with the direction of flow while the lamellar portion remains unaffected. On the other hand, when an aligned hexagonal phase is heated past the hexagonal to lamellar phase transition temperature, the aqueous cylinders merge in the $(1, 0)$ direction to form planar sheets parallel to the walls of the

Couette cell. This planar lamellar microstructure differs from the multi-lamellar vesicles observed more typically at this composition and temperature and is likely to be a non-equilibrium structure, kinetically trapped because of the high viscosity of the gel.

CTAB + Organic Dopant System

The third manuscript of this dissertation discusses the effects of non ionic organic dopants on the structure of cationic micelles of CTAB in water. The micelle formation in an aqueous solution of surfactant is known to be affected by the presence of organic additives.^{34, 35} A series of organic dopants (phenol, cresol, 4-ethyl phenol and 4-sec-butyl phenol) has been used for this study. Cryo-TEM has been used to map the transformation of CTAB micelles to vesicles and tubules as a range of phenolic derivatives are doped into the system. The addition of hydrotopes as well as more insoluble dopants to micelles to drive structural transitions represents an interesting approach to controlling functionality in complex fluids.

As the concentration ($M = \text{moles of dopant} / \text{moles of CTAB}$) of each of the dopants is increased in 50mM aqueous solution of CTAB, there is a systematic reduction in the curvature of the observed microstructures. For phenol and cresol the microstructure changes from globular micelles to rod-like micelles with low amounts of dopant concentration and at higher concentration of dopant the microstructure changes to long worm-like micelles. For 4-ethyl phenol and 4-butyl phenol, the microstructure transforms from globular micelles to worm-like micelles at lower concentrations of

dopant and to unilamellar vesicles and then bilamellar vesicles at higher dopant loading. The concentrations at which these morphological transitions take place reduce as the number of methyl substitutions on the phenolic ring is increased. These microstructure transitions are attributed to changes in the packing parameter of the surfactant complex as dopants penetrate to different degrees in the surfactant interfacial layer, resulting from a balance of interaction between the surfactant tails and the dopant aromatic chain and the hydrogen bonding of the hydroxyl group with surrounding water. The alignment of the hydroxyl dipoles reduces the electrostatic field around the CTAB head groups, decreases interlayer repulsive interactions and allows membrane fluctuations to stabilize the bilayered vesicles.

Summary

The detailed understanding of the microstructures, in surfactant systems, and its responses to external fields is utmost important for using these surfactant systems for templated nanostructured materials synthesis. The AOT/Lecithin/Water/ Isooctane gel system provides an excellent template for nanocomposites that combine material synthesis in spatially immobilized aqueous and organic nanodomains simultaneously. Doping with a polar organic additive offers a method of controlling shape and size of CTAB micelles. These micelles can then be used in the templated synthesis of mesoporous materials.^{36, 37} Altering the structure of the micellar system that serves as a template for the synthesis of mesoporous materials may provide an easy route to tailor the structure and properties of the mesoporous materials.

Figure captions

Figure 1 Chart illustrating the formation of various micelle morphologies corresponding to different packing parameters (from reference # 3).

Figure 2 Phase diagram of aqueous solutions of CTAB (from reference # 7).

Figure 3 Plot of viscosity and electrical conductivity, of the mixed surfactant system formed by 0.85 M AOT and 0.42 M lecithin in isooctane plus water, as the function of water content (W_0 , moles of water per unit moles of AOT) (from reference # 32).

Figure 4 Phase diagram for the mixed surfactant system, formed by 0.85 M AOT and 0.42 M lecithin in isooctane plus water, obtained from SANS measurements (from reference # 33).

Lipid	Critical packing parameter $v/a_0 l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: <i>SDS in low salt</i>	$< 1/3$	Cone	Spherical micelles
Single-chained lipids with small head-group areas: <i>SDS and CTAB in high salt, nonionic lipids</i>	$1/3-1/2$	Truncated cone	Cylindrical micelles
Double-chained lipids with large head-group areas, fluid chains: <i>Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG^a, dihexadecyl phosphate, dialkyl dimethyl ammonium salts</i>	$1/2-1$	Truncated cone	Flexible bilayers, vesicles
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: <i>phosphatidyl ethanolamine, phosphatidyl serine + Ca²⁺</i>	~ 1	Cylinder	Planar bilayers
Double-chained lipids with small head-group areas, nonionic lipids, poly (c/s) unsaturated chains, high T: <i>unsat. phosphatidyl ethanolamine, cardiolipin + Ca²⁺, phosphatidic acid + Ca²⁺, cholesterol, MGDG^b</i>	> 1	Inverted truncated cone or wedge	Inverted micelles

^aDGDC, digalactosyl diglyceride, diglucosyl diglyceride.

Figure 1 Chart illustrating the formation of various micelle morphologies corresponding to different packing parameters (from reference # 3).

Figure 2 Phase diagram of aqueous solutions of CTAB (from reference # 7).

Figure 3 Plot of viscosity and electrical conductivity, of the mixed surfactant system formed by 0.85 M AOT and 0.42 M lecithin in isooctane plus water, as the function of water content (W_0 , moles of water per unit moles of AOT) (from reference # 32).

Figure 4 Phase diagram for the mixed surfactant system, formed by 0.85 M AOT and 0.42 M lecithin in isooctane plus water, obtained from SANS measurements (from reference # 33).

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MANUSCRIPT I

Freeze Fracture Direct Imaging of a Viscous Surfactant Mesophase

I.1 Introduction

Above the critical micellization concentration (CMC) surfactant molecules self assemble into a variety of structures when dispersed in solvents. On the basis of the surfactant concentration¹, salinity² or temperature³, these structures vary as spherical or spheroidal micelles⁴, elongated rodlike⁵ or threadlike micelles⁶, ribbons⁷, discs^{8,9}, vesicles¹⁰ and ordered liquid crystalline phases¹¹.

Many experimental techniques have been used to study microstructures in colloidal systems, including self-diffusion NMR,¹² fluorescence,¹³ and scattering techniques such as small-angle neutron scattering (SANS),^{14,15} small-angle X-ray scattering (SAXS),¹⁶ and light scattering (static and dynamic).^{17,18} All these techniques come under the category of indirect imaging because the information on the aggregate size, shape and interaggregate interactions can only be interpreted using predetermined models. The information, averaged over the sample volume, thus makes data interpretation complex in the case of the coexistence of structures of different sizes or topologies.

Direct information about aggregate morphology in microstructured fluids can be obtained from light and transmission electron microscopy (TEM), so long as the objects of interest are in the applicable size range. In particular, direct imaging

cryogenic TEM (Cryo-TEM)^{19,20} and freeze fracture replication TEM (FFTEM)²¹ have emerged as artifact-free methods for observing diverse systems such as surfactant aggregates, polymer and polymer-surfactant solutions, and microemulsions, as well as biological and biomedical systems. These methods provide the ability to preserve microstructures by rapid vitrification of the solution containing the aggregates. In cryo-TEM, this is accomplished by forming a thin film of the sample on a specially prepared electron microscope grid. Plunging into a cryogen then vitrifies the sample. The vitrified sample is transferred to a cold stage without exposure to the environment and maintained at a temperature well below the amorphous-to-crystalline phase transition temperature of the solvent phase during the imaging. In FFTEM, a sample is sandwiched between conducting metal planchettes and then vitrified by contact with a cryogenic liquid. Peeling apart the planchettes cleaves the sample along a fracture plane. A metal replica of the fractured surface is obtained by vapor deposition of heavy metal and carbon on the fractured surface. The sample is then melted away to recover the replica. Properly washed and dried metal replica, morphology of which is controlled by the sample's microstructure, is then viewed using TEM at room temperature.²²

Most of the cryo-TEM work reported to date has involved water rich, especially water-continuous, systems. The basic technique²² involves blotting of the excess sample from the TEM grid, thus limiting its use to low-viscosity systems only. For organic-rich samples, the process of vitrification, typically achieved by plunging the sample containing the grid into liquid ethane at its freezing point, is complicated by

some solvent dissolution even at these very low temperatures.²³ This shortcoming can be overcome by using liquid nitrogen as a cryogen but to achieve vitrification at the concomitant low cooling rates, a cryo-protectant, which may perturb the original microstructure of the system, is often needed.²⁴ Additionally, at atmospheric pressure, the difference in melting point (-210 °C) and boiling point (-196 °C) of nitrogen is only 14°C. Any vapor films that forms at the sample-cryogen interface as a result of heat transfer from the sample will attenuate the cooling rate and prevent vitrification of the internal regions in the sample. The FFTEM method overcomes some of these limitations by protecting the sample from direct contact with the cryogen and by controlling the sample thickness by squeezing between the copper planchettes. The main disadvantage is that the replication process is tedious, and the replicas only provide information about surface topology in the fracture planes. In addition, the resolution of this method is limited by the grain size in the replica. In this manuscript a newly developed technique known as freeze fracture direct imaging (FFDI), originally conceptualized by Belkoura et. al.²⁵, has been used to image a highly viscous and organic rich mixture formed by an anionic surfactant bis(2-ethylhexyl) sodium sulfosuccinate (AOT), a zwitterionic surfactant phosphatidylcholine (lecithin), isooctane and water²⁶. This technique involves sample thinning, vitrification and fracturing followed by direct observation in a TEM, and therefore is a hybrid of the cryo-TEM and the FFTEM methods.

I.2 Materials and Methods

I.2.1 Chemicals and Materials

Phosphatidycholine (Lecithin, 95% purity) was purchased from Avanti Polar Lipids and stored at -20°C , and (AOT) and 2, 2, 4-trimethylpentane (isooctane, 99% purity) were purchased from Sigma Chemical Company. All the chemicals were used without any further treatment or purification. Copper planchettes (4.5mm, 3mm, and 0.1mm) were purchased from BAL-TEC and coated with a thin film of carbon. Microscope grids (600 hexagonal mesh) were purchased from Electron Microscopy Sciences.

Samples were prepared by gradually adding water to a clear solution of 0.8M AOT and 0.4M lecithin in isooctane. Vortex mixing and sonication accompanied each incremental water addition, until the solution became homogeneous and clear. Five samples with different water content ($W_0 = 30, 70, 130, 170, 200$; $W_0 = \text{mol water/mol AOT}$) were prepared.

I.2.2 Freeze Fracture Direct Imaging (FFDI)

Vitrified specimens are prepared in a manner delineated in Figure I.1. Approximately 1 μl of the sample is placed on a flat surface of a carbon coated copper planchette. A perforated TEM-grid (mesh size 600) is then placed on top of the sample. A second planchette (flat surface down) is placed on the grid to make a sandwich. The assembly is then squeezed using a tweezer, reducing the sample thickness and causing some of the sample to flow into unfilled regions on the grid. The sandwich assembly is then plunged into liquid ethane for vitrification of the sample film inside the assembly. The

copper planchettes are then taken apart, while in liquid ethane, causing the sample to get cleaved along a fracture plane on the grid. The grid is then recovered, and excess ethane blotted. The vitrified sample is then transferred into a liquid nitrogen cooled TEM holder using a cryo-transfer stage (Oxford Instruments CT-3500), designed for minimal air exposure and heat loss. The samples were observed on a JEOL 1200EX S/TEM, coupled with the TVIPS® F-224 slow-scan CCD (2048×2048 resolution) camera, with an accelerating voltage of 100 kV at about -170 °C and at an underfocus of 2-4 µm for phase contrast enhancement. Each sample was imaged repeatedly three to four times and over more than 50 images per sample was collected for the detailed analysis.

I.3 Results and Discussions

A control sample was first imaged using FFDI and compared with the cryo-TEM image to test the cooling rates in the freezing step used for the FFDI technique. The sample is comprised of a mixture of two surfactants, cetyl trimethyl ammonium bromide (CTAB) (64 mM) and dodecyl benzene sulfonic acid (HDBS) (36 mM), in water. This system is known to form vesicles in the size range of 30-200 nm.²⁷ A comparison is shown in Figure I.2. Images taken using the FFDI technique show vesicles that look similar to that shown by cryo-TEM, and help establish the efficacy of the freezing process. Additional diffraction experiments with water in the sandwich layer confirm that the water layer is indeed vitrified in the FFDI process.

The surfactant system formed by AOT/lecithin/isooctane and water has been characterized extensively using SANS. At low water contents ($W_0 < 50$, where $W_0 = \text{mol water/mol AOT}$) and 25°C, a water-in-oil microemulsion is formed, with the water droplets stabilized in the continuous organic phase by a surfactant interfacial layer. As the water content is increased to $W_0 > 50$, these droplets grow and coalesce to form a bicontinuous system, with a low-shear viscosity of the order of 10^5 poise at 25°C. SANS data reveal that the water channels are arranged in a polycrystalline hexagonal array. Further increase in water content or temperature transforms the hexagonal phase to a lamellar phase. At intermediate temperatures and water contents, both phases coexist, as illustrated in Figure I.3. The high viscosity gel phase remains intact for water contents as large as $W_0 = 250$. This surfactant system is so viscous and rich in the organic component that our attempts to directly image this using cryo-TEM have not succeeded. The key bottlenecks are the blotting of the very viscous sample to an acceptable thickness on the grid, and the presence of a large amount of isooctane that comes into direct contact with the liquid ethane cryogen.

An FFDI image of a microemulsion phase, shown in Figure I.4, clearly shows the presence of droplets. Because this microemulsion phase is very close to the gel formation threshold, some clusters of droplets are also visible. We speculate that these clusters come together and eventually form the aqueous channels.

Figure I.5 is an FFDI image of a $W_0=70$ sample and clearly show striations. These striations are flexible aqueous cylinders packed in hexagonal array and observed

normal to the cylinder axes. The spacing between the (1 0) plane from FFDI ($\sim 10 \pm 2.1$ nm) matches well with the previous small angle neutron scattering (SANS $\sim 12 \pm 0.4$ nm) results²⁶. FFDI images of the $W_0=130$ sample are shown in Figure I.6. The (1 0) plane spacing from FFDI ($\sim 9 \pm 2.7$ nm) doesn't quite match with the previous SANS ($\sim 18 \pm 0.5$ nm) results²⁶. This could be attributed to the oblique view of the microstructure during FFDI visualization. Cylinders with their axes arranged parallel to as well as normal to the plane of the grid are seen. This image provides direct evidence of the columnar hexagonal arrangement of these water cylinders. With the use of SANS, both these samples were interpreted as having a columnar hexagonal microstructure. FFDI has been successful in capturing direct images of these microstructures and confirm the SANS results.

An FFDI image of the $W_0=170$ sample, shown in Figure I.7a reveals the presence of a multi-lamellar vesicle, or onion-like structure (Figure I.7b). None of the onion-like structures observed showed noncircular morphologies, implying that these are likely not rolled cylinders. This is also consistent with our SANS observations that shearing of the $W_0=170$ sample did not produce any alignment.²⁸ Due to the probe length scale (several angstroms to few nanometers) involved with the SANS technique, it cannot see the overall curvature (few hundreds of nm) of the multilamellar wall of an onionlike structure and gives the similar results as in a case of a planar lamellar structure. This is further justified by the exact matching of the FFDI ($\sim 17 \pm 1.6$ nm) lamellar plane spacing with the previous SANS ($\sim 16.98 \pm 0.5$ nm) results²⁶. Direct imaging using FFDI reveals this important distinction between the structures. An

FFTEM image (Figure I.7c), showing large spherical structure in $W_0=170$ gel system, is also reported here to compliment the FFDI results. Similar multilamellar vesicles were found in the samples containing a water content of $W_0=200$. This is shown in Figure I.8.

Polarized light microscopy has been used to confirm the presence of these vesicles. The telltale signature of an object with molecules whose optic axes are placed with spherical symmetry, such as multi-lamellar vesicles, are the Maltese crosses (Figure I.9)²⁹, which provide additional confirmation for the presence of onionlike structures at these water contents.

While onion-like structures have been observed at these water contents and at 25°C, such morphology need not be pervasive over the entire temperature-composition space where a lamellar structure has been observed using SANS. The examination of microstructures over a wider temperature range using FFDI remains a future goal of our research.

I.4 Conclusions

FFDI is a modified specimen preparation technique, combining cryo-TEM and freeze fracture replication techniques, especially suitable for highly viscous or organic rich samples. FFDI was used to image the microstructures formed in the ternary system formed by AOT/lecithin/Isooctane, and water. Microemulsion droplets are observed at low water contents. As the water content is increased, a hexagonal phase is observed.

At high water contents, these direct images show the presence of multilamellar vesicles and not planar sheet-like lamellar structures. This direct image provides a simple way to resolve the microstructure beyond the previously obtained SANS data.

Figure Captions

Figure I.1. Schematic of FFDI sample preparation method (a) sample is placed on copper planchette (b) TEM grid is placed on the sample (c) a second planchette is used to squeeze the sample (d) the sandwich assembly is plunged into liquid ethane (e) the planchettes are peeled off in liquid ethane, cleaving the sample along fracture planes. (f) Relative sizes of planchettes and grids.

Figure I.2. Control sample containing CTAB/HDBS vesicles: (a) cryo-TEM image, (b) FFDI image. The scale bar is 100 nm.

Figure I.3. Phase diagram for 0.85M AOT and 0.42M lecithin in isooctane plus water system obtained from SANS measurements.

Figure I.4. (a) FFDI image of a microemulsion phase ($W_0=30$) showing water droplets (light gray regions), (b) illustration of the microstructure. The scale bar is 100 nm.

Figure I.5. (a) FFDI image of a gel phase ($W_0=70$) showing striated water cylinders (light gray regions). (b) Illustration of the microstructure and the perspective of the observation. The scale bar is 100 nm.

Figure I.6. (a) FFDI image of a gel phase ($W_0=130$) showing striated water cylinders (light gray regions) and an inset illustrating the microstructure and the perspective of observation. (b) FFDI image of a gel phase showing hexagonally arranged water cylinders (light gray regions). The inset illustrates the perspective of the observation. The scale bar is 100 nm.

Figure I.7. (a) FFDI image of a gel phase ($W_0=170$) showing onionlike structures, (b) illustration of the microstructure, (c) FFTEM image showing large spherical structures. The scale bar is 100 nm.

Figure I.8. (a) FFDI image of a gel phase ($W_0=200$) showing multilamellar vesicles. The inset illustrates the microstructure. The scale bar is 100 nm.

Figure I.9. $W_0=200$ sample viewed through cross polarizers. The arrows show the Maltese crosses.

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(a)

(b)

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(a)

(b)

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(a)

(b)

Figure I.5. (a) FFDI image of a gel phase ($W_0=70$) showing striated water cylinders(light gray regions). (b) Illustration of the microstructure and the perspective of the observation. The scale bar is 100 nm.

(a)

(b)

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(a)

(b)

(c)

Figure I.7. (a) FFDI image of a gel phase ($W_0=170$) showing onionlike structures, (b) illustration of the microstructure, (c) FFTEM image showing large spherical structures. The scale bar is 100 nm.

Figure I.8. (a) FFDI image of a gel phase ($W_0=200$) showing multilamellar vesicles. The inset illustrates the microstructure. The scale bar is 100 nm.

Figure I.9. $W_0=200$ sample viewed through cross polarizers. The arrows show the Maltese crosses.

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Manuscript II

Shear-Response of a Coexisting Lamellar/Hexagonal Surfactant Mesophase

II.1 Introduction

Shear induces a wide variety of structural transformations in complex fluids. Shear flow can shift phase boundaries¹, deform microstructures and induce the formation of entirely new shear-induced structures (SIS)²⁻⁵. Shear can also induce, breakup, or change the symmetry of crystalline order⁶⁻⁸. Well known shear-influenced phenomena include micellar growth^{9,10}, shear induced melting^{11,12}, shear induced ordering, phase segregation and liquid-crystal transitions¹³⁻¹⁶.

Surfactant systems commonly form lyotropic liquid crystalline mesophases of different microstructure. On a macroscopic length scale these microstructures are usually not uniformly aligned, and a polydomain structure is present^{12,17,18}. Shear is known to have a strong effect on the orientation and the structure of liquid crystalline phases⁷. Shear studies on cubic phases,^{19,20} hexagonally packed rod like micelles^{18,21} and lyotropic lamellar phases^{22,23} in liquid crystalline solutions of stiff macromolecules and block copolymer melts²⁴ have shown shear induced alignment and variety of responses involving phase transitions from isotropic to ordered²⁵, ordered to isotropic²⁶ and ordered to ordered²⁷ as well as formation of entirely new structures such as multilayer vesicles (MLVs) by shearing a lamellar phase^{23,28-31}. Many experimental techniques such as flow birefringence^{32,33}, optical and electron microscopy^{34,35}, X-ray scattering¹², small angle light and neutron scattering^{22,36}, and

nuclear magnetic resonance (NMR)^{37,38} have been developed to monitor these changes.

In this manuscript results are reported of small angle neutron scattering experiments performed in a Couette flow cell on a highly viscous surfactant system consisting of bis(2-ethylhexyl) sodium sulfosuccinate (AOT), phosphatidylcholine (lecithin), 2,2,4-trimethylpentane (isooctane), and water^{39,40}. The combination of the anionic surfactant AOT, which forms reverse micelles in non-polar solvents, and a zwitterionic surfactant lecithin, which tends to form bilayers in non polar solvent, leads to a highly rigid gel that shows a variety of microstructural arrangements as the water content or the temperature of the system is varied. The gel mesophase has a hexagonal columnar structure (H_{II}) at W_0 (moles water/ moles AOT) values of 50-100 at 25 °C. As the water content is increased further, both the columnar hexagonal and lamellar (L_α) phases coexist. At $W_0 = 170$ and above a lamellar phase is produced. The transition from hexagonal to lamellar microstructures also occurs as the temperature is increased with the lower temperatures favoring the hexagonal phase (Figure II.1). Small Angle Neutron Scattering (SANS) has been used to monitor changes in microstructure alignment when each of these phases is subjected to steady shear. Novel results from shearing of the H_{II} phase as well as examining the impact of shear on the mixed hexagonal/lamellar phase are reported.

II.2 Experimental Details

II.2.1 Chemicals

The samples are composed of a quaternary mixture of; 2, 2, 4 –trimethylpentane (isooctane), bis (2-ethylhexyl) sodium sulfosuccinate (AOT), phosphatidycholine (lecithin) and deuterium oxide. Isooctane and AOT were purchased from Sigma Aldrich, Lecithin (95% pure) was purchased from Avanti Polar Lipids and deuterium oxide was purchased from Cambridge Isotopes Laboratory. All chemicals were used without further treatment or purification.

II.2.2 Sample Preparation

A solution containing 0.85 M AOT and 0.42 M of lecithin in isooctane is prepared. D₂O is added to this solution until the desired W_0 value ($W_0 = 70, 90$ and 170 for these experiments) is reached. The sample is then sonicated in a warm water bath ($\sim 38^\circ\text{C}$) and vortexed until a clear yellow solution/gel is obtained. The samples are removed from the water bath, centrifuged at 1000 RCF (Relative Centrifugal Force) to remove air bubbles, and allowed to cool to ambient conditions. The zero shear viscosity of each of the sample is in the range of 10^5 - 10^6 Pa.s⁴¹

II.2.3 Experimental Procedure

SANS experiments were performed on the 30 m NG3 beam line at the Center for Neutron Research, National Institute of Standards and Technology (Gaithersburg, MD). The SANS intensity, $I(q)$, was recorded on a two dimensional detector as a

function of the magnitude of the scattering vector q ($q = 4\pi \sin(\theta/2)/\lambda$ where θ is the scattering angle and λ the neutron wavelength = $6 \pm 0.9 \text{ \AA}$). The detector angle was set to 0° and the sample-to-detector distance was set to 4.5 m. The beam diameter was set at 1.27 cm. For this experimental setup, the range of the scattering vector q was 0.0057 to $0.1039 \text{ \AA}^{-1}$.

The NIST SANS Couette-type shear cell⁴² consists of an inner quartz cylindrical stator (O.D. = 60mm) and an outer quartz cylindrical rotor (I.D. = 61mm). Approximately 11 ml of bubble-free sample was placed in the outer cup and the inner stator was lowered. This method gently shears the sample in a directional orthogonal to the actual experiments. The high viscosity of our samples precludes the relaxation of this effect prior to the outer cup being rotated. The stator was lowered slowly ($\sim 0.1 \text{ cm/min}$) to minimize this effect. The shear rates were varied from 0 s^{-1} to 116.7 s^{-1} . The maximum strain rate was limited by the onset of 'tearing' in the gel. At every strain rate, the samples were sheared for 90 sec, before any SANS data acquisition. Separate Couette flow experiments where the sample viscosity was monitored upon an abrupt change of shear rate showed that the viscosity relaxed to a steady value within a few seconds⁴³. The samples were also allowed to equilibrate at each temperature for 15 minutes before the SANS data were acquired.

Two beam configurations were used - the radial direction, which explores the velocity-vorticity plane, and the tangential direction, which explores the velocity gradient-vorticity plane (Figure II.2). Data were corrected for empty cell scattering, detector

sensitivity, background, and the transmission of each sample, and were then placed on an absolute scale.

II.3 Results and Discussions

Our previous analysis of the shear behavior of the hexagonal phase of the mixed surfactant system showed preferential alignment of hexagonally packed cylinders along the flow direction⁴³. Figure II.3 (a) reveals that as the strain rate increases, the anisotropy determined by the spot intensity increases. The anisotropy is quantified by plotting intensity (I) versus the scattering vector (q) scan along the two perpendicular directions, as shown by the arrows in Figure II.3 (a). The scan along the vertical direction, shown in Figure II.3B, reveals the increase in alignment of the cylinders along the flow direction with an increase in shear rate. The value of q for the primary peak displayed by the hexagonal phase shifts upward from $q = 0.040 \pm 0.002 \text{ \AA}^{-1}$ to $q = 0.046 \pm 0.004 \text{ \AA}^{-1}$, indicating a closer packing of the cylinders, from (1,0) plane spacing of $15.7 \pm 0.16 \text{ nm}$ to $13.6 \pm 0.23 \text{ nm}$, because of shear. The change in the packing length scales could be explained by the formation of larger crystals ($88 \pm 6.5 \text{ nm}$) with less surface activity than smaller crystals ($56 \pm 3.6 \text{ nm}$) and large surface activity. The crystal size was obtained by analyzing the full width at half maximum, and using the Scherer's equation, of the scattering peaks before and after shear. The scan along the horizontal direction, shown in figure 3C, shows no change in intensity except for that caused during sample loading. In both the cases the aligned phase has closer packing of cylinders with an intensity maximum at higher q, than the unaligned phase.

The lamellar phase, on the other hand, does not respond to strain rates as high as 389 Hz (Figure II.4A), consistent with our findings from freeze fracture direct imaging that these are multi-lamellar vesicles (Figure II.4B) instead of planar lamellar sheets⁴⁴. We do not see any alignment of lamellar phase even at strain amplitude of 3.89, much smaller than the critical strain amplitude of 20 which is required for a transition from planar lamellar to multilamellar vesicles 'onions' in a sample of low viscosity²⁸. A high viscosity system would require much larger strain amplitude for the lamellar to onion transition than a low viscosity system. It indicates that the multilamellar vesicle structure is the original microstructure in this case rather than a consequence of shearing a planar lamellar phase.

The $W_0=90$ sample, chosen for this study, is hexagonal at 25 °C. Between 55 °C and 75 °C both the hexagonal and lamellar phases coexist. (Figure II.5) ³⁹. At 57 °C, the scattering pattern in the tangential direction prior to shear consists of two distinct diffuse rings (Figure II.6A). The isotropic rings are indicative of a polycrystalline structure in the sample. The outer ring corresponds to the lamellar phase while the inner ring corresponds to the hexagonal phase*. As this system is sheared and then allowed to relax, the characteristic 6-spot pattern is generated in the hexagonal region with no effect of shear on the lamellar ring (Figure II.6 B). When this phase is heated to 70 °C, a single ring develops with distinct spots at 0 and 180, indicative of an aligned lamellar phase (Figure II.6 C). As there is no shearing involved in this process we can also quantify the results in tangential geometry data. The data clearly show the

increase in the intensity of the spots in the lamellar ring with the increase in temperature (Figure II.6 D). The (1, 0) planes in the hexagonal structure merge to form the planar lamellar sheets that are parallel to the cell walls, as illustrated in Figure II.7.

The microstructure of the aligned lamellar phase produced by heating the shear-aligned hexagonal phase is different from that produced by incrementally adding water, vortex mixing, and then increasing the temperature to 57°C. The former produces plane lamellar sheets while the latter results in multi-lamellar vesicles. The planar phase is likely a non-equilibrium structure, trapped kinetically because of the high viscosity.

II.4 Conclusions

A four-component gel system formed by AOT, lecithin, isooctane and water shows a very unique behavior under shear. The hexagonal microdomains of this gel get aligned with shear. On the other hand the lamellar microdomains do not show any alignment under shear because the original structure is multi-lamellar vesicles rather than planar lamellar sheets. An aligned lamellar micro phase, consisting parallel sheets, in this gel system can be obtained by heating an aligned hexagonal microphase. The positive response of the gel microstructure to the shear and the retention of the alignment after removal of the shear make this gel system a potential candidate for nanostructured material synthesis.

Figure Captions

Figure II.1 Phase behavior of the 0.82M AOT/0.4M lecithin/isooctane/water system determined by SANS. (H) represents hexagonal microstructure, (L) represents lamellar microstructure (●) represents the microstructures examined in this study.

Figure II.2 (a) The Couette shear cell geometry; the outer cylinder rotates. (b) The planes examined in the radial and tangential directions.

Figure II.3 (a) The two dimensional SANS patterns for $W_0=70$ at 25°C in radial geometry at different shear rates. (b) The intensity (I) versus scattering vector (q) plot, a scan along vertical direction, for different shear rates. (c) The intensity (I) versus scattering vector (q) plot, a scan along horizontal direction, for different shear rates.

Figure II.4 (a) Results of the Shear-SANS studies on the $W_0=170$ system at 41°C . (a, a') Radial and tangential profiles before shearing. (b, b') Radial and tangential profiles at $\gamma = 389 \text{ s}^{-1}$. (c, c') Radial and tangential profiles after the cessation of shear. (b) A TEM image of $W_0=170$ sample showing multilamellar vesicles.

Figure II.5 Scattering Intensity vs. q data for $W_0=90$ sample at different temperatures. The scattering peak at $q = 0.041 \text{ \AA}^{-1}$ corresponds to hexagonal phase and the scattering peak at $q = 0.053 \text{ \AA}^{-1}$ corresponds to lamellar phase. The data is intentionally shifted on intensity axis for better observation of peak q values.

Figure II.6 Tangential direction Shear-SANS patterns of the $W_0=90$ system. (a) before shearing at 57°C . (b) at cessation of shear after shearing the sample up to 116.7 s^{-1} at 57°C . (c) after heating the sample to 70°C (d) Sector averaged ($\theta = 0^\circ \pm 2^\circ$) intensity (I) versus scattering vector (q) plot of figure 6b and 6c.

Figure II.7 An illustration of the merging of the (1,0) cylinders to planar sheets. An inset shows the packing of the planar sheets inside the Boulder flow cell.

Figure II.1 Phase behavior of the 0.82M AOT/0.4M lecithin/isooctane/water system determined by SANS. (H) represents hexagonal microstructure, (L) represents lamellar microstructure (•) represents the microstructures examined in this study.

Figure II.2 (a) The Couette shear cell geometry; the outer cylinder rotates. (b) The planes examined in the radial and tangential directions.

Figure II.3 (a) The two dimensional SANS patterns for $W_0=70$ at 25°C in radial geometry at different shear rates. (b) The intensity (I) versus scattering vector (q) plot, a scan along vertical direction, for different shear rates. (c) The intensity (I) versus scattering vector (q) plot, a scan along horizontal direction, for different shear rates.

Figure II.3 Continued

Figure II.4 (a) Results of the Shear-SANS studies on the $W_0=170$ system at 41°C . (a, a') Radial and tangential profiles before shearing. (b, b') Radial and tangential profiles at $\gamma = 389 \text{ s}^{-1}$. (c, c') Radial and tangential profiles after the cessation of shear. (b) A TEM image of $W_0=170$ sample showing multilamellar vesicles.

Figure II.5 Scattering Intensity vs. q data for $W_0=90$ sample at different temperatures. The scattering peak at $q = 0.041$ Å⁻¹ corresponds to hexagonal phase and the scattering peak at $q = 0.053$ Å⁻¹ corresponds to lamellar phase. The data is intentionally shifted on intensity axis for better observation of peak q values.

Figure II.6 Tangential direction Shear-SANS patterns of the $W_0=90$ system. (a) before shearing at 57°C . (b) at cessation of shear after shearing the sample up to 116.7 s^{-1} at 57°C. (c) after heating the sample to 70°C (d) Sector averaged ($\theta = 0^\circ \pm 2^\circ$) intensity (I) versus scattering vector (q) plot of figure 6b and 6c.

Figure II.7 An illustration of the merging of the (1,0) cylinders to planar sheets. An inset shows the packing of the planar sheets inside the Boulder flow cell.

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* The ratio of q values for the primary hexagonal and lamellar peaks can be predicted using a simple geometric calculation, and mass conservation for all components in the system,

$$\text{This ratio} = \frac{q_{\text{hexagonal}}}{q_{\text{lamellar}}} = \sqrt{\frac{8}{3}} \pi \left[\frac{\sqrt{\phi_{\text{Water}} + \phi_{\text{Surfactant}}} - \sqrt{\phi_{\text{Water}}}}{\phi_{\text{Surfactant}}} \right].$$

Here ϕ_{Water} and $\phi_{\text{Surfactant}}$ are the volume fractions of these components respectively. For $W_0 = 90$, this ratio is predicted to be 0.805, which matches with the experimental number of 0.8.

Manuscript III

Microstructure Evolution in Aqueous Solutions of Cetyl Trimethyl Ammonium Bromide (CTAB) and Phenol Derivatives

III.1 Introduction

Surfactants self assemble to form a range of microstructures when present in solution above the critical micelle concentration (CMC) ¹. The structure of surfactant micelles depends on the architecture of the surfactant molecule, the concentration of the surfactant as well as the solution environment ², including the temperature, pressure and the presence of interacting species and their concentrations^{3,4}. These interacting species could be other surfactants, inorganic and organic salts, hydrotopes or nonionic organics.

Mixtures of surfactants provide an additional compositional degree of freedom and expand the range of observed microstructures ⁵. The discovery of the spontaneous formation of vesicles in a mixture of anionic and cationic surfactants is an example of complex interactions in mixed surfactant systems^{6,7}. The effect of inorganic and organic salts on the micellar structure of surfactant self assembly has also been studied extensively ⁸⁻¹⁰. When inorganic salts dissociate in a solvent, charge screening of ionic head groups by counterions promotes the transition from high curvature to low curvature micellar structures. A good example is the transition from spherical to worm like micelles in aqueous solutions of cationic surfactant CTAB with the addition of KBr ¹¹. Dissociation of organic salts produces a surface active species as well as counterions and potentially has a more dramatic effect than addition of ionic inorganic

salts. The surface-active species tends to locate in the interfacial layer, affecting the overall surfactant packing parameter, $P = v/a_0l_c$ (v is the volume occupied by the tail group, a_0 is the area/head group and l_c the length of the hydrocarbon tail), and the counterion provides charge screening. Microstructure changes upon addition of dissociating organic salts are observed at much lower salt to surfactant ratios than their inorganic counterparts^{12,13}.

Recent studies show that the solubilization of small molecules in micelles often leads to changes in micellar structure¹⁴⁻¹⁶. Alcohols are by far the most studied solubilizes¹⁷⁻²¹. Alcohols are interesting because their polarity and ability to hydrogen bond with the surrounding aqueous environment keep them at the interfacial layer instead of going into the core of the micellar structure as bulk organics. Aromatic compounds are also of great interest as they show similar kind of polar behavior as alcohols. Hedin and coworkers reported the elongation of CTAB micelles upon the solubilization of benzene¹⁶. Zhang et al. reported the elongation of micelles through the solubilization of benzyl alcohol in CTAB/KBr micellar system²².

In this manuscript effect of nonionic but polar aromatic dopants on the micellar structure of surfactants in solution has been explored. The dopants are phenol and para-substituted phenolic derivatives like cresol, 4-ethyl phenol and 4-tert-butyl phenol, while the surfactant is cetyl trimethyl ammonium bromide (Figure III.1). Phenol has a solubility of ~ 8% w/w in water at 25°C. The remaining dopants used in this study are essentially insoluble (< 2% by wt.) in water at 25°C. All the phenols

used in this study have a very low dissociation constant ($pK_a \sim 10$) in water.

Counterion effects are therefore expected to be negligible. However the polarity of the molecule and its interaction with the surfactant tails in the interfacial region can play a significant role on the micellar structure. The effect of this systematic increase in methyl substitution on the micellar structure of CTAB in water has been investigated using Cryogenic Transmission Electron Microscopy (Cryo-TEM).

A cationic surfactant such as CTAB has been widely investigated for its relevance in templated synthesis of mesoporous materials.²³ Controlling the template mesopore geometry using organic dopants could be very effective. Also, the incorporation of phenolic molecules in micelles creates confined environment for chemical and enzymatic synthesis of novel polyphenolics.²⁴ The polymer synthesis coupled with mesoporous materials synthesis could lead to the development of novel polymer-ceramic nanocomposites.²⁵

III.2 Experimental Section

III.2.1 Chemicals

All chemicals used in this study were purchased from Sigma Aldrich and used without further treatment or purification. The water used in the study was deionized and was twice distilled.

III.2.2 Sample Preparation

An aqueous solution of 50mM CTAB (2% by weight) was prepared in 0.1M 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer, pH 5.3. The mildly acidic condition suppresses any potential dissociation of the dopants. 17mM to 150mM of phenolic dopant is then dissolved in the CTAB solution with the dopant to CTAB molar ratio (M) ranging from 0.33 to 3. The upper bound on M was dictated by the point at which an isotropic single phase could no longer be maintained. The solution was then sonicated for half an hour for complete mixing of the constituents. The samples were then equilibrated at 25°C for two weeks before imaging.

III.2.3 Cryogenic TEM

A 2-5 μ l drop of the sample is placed on a specially prepared holey carbon grid. Excess liquid is blotted, leaving sample liquid films of thickness below 200nm spanning the grid holes. This processing is done in a controlled environment, where the temperature is maintained at 25°C and humidity at greater than 95% to suppress any water evaporation during sample preparation. The grid is then plunged into liquid ethane maintained at -183°C (its freezing point) in a liquid nitrogen bath. Contact with the cryogen rapidly solidifies the sample into an amorphous state, preserving the microstructures. The sample is withdrawn, excess ethane blotted, then transferred to a cold stage (Oxford Instruments CT 3500J), and viewed on a JEOL1200EX S/TEM using phase contrast microscopy. The sample temperature is maintained at -170°C during imaging to prevent the amorphous to crystalline transformation and to

minimize sublimation or beam damage. Images are captured on a TVIPS F-224 slow-scan CCD (2048×2048 resolution) camera

III.3 Results and Discussions

Phenol/CTAB

A systematic change from high curvature globular micelles to low curvature rod like micelles and then worm like micelles is observed with an increase in phenol concentration. Figure III.2 shows the presence of globular micelles of about 5-6nm in diameter in 50mM solution of CTAB in water. At $M=0.33$, some short rod like micelles (Figure III.3a) can be seen in addition to the globular micelles. At $M=1$, long worm like micelles can be seen coexisting with globular micelles (Figure III.3b). Further increase in phenol concentration to $M=3$ shows the presence of long worm like micelles throughout the sample (Figure III.3c), and no globular micelles.

This change in microstructure can be understood by following expected changes in the surfactant packing parameter, $P = v/a_0l_c$ (v is the volume occupied by the tail group, a_0 is the area/head group and l_c the length of the hydrocarbon tail) as M increases. The amphiphilic nature of phenol orients it in the interfacial layer, with the benzene ring interacting with the CTAB surfactant tail and the hydroxyl group hydrogen bonding with the surrounding water. This increases the effective volume of the tail region and P , leading to structures of progressively lower curvature. Also it could be possible that the CTAB head group repulsions may be decreased by the introduction of the polar dopant.

Cresol/CTAB

At $M = 0.33$, Figure III.4a shows mostly rod like micelles. At $M=1$, worm like micelles are present (Figure III.4b). Addition of cresol results in morphology changes that parallel that in phenol, but at systematically lower values of M . This suggests that the addition of a methyl group on the benzene ring increases the effective volume of the tail region and reduces the surfactant packing parameter.

4-Ethyl Phenol/CTAB

Figure III.5a is an image of the CTAB/4-ethylphenol system at $M=0.33$. Long wormlike micelles are seen throughout the sample. This is a direct evidence that the progressive addition of 4-ethylphenol promotes micellar growth in the system. Thus, the addition of phenols to CTAB micelles leads to structural transitions that mimic the transitions observed when ionic hydrotopes are added to CTAB²⁶⁻²⁹ and other cationic and non-ionic surfactants.

Interestingly, as the dopant to surfactant molar ratio is increased to $M=1$, polydispersed unilamellar vesicles are observed (Figure III.5b). In addition, disk-like objects are also seen. Mixed micelles transform to bilayer disks as the dopant concentration is raised. When the disks reach a critical size, dictated by a balance between the bilayer bending modulus and edge energy, they fold up into vesicles.³⁰ Beyond these levels, 4-ethylphenol is not a dopant but rather the major component of the system. At $M=3$ (Figure III.5c), bilamellar vesicles are observed. Oblong shaped

or tubular vesicles are also observed at $M=3$ (Figure III.5d). The tubule structure shows both entanglements, crossovers, and a connection to a large globular type vesicle structure (indicated by the arrows in Figure III.5d). These tubular structures are interesting, but are potentially the result of inhomogeneities in concentration in the sample. Gentle mixing after two weeks followed by cryo-TEM imaging shows bilayered vesicles at these dopant/surfactant ratios.

4-tert-Butyl Phenol/CTAB

Vesicles along with some discs are already present at $M=0.33$ for 4 butyl phenol (Figure III.6a). Interestingly, bilamellar vesicles are observed at $M=1$ (Figure III.6b). The systematic formation of bilayered vesicles implies that the energy penalty associated with forming a layer away from the spontaneous curvature is compensated by reduction in net repulsion between the layers, leading to thermal fluctuation induced stability^{31,32}. This reduction in repulsive interaction for non-ionizable dopants could be due to the increase in interfacial dielectric constant as the hydroxyl groups align to minimize the electrostatic field^{31,32}.

III.4 Conclusions

Doping with a polar organic additive offers a method of controlling shape and size of CTAB micelles. These micelles can then be used in the templated synthesis of mesoporous materials. Altering the structure of the micellar system that serves as a template for the synthesis of mesoporous materials may provide an easy route to tailor the structure and properties of the mesoporous materials²⁵. It is important to note that

the studies described here are not at very dilute surfactant concentrations, but are at concentrations typically used in mesoporous ceramic synthesis^{23,33}.

Figure captions

Figure III.1 Structures of cetyl trimethyl ammonium bromide (CTAB), phenol, cresol, 4-ethyl phenol and 4-tert-butyl phenol.

Figure III.2 Cryo TEM micrograph of aqueous solution of 50mM CTAB at 25°C, showing micelles of 5-6 nm in size. The scale bar corresponds to 100nm.

Figure III.3 Cryo-TEM micrograph of aqueous solution of 50mM CTAB and (a) 17mM phenol ($M=0.33$) – globular micelles (5-6nm) with some rod like micelles (diameter: 5-6nm, length: 30-40 nm) (marked by a box) are observed; (b) 50mM phenol ($M=1$) – few worm like micelles (marked by an arrow) are present with globular micelles; (c) 150mM phenol ($M=1$) – only worm like micelles are present. The scale bar corresponds to 100nm.

Figure III.4 Cryo-TEM micrographs of aqueous solution of 50mM CTAB and (a) 17mM cresol ($M=0.33$) – mostly rod shaped micelles (marked by a box) (length: 30-40 nm, diameter: 5-6 nm) are observed; (b) 50 mM cresol ($M=1$) – mostly worm like micelles (marked by an arrow) are present with very few vesicular structures (marked by a box). The scale bar corresponds to 100nm.

Figure III.5 Cryo-TEM micrographs of aqueous solution of 50mM CTAB and (a) 17mM 4-ethyl phenol ($M=0.33$) – mostly worm like micelles (diameter: 5-6 nm) (marked by an arrow) are observed; (b) 50 mM 4-ethyl phenol ($M=1$) – mostly unilamellar vesicles (marked by an arrow) are present with very few disc shaped structures (marked by a box); (c) 150 mM 4-ethyl phenol ($M=3$) – bilayered vesicles and (d) tubular structures (marked by an arrow) are present. The scale bar corresponds to 100nm.

Figure III.6 Cryo-TEM micrographs of aqueous solution of 50mM CTAB and (a) 17mM 4-tert-butyl phenol ($M=0.33$) – primarily unilamellar vesicles (marked by an arrow) with few disc shaped structures (marked by a box) are observed; (b) 50 mM 4-tert-butyl phenol ($M=1$) – two layered vesicles are observed throughout the sample. The scale bar corresponds to 100nm.

Phenol

Cresol

4-Ethyl Phenol

4-Butyl Phenol

Figure III.1 Structures of cetyl trimethyl ammonium bromide (CTAB), phenol, cresol, 4-ethyl phenol and 4-tert-butyl phenol.

Figure III.2 Cryo TEM micrograph of aqueous solution of 50mM CTAB at 25°C, showing micelles of 5-6 nm in size. The scale bar corresponds to 100nm.

Figure III.3 Cryo-TEM micrograph of aqueous solution of 50mM CTAB and (a) 17mM phenol ($M=0.33$) – globular micelles (5-6nm) with some rod like micelles (diameter: 5-6nm, length: 30-40 nm) (marked by a box) are observed; (b) 50mM phenol ($M=1$) – few worm like micelles (marked by an arrow) are present with globular micelles; (c) 150mM phenol ($M=1$) – only worm like micelles are present. The scale bar corresponds to 100nm.

Figure III.3 Continued

Figure III.4 Cryo-TEM micrographs of aqueous solution of 50mM CTAB and (a) 17mM cresol ($M=0.33$) – mostly rod shaped micelles (marked by a box) (length: 30-40 nm, diameter: 5-6 nm) are observed; (b) 50 mM cresol ($M=1$) – mostly worm like micelles (marked by an arrow) are present with very few vesicular structures (marked by a box). The scale bar corresponds to 100nm.

Figure III.5 Cryo-TEM micrographs of aqueous solution of 50mM CTAB and (a) 17mM 4-ethyl phenol ($M=0.33$) – mostly worm like micelles (diameter: 5-6 nm) (marked by an arrow) are observed; (b) 50 mM 4-ethyl phenol ($M=1$) – mostly unilamellar vesicles (marked by an arrow) are present with very few disc shaped structures (marked by a box); (c) 150 mM 4-ethyl phenol ($M=3$) – bilayered vesicles and (d) tubular structures (marked by an arrow) are present. The scale bar corresponds to 100nm.

Figure III.5 Continued

Figure III.6 Cryo-TEM micrographs of aqueous solution of 50mM CTAB and (a) 17mM 4-tert-butyl phenol ($M=0.33$) – primarily unilamellar vesicles (marked by an arrow) with few disc shaped structures (marked by a box) are observed; (b) 50 mM 4-tert-butyl phenol ($M=1$) – two layered vesicles are observed throughout the sample. The scale bar corresponds to 100nm.

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CONCLUSIONS

The detailed understanding of the microstructures, in surfactant systems, and its responses to external fields is of utmost importance for using the self assembly in surfactant systems for templated nanostructured materials synthesis. Various experimental techniques are available in the literature to explore the microstructures in surfactant systems. These techniques can be categorized into two broad categories of indirect and direct imaging techniques. In this dissertation it has been showed that a combination of indirect and direct imaging techniques needs to be explored in order to completely understand the microstructures in surfactant systems.

Freeze Fracture Direct Imaging (FFDI), a modified sample preparation technique, has been demonstrated as a powerful direct imaging technique to visualize highly viscous and organic rich samples. FFDI was used to image the microstructures formed in the ternary system formed by AOT/lecithin/Isooctane, and water. FFDI results do not only complement the results of previously done small angle neutron scattering (SANS) experiments but also resolves the issue about the presence of either multilamellar vesicles or planar lamellar phase at high water contents. Due to the probe length scale (several angstroms to few nanometers) involved with the SANS technique, it cannot see the overall curvature (few hundreds of nm) of the multilamellar wall of an onion like structure and gives the similar results as in a case of a planar lamellar structure. FFDI provides a simple way to resolve this issue.

The ternary system formed by AOT/lecithin/Isooctane, and water also shows a very unique behavior under shear. The hexagonal microdomains of this gel get aligned with shear. On the other hand the lamellar microdomains do not show any alignment under shear because the original structure is multi-lamellar vesicles rather than planar lamellar sheets. An aligned lamellar micro phase, consisting parallel sheets, in the gel system can be obtained by heating an aligned hexagonal microphase.

The positive response of the gel microstructure to the shear and the retention of the alignment after removal of the shear make this gel system a potential candidate for nanostructured material synthesis. The gel system provides an excellent template for nanocomposites that combine material synthesis in spatially immobilized aqueous and organic nanodomains simultaneously.

Cryo-TEM has been used extensively to explore the effect of phenolic dopants on the shape and size of Cetyl trimethyl ammonium bromide (CTAB) micelles formed in water. CTAB micelles gradually transform from high curvature structures (globular micelles) to low curvature structures (vesicles), either by increasing the dopant concentration or by increasing the dopant size. A transformation from globular micelles to elongated micelles, to disks, to vesicles, and subsequently to bilayered vesicles and tubular structures has been observed.

CTAB micelles have been used extensively for templated synthesis of mesoporous materials. Doping with a polar organic additive offers a method of controlling shape

and size of CTAB micelles. Altering the structure of the micellar system that serves as a template for the synthesis of mesoporous materials may provide an easy route to tailor the structure and properties of the mesoporous materials.

APPENDIX

List of all the co-authored publications and scientific meetings representations:

Publications

1. V. Agarwal, M. Singh, C. Ford, G. McPherson, V. John, A. Bose, "Microstructure Evolution in Aqueous Solutions of Cetyl Trimethyl Ammonium Bromide (CTAB) and Phenol Derivatives" Preparing for submission in Langmuir 2004.
2. V. Agarwal, M. Singh, G.L. McPherson, V. T. John, A. Bose, "Shear-Response of a Coexisting Lamellar/Hexagonal Surfactant Mesophase", *Submitted to* Langmuir 2004.
3. M. Singh, C. Ford, V. Agarwal, G. Fritz, A. Bose, V. John, G. McPherson, "Structural Evolution in Cationic Micelles Upon Incorporation of a Polar Organic Dopant" Langmuir 2004, 20, 9931-9937.
4. M. Singh, G. Tan, V. Agarwal, G. Fritz, K. Maskos, A. Bose, V. John, G. McPherson, "Structural Evolution of A Two Component Organogel" Langmuir 2004, 20, 7392-7398.
5. M. Singh, V. Agarwal, D. D. Kee, G. L. McPherson, V. T. John, A. Bose, "Shear-induced Orientation of a Rigid Surfactant Gel Mesophase", Langmuir 2004, 20, 5693-5702.
6. V. Agarwal, V. T. John, A. Bose, "Freeze Fracture Direct Imaging (FFDI) of a Viscous Surfactant Mesophase", Langmuir 2004, 20, 11-15.
7. L. Liu; M. Singh; V. Agarwal; A. Bose; V. T. John; "Shear-Induced Alignment and Nanowire Silica Synthesis in a Rigid Crystalline Surfactant Mesophase", Journal of American Chemical Society (JACS) 2004, 126, 2276-2277.
8. M. Singh; V. Agarwal; C. Ford; L. Liu; G. L. McPherson; P. Johnson; A. Bose; V.T. John; M. Sennett; "Enzymatic Polymerization in Spontaneously Formed CTAB/HDBS Vesicles Bilayers", Polymeric Materials: Science and Engineering 2003, 88, 112.
9. B. Simmons, L. Liu, V. John, C. Taylor, D. Schwartz, G. McPherson, A. Bose and V. Agarwal, Synthesis, Functionalization and Surface Treatment of Nanoparticles, 2003, 51.
10. B. Simmons, V. Agarwal, M. Singh, G. L. McPherson, V. T. John, A. Bose, "Phase Transition Dynamics and Microstructure Evolution in a Crystalline

Surfactant Mesophase Using Time-Dependent Small-Angle Neutron Scattering" Langmuir 2003, 19(15), 6329-6332.

11. B. Simmons, V. Agarwal, G. L. McPherson, V. T. John, A. Bose, "Small Angle Neutron Scattering Study of Mixed AOT + Lecithin Reverse Micelles, , Langmuir 2002, 18, 8345.
12. B. Simmons, G. C. Irvin, V. Agarwal, A. Bose, V. T. John, G.L. McPherson, N. P. Balsara, "Small Angle Neutron Scattering Study of Microstructural Transitions in a Surfactant-Based Gel Mesophase", Langmuir 2002, 18, 624.
13. L. Limin, S. Li, B. Simmons, M. Singh, V. T. John, G. L. McPherson, V. Agarwal, P. Johnson, A. Bose, N. Balsara, "Nanostructured Materials Synthesis in a Mixed Surfactant Mesophase" Journal of Dispersion Science and Technology 2002, 23(1-3), 441-442.

Scientific Meetings Representations

(Oral presentations)

- V. Agarwal, M. Singh, G. L. McPherson, V. T. John, A. Bose, "Imaging of soft colloids" *ACS 78th Colloid and Surface Science Symposium*, Yale University, 2004.
- V. Agarwal, M. Singh, G. L. McPherson, V. T. John, A. Bose, "Microstructure Evolution of Cationic Micelles upon Incorporation of an Organic Dopant" *ACS 78th Colloid and Surface Science Symposium*, Yale University, 2004.
- V. Agarwal, M. Singh, G. L. McPherson, V. T. John, A. Bose, Shear Induced Microstructure Alignment of a Surfactant Based Mesophase, *Annual AIChE Meeting*, San Francisco, CA, November 2003.
- V. Agarwal, M. Singh, G. L. McPherson, V. T. John, A. Bose, "Visualization of soft colloids using Freeze Fracture Direct Imaging (FFDI) Electron Microscopy" *American Chemical Society(ACS) Colloid and Surface Science Symposium*, Georgia Tech., July 2003.
- G. Tan; M. Singh; L. Liu; V. T. John; V. Agarwal; A. Bose; Self-Assembly of Organogels and Transcription to Materials Synthesis, *Annual AIChE Meeting*, San Francisco, CA, 2003.
- V. T. John; M. Singh; L. Liu; C. Ford; V. Agarwal; A. Bose; A Biomimetic Approach to Polymer-Ceramic Nanocomposites, *Annual AIChE Meeting*, San Francisco, CA, 2003.

- M. Singh; V. Agarwal; V. T. John; G. L. McPherson; D. De Kee; A. Bose; Shear-induced orientation of a rigid surfactant gel mesophase, 77th ACS Colloid and Surface Science Symposium, Atlanta, GA, 2003.
- M. Singh; V. Agarwal; C. Ford; L. Liu; G.L. McPherson; A. Bose; V. T. John; M. Sennett; Enzymatic polymerization in spontaneously formed CTAB/HDBS vesicle bilayers. 225th ACS National Meeting, New Orleans, LA, 2003.
- V. Agarwal, M. Singh, B. Simmons, G. L. McPherson, V. T. John, A. Bose, "Microstructure Evolution in a Self Assembled Surfactant Mesophase", *Self Assembly-the future*, Mass Marittima, Italy, 2002.
- V. Agarwal, M. Singh, G. L. McPherson, V. T. John, A. Bose, "Shear Induced Microstructural Alignment of a Mixed Surfactant Mesophase", *13th New England Complex Fluids Workshop*, Harvard University, MA, 2002.
- V. Agarwal, M. Singh, B. Simmons, G. L. McPherson, V. T. John, A. Bose, "Microstructure Determination of a Self Assembled Surfactant Mesophase Using Small Angle Neutron Scattering (SANS)", *ACS Colloid and Surface Science Symposium*, Ann Arbor, Michigan, July 2002.
- V. Agarwal, B. Simmons, G. L. McPherson, V. T. John, A. Bose, "Microstructure Evolution in a Surfactant Based Gel Mesophase", *AIChE Annual Meeting*, Reno, NV, November 2001.

(Poster presentations)

- V. Agarwal, M. Singh, G. L. McPherson, V. T. John, A. Bose, "Freeze Fracture Direct Imaging (FFDI) of a Self Assembled Surfactant Mesophase" *Gordon Research Conference on Chemistry of Supramolecular Assemblies*, August 2003.
- V. Agarwal, B. Simmons, G. L. McPherson, V. T. John, A. Bose, "Characterizing A Novel Mixed Surfactant Based Mesophase", *Gordon Research Conference on Chemistry of Supramolecular Assemblies*, August 2001.

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