Notes

Phase Transition Dynamics and Microstructure Evolution in a Crystalline Surfactant Mesophase Using Time-Dependent Small-Angle Neutron Scattering

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Introduction

In the presence of water and oil, surfactants spontaneously self-assemble into a variety of well-known microstructures, including lamellae,[1] intercontiguous networks,[2] well-defined spherical droplets,[3] or disordered/ordered bicontinuous networks of both phases.[4] Such self-assembled microstructures have been used effectively as structure-directing templates in a variety of materials synthesis applications[5] and are of relevance for their potential applications in the development of structured materials.

Our focus is the self-assembly of a surfactant mixture containing the twin-tailed anionic surfactant bis(2-ethylhexyl) sodium sulfosuccinate (AOT) and the zwitterionic surfactant lecithin, both shown in Figure 1. AOT typically forms spherical water-in-oil microemulsions.[6] Lecithin tends to form interfaces with mimimal curvatures, such as flexible bilayers and vesicles, in aqueous systems. In nonpolar organic solvents, lecithin forms wormlike cylindrical reverse micelles that can incorporate water up to a water/lecithin molar ratio of 20.[7] When these surfactants with differing packing parameters (and therefore tendencies to form structures with differing spontaneous curvatures) are mixed, the additional compositional degree of freedom allows a range of new microstructures to be realized.

When AOT and lecithin are dissolved in isooctane at concentrations of 0.85 and 0.42 M, respectively, the solution behaves as a Newtonian fluid with a viscosity of 0.7 Pa·s at 25 °C. As water is added, the viscosity increases and the system achieves an optically clear but rigid gellike state at a molar ratio of water to AOT, W_o, of about 70. This highly rigid, optically clear structure, with low shear viscosities up to 10^5 Pa·s, persists until a W_o of over 200. Since these rigid structures contain immobilized pools of both water and oil in nearly equal proportions, they are conducive to ordered materials synthesis over extended length scales.[8] Therefore, we have sought to understand their microstructure. Our earlier work using small-angle neutron scattering (SANS) has shown that these systems are crystalline mesophases with columnar reverse hexagonal (H_{II}) and/or lamellar (L_α) ordering.[9] At lower water contents and temperatures, the reverse hexagonal order exists. Upon heating or increasing the water content, the structure transitions to the lamellar phase through an intermediate coexistence region.

Since the transition from the hexagonal to the lamellar phase is completely reversible with temperature, a rapid temperature quench is a potential route for determining the dynamics of this transition as well as monitoring the evolution of microstructures as the system goes from one state to another. Understanding the rate at which one self-assembled microstructure evolves from another and examining intermediate-state structures can open up new avenues for modifying the morphology in materials synthesis.

The technique used to probe phase transition dynamics must capture a statistically meaningful amount of data within a time period that is short enough to produce an "instantaneous snapshot" of the system. Thus, if microstructure reorganization rates are slow compared to the collection times for statistically significant data acquisition in neutron scattering experiments, the temporal evolution of diffraction peak patterns may be used to understand microstructure evolution. An additional constraint is that the fastest time constant that can be probed must be much larger than the time scale of the imposed temperature change. The experiment is relatively simple and involves taking a system to the lamellar phase at a high temperature (65 °C), quenching it to ambient temperature (25 °C), where the equilibrium structure is predominantly hexagonal, and monitoring the diffraction spectra to understand the temporal evolution of microstructures during the transition. This short paper describes our results on such experiments.

Materials and Methods

Chemicals. Lecithin (95% purity; extracted from soybeans) was obtained from Avanti Polar Lipids, Inc. Bis (2-ethylhexyl) sodium sulfosuccinate (AOT) and 2,2,4-trimethylpentane (isooctane, 99% purity) were purchased from Sigma−Aldrich.

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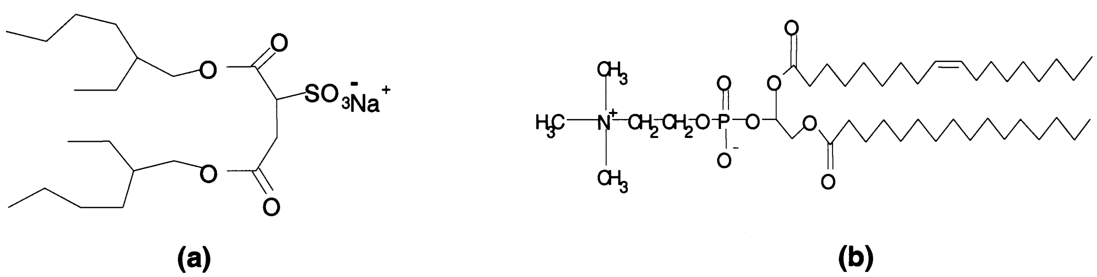

(a) (b)

Figure 1. Chemical structures of (a) AOT and (b) lecithin.

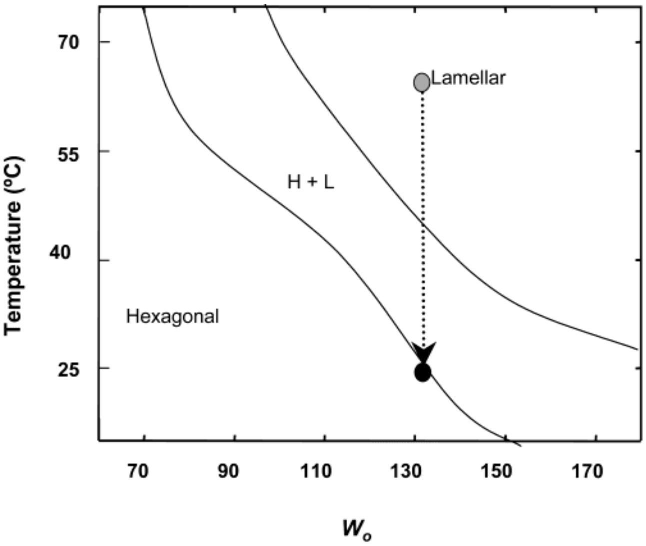

Figure 2. Phase diagram showing equilibrium microstructures in the AOT/lecithin/isooctane/water system as temperature and water content are varied. The dashed arrow shows the trajectory of the temperature quench used in this experiment.

Deuterium oxide (99.9%) was purchased from Cambridge Isotopes Laboratory. All chemicals were used without further treatment and/or purification.

Experimental Details. The sample consists of an AOT/lecithin/D_2O/isooctane gel. An isooctane solution containing 0.84 M AOT and 0.42 M lecithin is prepared. D_2O is then added progressively, until the W_0 reaches 130 (W_0 = mol of D_2O/(mol of AOT)). The sample was first equilibrated at 65 °C in a holder that was outside the beam line. The sample was then placed in the sample holder thermostated at 25 °C, and in the beam line, and allowed to cool to this temperature. The experimental path is illustrated in Figure 2.

SANS measurements were carried out at the NIST Center for Neutron Research in Gaithersburg, MD, on the 30 m NG3 beamline. The SANS intensity, I_q, was recorded as a function of the scattering vector q (=$[4\pi \sin(\theta/2)]/\lambda$ with θ defined as the scattering angle and λ the neutron wavelength, equal to 6 ± 0.9 Å). The detector angle was set at 2°, and the sample-to-detector distance was set to 6 m. The range of the scattering vector q was therefore 0.007−0.1039 $Å^{-1}$. Samples were contained in closed stainless steel cells with quartz windows that provided a path length of 2 mm. The AOT/lecithin/D_2O/isooctane system scatters strongly and shows very pronounced and distinct diffraction patterns for the H_{II} and L_α phases that can be captured within 10 s. Therefore, it is feasible to monitor kinetics with time constants of the order of minutes or higher. SANS data were taken at 40 s intervals from the time the sample was placed in the beamline until the system had attained equilibrium; that is, there was no further change in the SANS profile for ∼5 min. Any nonzero scattering at high "q" was assigned to incoherent scatter and was subtracted from the resultant profiles. As shown below, the time constant associated with the temperature change is of the order of 2 min. This represents the lower bound on the process rates that can be probed using our temperature quench method.

Results and Discussion

Figure 3 presents the data obtained by taking chronological 10 s snapshots at 40 s intervals, as the sample cools from 65 to 25 °C. The inset, with the data plotted on a log−log scale, illustrates that the first SANS profile exhibits the characteristic peaks of a lamellar microstructure—a prominent peak at $q = 0.043$ $Å^{-1}$ and a higher order peak at $q = 0.084$ $Å^{-1}$, in good agreement with our previous work.[9] As the sample is cooled to 25 °C, the primary peak associated with the lamellar phase decreases in intensity and a new peak, not observable until approximately 120 s, emerges at $q = 0.033$ $Å^{-1}$, exactly at the d spacing corresponding to the [10] plane of the observed equilibrium hexagonal structure.[9] This peak progressively increases in intensity without a shift in position. Assuming that the surfactant layer thickness is the same in the lamellar and hexagonal phases, a straightforward calculation from geometric considerations at a fixed W_0 [9] gives the ratio of the primary peak locations for the equilibrium hexagonal and lamellar structures as

$$\frac{q_{\text{hexagonal}}}{q_{\text{lamellar}}} = \sqrt{\frac{8}{\sqrt{3}\pi}}\left[\frac{\sqrt{\phi_{\text{water}}+\phi_{\text{surfactant}}}-\sqrt{\phi_{\text{water}}}}{\phi_{\text{surfactant}}}\right] \qquad (1)$$

Here ϕ_{water} and $\phi_{\text{surfactant}}$ are the volume fractions of these components, respectively. For $W_0 = 130$, $\phi_{\text{water}} = 0.602$ and $\phi_{\text{surfactant}} = 0.095$. Equation 1 gives $q_{\text{hexagonal}}/q_{\text{lamellar}} = 0.75$, in good agreement with the experimental ratio of 0.76.[9] Therefore, the evolving peak is associated precisely with the equilibrium hexagonal phase. Clearly, within the temporal resolution of these SANS experiments, the hexagonal phase nucleates at exactly the equilibrium d spacings. There is no relaxation of the structural characteristics of either the lamellar or hexagonal phases, and only the relative amounts of each of these evolve over time as the sample temperature changes. In addition, no other intermediate microstructures are observed.

The intensities of the primary peaks associated with each phase represent reasonable measures of the amount of that phase at any time. Figure 4 shows the time variation of the sample temperature,[10] as well as the primary scattering peak intensities of the lamellar and hexagonal phases. The sample temperature displays a characteristic single-exponential decay, with a time constant of the order of 150 s. The scattering peak intensities show different kinetics, varying slowly in the beginning, decaying fast, and then varying slowly at large times. The phase transition kinetics does not simply follow but lags behind the sample temperature trajectory. Therefore, the transi-

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[10] The variation of sample temperature over time is measured in a scattering cell in our laboratory. The cell containing the sample is equilibrated at 65 °C in an oven and then placed in an aluminum holder exposed to air at room temperature. A thermocouple placed within the sample is used to monitor the temperature over time.

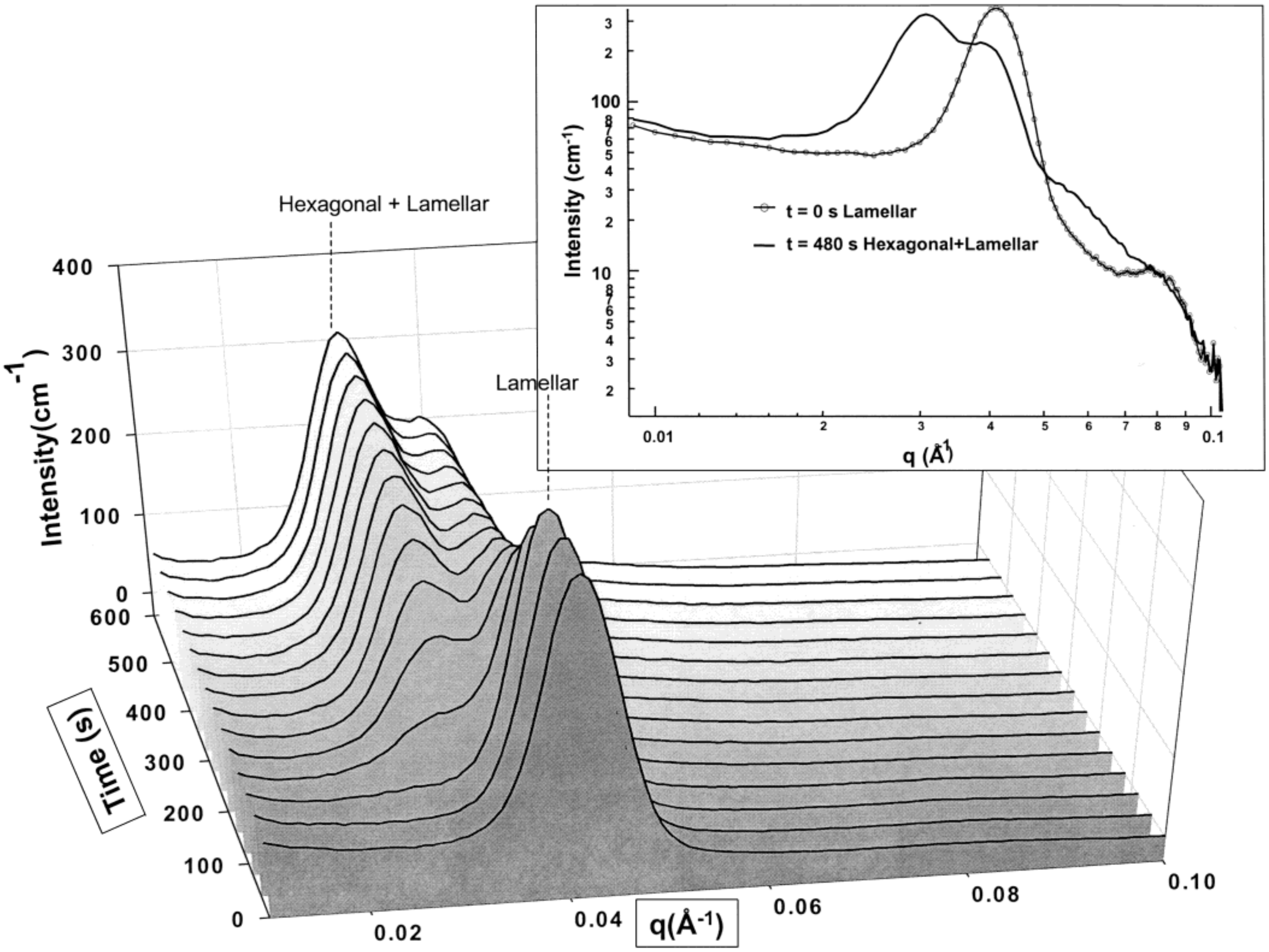

Figure 3. Scattering intensity profiles showing the temporal evolution from the lamellar to the hexagonal phase. Each profile at a given time is obtained by averaging the scattering intensity over 10 s. The inset shows the pattern at the start, and after the relaxation is complete, on a logarithmic scale. The higher order peaks for the hexagonal and lamellar phases are evident.

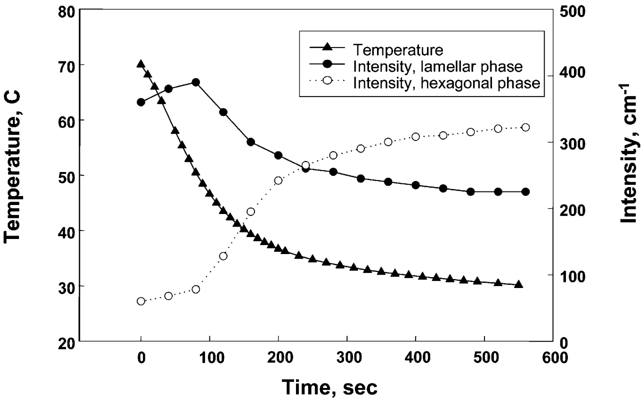

Figure 4. Lamellar and hexagonal phase primary peak intensity as a function of time. The time dependence of the sample temperature is also shown to indicate that the microstructure evolution is slower and follows a different kinetics than the sample temperature.

tions observed in the diffraction patterns do not represent a series of equilibrium states corresponding to the current temperature of the sample (this would be the case if the phase transition kinetics was fast compared to the temperature change in the system). There is no further change in the intensities after 440 s. The SANS profile from this point onward is characteristic of the equilibrium data at 25 °C. These data set the upper bound for the time constant associated with the lamellar to hexagonal phase transition at ~7 min.

Neutron scattering data can be used to get measurements of the water pool dimensions in the lamellar and hexagonal phases. For $W_0 = 130$, the water layer thickness for the lamellar phase, d_w, is 8.6 nm. The water cylinder diameter for the hexagonal phase, D_w, is 17.9 nm. The microstructures are drawn to scale in Figure 5, illustrating the change in the characteristic d spacing between the lamellar and the hexagonal microstructures. The mechanistic details of this transition are unclear, but certainly involve cooperative transport and rearrangement of surfactants at the oil–water interface, as well as movement of isooctane and water. In a related study of the SANS characterization of equilibrium hexagonal and lamellar structures of a quaternary system of a phospholipid, a lipid-grafted polymer, a cationic surfactant, and water, Firestone and co-workers have proposed a mechanistic scheme where fluctuations of the lamellar interfaces lead to defect formation and break-off of the layers to fold into the columnar structures of the hexagonal phase.[11] Such rearrangements may be applicable here too, but the domains adjust to maintain the characteristic crystallographic d spacings specified by eq 1 at a fixed system composition.

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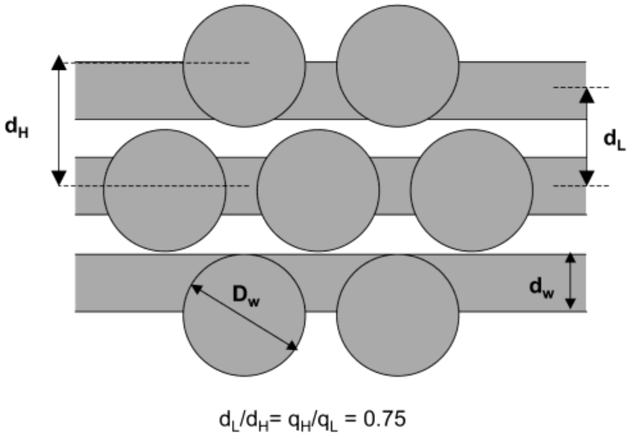

Figure 5. End-view representation of the hexagonal microstructure superimposed on the lamellar microstructure, drawn to scale.

Conclusions

Time-dependent SANS experiments are capable of capturing the transition from one microstructure to another following a temperature quench. Within the time resolution of these SANS measurements, we observe that the hexagonal phase nucleates and remains at the equilibrium crystallographic *d* spacings, and there is no relaxation of the lamellar *d* spacing over time. Only the relative amounts of each phase evolve with time. No other intermediate states are observed. The phase change is complete within 7 min. Therefore, the upper bound for the time constant associated with this lamellar to hexagonal phase transition is of the order of 7min.

There are potential applications of such time-dependent microstructural transitions. If inorganic ceramics (for example, silica) are nucleated in the water domains at high temperatures, where hydrolysis and condensation rates are high, and the system is then quenched to ambient conditions, it would be interesting to determine the final morphology of the material. Such experiments may lead to the development of new structures of ceramics, polymers, and polymer−ceramic nanocomposites.

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