TEM INVESTIGATIONS OF SELF-ASSEMBLY THROUGH PHYSICAL SYNTHESIS

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A novel way of enlarging the realm of surfactant solution microstructure is the "physical synthesis" of new microstructures and surfactant-templated materials by mixing simple surfactants\(^1\) or surfactant and inorganic and ionic species.\(^2\) Mixing can often produce properties not possessed by any one species alone. As we have recently shown, mixtures of single-tailed cationic and anionic surfactants associate in solution to form a quasi-double-tailed catanionic surfactant that forms bilayers rather than the simple micelles each species would form on its own. Mixed surfactant systems apparently produce new microstructures by altering the intermolecular and interaggregate forces in ways impossible for single component systems.\(^1\) In addition to spontaneous vesicles, we have found other new microstructures including dilute lamellar and L\(_3\) phases depending on the details of the surfactant mixture. Surfactant interactions with ionic species also play an important role in the in synthesis of a new M41S family of mesoporous silicas,\(^2\) and are likely to be important in the templating of biominerals at interfaces. By understanding the molecular and chemical basis of these interactions, we can begin to tailor new microstructured and/or biomimetic materials by controlling surfactant aggregation and phase behavior through physical synthesis rather than through much more elaborate chemical synthesis.

In mixed surfactant systems, microstructure is often so unexpected as to make it difficult to construct a model to explain scattering or other data; or worse, a model built on simple structural concepts leads to erroneous interpretation of experimental results. Electron microscopy is the only technique with sufficient resolution to elucidate the microstructure present in catanionic surfactant mixtures. Of particular interest will be the nature of the phases with which the vesicles are in equilibrium. Our preliminary work shows that the vesicles, which exist as a single equilibrium phase at low surfactant concentrations, are in equilibrium with lamellar liquid crystals at higher surfactant concentrations (Fig. 1). In addition, there are theoretical reasons why a vesicle phase (consisting of a dispersion of spontaneously curved bilayers) might be under some conditions be found in equilibrium with a collection of connected spontaneously curved bilayers, which is one model for what is known as the L\(_3\) phase. We have recently found such an L\(_3\) phase in dilute aqueous mixtures of cetyl trimethylammonium tosylate (CTAB) and sodium octyl sulfonate (SOSO). Fig. 2 shows a freeze-fracture electron micrograph of this phase, which shows the characteristic bicontinuous textures seen in such materials, while Fig. 3 shows a phase diagram of the CTAB-SOSO mixture that reveals two L\(_3\) phases, roughly symmetrically located around the equimolar CTAB-SOSO. This type of phase diagram is unique: very few L\(_3\) phases have been seen in ternary mixtures, and no phase diagrams have multiple L\(_3\) phases.

Freeze-fracture and cryoelectron microscopy are also necessary to visualize the mechanisms and intermediates of mesoporous silicate formation and microstructure transitions as hypothesized by Monnier et al.\(^2\) In mixed silicate-surfactant systems, mesoporous materials can be synthesized at surfactant concentrations as low as 1%. The single chain alkyltrimethylammonium bromide surfactants used in the syntheses typically form isotropic micellar phases at these concentrations in the absence of silicates. In the CTAB-water (cetyltrimethylammonium bromide) phase diagram at typical mesophase synthesis conditions, the isotropic micellar phase is stable up to a CTAB concentration of about 25\% by weight at which the hexagonal phase begins. For CTAB concentrations above 70\%, the preferred microstructure is lamellar. However, as is clear from Fig. 4, in the presence of silicates, a 6 wt\% solution of CTAB forms well-defined lamellar aggregates. These studies will show if the surfactant microstructure changes during the synthesis in response to the charge of the silicon anions.\(^2\)

FIG. 1. Equilibrium vesicles formed from catanionic mixtures of sodium dodecylbenzenesulfonate and cetyltrimethylammonium tosylate. Characteristic dimensions are about 100 nm.

FIG. 2. L₃ phase formed from catanionic mixtures of sodium octyl sulfonate and cetyltrimethylammonium tosylate. The characteristic bicontinuous texture is obvious.

FIG. 3. Preliminary phase diagram of the SOSO-CTAB surfactant mixture. What is surprising is that there are two L₃ phases roughly symmetrically located about the equimolar line.

FIG. 4. Mesoporous silicate reaction intermediates. CTAB, at the 6 wt% concentration chosen forms spherical micelles. However, in the presence of silicate anions, the surfactant forms bilayers.