SELF-ASSEMBLY OF SILICATE/SURFACTANT MESOPHASES

SCOTT A. WALKER, J.A. ZASADZINSKI
Dept. of Chemical Engineering, University of California, Santa Barbara, CA 93106

ABSTRACT

The synthesis of silicate/surfactant mesophases is driven by cooperative assembly of organic surfactant and inorganic silicate species, and the resultant mesophase morphology can be controlled by synthesis conditions (i.e., CTAB concentration in precursor solution and SiO₂-CTAB mole ratio). The self-assembly process of these mesophases is driven complexation of the polyionic silicate species with several CTAB cations to form a multi-tailed surfactant. One of these mesophases is a novel rippled lamellar phase in which the ripple wavelength and lamellar spacing are similar to the hexagonal mesophase rod center-to-center spacing; each of these dimensions are consistent with the length of two CTAB molecules.

INTRODUCTION

Mesophases composed of silicate and surfactant are widely used as precursor solutions in the production of many types of mesoporous materials, most notably the MCM-type mesoporous materials.1 Mesoporous materials are ordered arrays of long-length scale pores with diameters ranging from 20 Å to greater than 500 Å.2 These materials are used in a wide range of applications, including molecular sieves, catalysts, and sorption media, each of which make use of the large surface area available, which may range above 500 m²/g.1 Naturally, mesoporous materials are found in many silicas, aluminas, and clays. Also, in natural biomineralization processes, microorganisms produce bones and shells by depositing inorganic species (e.g. silica) in the presence of surfactant structures.3

Recently, there has been much interest in determining the mechanism(s) involved in mesophase formation.4,5 Many proposed mechanisms suggest that an initial liquid crystal phase of surfactant (organic) molecules exists prior to the addition of the silicate species; this liquid crystal phase serves as a template into which silicate self-assembles.4,5 However, recent studies indicate that a preexisting liquid crystal phase is not necessary for the formation of several different mesophases; this model shows that the self-assembly into the mesophase is driven by a cooperative biphase organization of the inorganic silicate species and the organic surfactant species.5 The motivation for this study is to characterize and visualize by freeze-fracture electron microscopy the different mesophases produced.

MATERIALS AND METHODS

Materials

Cetyl trimethylammonium bromide (CTAB), trimethyllybenzene (TMB), and tetramethylammonium hydroxide (TMAOH) were obtained from Aldrich Chemicals (Milwaukee, WI). The silica source was CAB-O-SIL M-5 (Scintillation grade, Kodak). A TMA-silicate solution (0.5 TMA/SiO₂, 10 wt% silica) was prepared with a 25 wt% aqueous solution of TMAOH and CAB-O-SIL M-5. The precursor silicate solution also contained methanol at high pH, which helps stabilize the silica species, which is polyanionic, to the double-four-ring cubic octamer silicate unit.6

Sample Preparation

The hexagonal mesophase was formed by the addition of the cubic, octameric silicate oligomer solution and TMB to an isotropic 12.8 wt% CTAB/water solution at 25°C. The resultant
mixture had the following molar composition: 1.4 SiO₂ - 196 Water - 0.5 (TMA)₂O - 0.5 (C₁₆TMA)₂O - 18.8 CH₃OH - 1.2 TMB. The lamellar mesophase was formed by the addition of the cubic, octameric silicate oligomer solution and TMB to an isotropic 6.8 wt% CTAB/water solution at 25°C, to form the following molar composition: 1.4 SiO₂ - 196 Water - 0.5 (TMA)₂O - 0.25 (C₁₆TMA)₂O - 18.8 CH₃OH - 1.2 TMB. The initial lamellar mesophase material did not contain methanol, and was synthesized in the same fashion; its molar composition was 3.6 SiO₂ - 281.5 Water - 0.5 (TMA)₂O - 0.5 (C₁₆TMA)₂O - 1.0 TMB.

Freeze-Fracture Transmission Electron Microscopy (FF-TEM)

Samples for freeze-fracture transmission electron microscopy (FF-TEM) were prepared by placing ~0.5 µL of sample between two thin (0.1 mm) copper freeze-fracture planchettes (Balzers Union, BU-012-056T, Hudson, NH). The sandwiches were vitrified by plunging them into a bath of liquid propane or ethane cooled by a surrounding bath of liquid nitrogen. The vitrified specimens were transferred under liquid nitrogen to a Balzers 400 freeze etch device, fractured under vacuum (<10⁻⁷ mbar) at -170°C and then immediately shadowed with a 1.5 nm thick layer of platinum deposited at a 45° angle with respect to the fracture surface, followed by a 20 nm thick layer of carbon deposited normal to the surface to create a permanent replica of the fractured surface. The replicas cleaned according standard procedures and imaged with a JEOL 100CX II electron microscope in the conventional transmission mode at 100 kV.

RESULTS AND DISCUSSION

CTAB in aqueous solution forms a variety of phases depending on its concentration and temperature. At 25°C, an isotropic spherical micellar phase exists at CTAB concentrations of 7 wt%, and an isotropic cylindrical micellar phase exists at 13 wt%, as indicated by ²H NMR spectroscopy. The hexagonal phase for CTAB/water solutions exists at higher concentrations, above 25 wt% and above 25°C. Lamellar phases exist only for CTAB concentrations above ~80 wt%.

The silicate/surfactant mesophases are formed by mixing together two separate precursor solutions, an organic CTAB micellar solution and an inorganic silicate (4.0 wt%) solution.

The addition of the silicate solution at a 3.6:1 SiO₂-CTAB mole ratio to an aqueous dispersion of 13 wt% CTAB resulted in the immediate precipitation of a lamellar phase, as indicated by ²H NMR spectroscopy (not shown), surrounded by a dilute phase. FF-TEM of the surrounding aqueous region revealed that the solution contained a dispersion of bilayer vesicles, as shown in freeze-fracture electron micrograph in Fig. 1. Both unilamellar vesicles and multilamellar vesicles are present. The arrows point to small spherical structures that appear only on the vesicle bilayers themselves; these smaller features may be vesicles of higher curvature. The existence of bilayers in a CTAB/silicate solution at CTAB concentrations that normally form cylindrical micelles was our first indication that some unique, interesting phase was forming due to the presence of silicate.

The synthesis of two other CTAB/silicate mesophases, that of an hexagonal phase and a lamellar phase, were carried out and characterized by ²H NMR spectroscopy. The interesting aspect of these syntheses is that the formation of the actual mesophase type could be controlled by the synthesis conditions, specifically the original concentration of CTAB in the precursor solution and therefore the silicate/CTAB mole ratio.

Addition of silicate solution (purely cubic octamers of silica) at a 2.8:1 SiO₂-CTAB mole ratio to an aqueous dispersion of 13 wt% CTAB (precursor solution) resulted in the formation of a mesophase which had a ²H quadrupole splitting of 12.7 kHz as observed by ²H NMR spectroscopy. This quadrupole splitting is consistent with an hexagonal phase, similar to the quadrupole splitting in lyotropic liquid crystal (LLC) hexagonal phases. The final molar composition of this mesophase was 1.4 SiO₂ - 196 Water - 0.5 (TMA)₂O - 0.5 (C₁₆TMA)₂O - 18.8 CH₃OH - 1.2 TMB. FF-TEM of this mesophase revealed an assembly of rod-like aggregates (Fig. 2A) and region of more ordered, well-aligned cylindrical aggregates (Fig. 2B). These micrographs are consistent with an hexagonal mesophase of CTAB rod micelles. The Fourier Transform (FT)
of the image in Fig. 2B (right inset) allows calculation of the repeat spacing, which turns out to be 7.0±0.5 nm. X-ray diffraction (XRD) data (not shown) has indicated that the actual rod center-to-center spacing is 4.0 nm. Although there seems to be a discrepancy in the repeats measured in the two techniques, the 7.0±0.5 nm spacing from FF-TEM is consistent with a minimum energy fracture plane that has propagated along the staggered path 1 in Fig. 2B (left inset) and which can be shown, using simple geometry, to correspond to a 4.0±0.3 nm rod center-to-center spacing. It is possible, of course, that the 7 nm periodicity reflects the closest spacing between less densely packed rods (Fig. 2B, inset path 2), however, this is not expected to be the energetically preferred fracture plane. One interesting feature of this hexagonal mesophase, one which distinguishes it from the lamellar mesophase, is that FF-TEM has revealed regions in which the hexagonally close-packed rods have fractured end-on, perpendicular to the fracture direction, as seen in Fig. 2C. The small bumps and divots in the micrograph are presumably rod micelles that have fractured end-on. Although there does not appear to be a large, long-length scale hexagonal array of rod micelles, there are various regions in which it appears some rods are hexagonally packed, as indicated by the arrow. There is no obvious layering as we observe in the lamellar samples (Fig. 3).

As mentioned previously, the appropriate synthesis conditions can drive an isotropic CTAB precursor solution to a lamellar mesophase upon the addition of silicate. The addition of silicate solution (purely cubic octamers of silica) at a 5.6:1 SiO₂:CTAB mole ratio to an aqueous dispersion of 7 wt% CTAB (precursor solution) resulted in the formation of a mesophase which had a 2H quadrupole splitting of 27.8 kHz as observed by 1H NMR spectroscopy. This quadrupole splitting is consistent with a lamellar phase, similar to the quadrupole splitting in LLC lamellar phases. The final molar composition of this mesophase was 1.4 SiO₂ - 196 Water - 0.5 (TMA)₂O - 0.25 (C₆H₄TMA)₂O - 18.8 CH₃OH - 1.2 TMB. FF-TEM of this mesophase showed what initially appeared to be a typical lamellar phase, with lamellae stacked in layers and several breaks and downsteps to lower sheets. The layering of the system could be seen in fractured cross sections. However, more detailed analysis of this mesophase revealed the existence of a novel lamellar phase, with the lamellar sheets themselves having undulations with a characteristic periodicity, as shown in Fig. 3. Fig. 3A shows these clearly visible undulations, whose directionality is preserved over many lamellar surfaces. The internal lamellar spacing is much more easily observed in Fig. 3B. The FT of the image (inset, Fig. 3B) indicates two periodicities corresponding to (1) approximately 4.0 nm wavelength undulations on the lamellar surfaces and (2) approximately 4.0 nm spacing as evidenced by the terraced discontinuities which range from a
few to tens of layers thick. We have interpreted this novel microstructure to be a type of rippled lamellar phase. The undulation wavelength and the bilayer spacing both are likely closely associated with the hexagonal mesophase, which also has a characteristic spacing of approximately 4.0 nm. The ripple undulation wavelength, lamellar thickness, and hexagonal rod spacing are likely set by the length of two CTAB molecules. Since the undulations do not extend through the layers to form discrete cylindrical aggregates, as supported by $^1$H NMR spectroscopy, this suggests that the undulations in the layers have a fairly small amplitude or the surfactant orientation does not vary significantly across the bilayer surface.

Figure 2. Freeze-fracture electron micrographs of silicate-surfactant hexagonal mesophase. (A) A region of close-packed cylindrical aggregates with reduced long range order, a common feature of these samples. (B) A region of well-aligned cylindrical aggregates. Right inset: Fourier Transform (FT) of image. Left inset: Possible fracture paths. (C) A region in which the rods have fractured end-on. Molar composition: 1.4 SiO$_2$ - 196 Water - 0.5 (TMA)$_2$O - 0.5 (C$_{16}$TMA)$_2$O - 18.8 CH$_3$OH - 1.2 TMB. Final CTAB concentration 7.5 wt%.
Figure 3. Freeze-fracture electron micrographs of silicate-surfactant lamellar mesophase. (A) A region clearly showing the novel ripple undulations existing on the lamellar sheets. The ripple directionality is preserved over several lamellar surfaces. (B) A region showing two distinct periodicities, as seen in the FT. The lamellae are clearly seen in this region. Molar composition: 1.4 SiO₂ - 196 Water - 0.5 (TMA)₂O - 0.25 (C₁₆TMA)₂O - 18.8 CH₃OH - 1.2 TMB. Final CTAB concentration 6.8 wt%.

The self-assembly of CTAB into unexpected phases upon addition of the polyanionic silicate species can be explained by a simple geometric packing argument as developed by Israelachvili and coworkers.⁹ Each surfactant molecule has a characteristic hydrophobic volume, v, hydrocarbon tail length, l, and optimal headgroup area, a. A packing parameter, p, defined as p = v/la, determines the characteristic packing shape and therefore the most likely aggregate into which the surfactant molecule self-assembles. For p < 1/3, the packing shape resembles a cone, and such surfactant shapes most easily pack into spherical micelles. Rod micelles are formed for 1/3 < p < 1/2, in which the packing shape resembles a truncated cone. Upon increasing the packing parameter to 1/2 < p < 1, the surfactant packs into a truncated cone-like geometry that resembles a cylinder more than a cone. Vesicles are the preferred aggregate for this type of shape. Finally, for p ~ 1, a cylindrical packing shape results, and flat lamellar sheets are formed. Typically, single-tailed surfactants (e.g. CTAB) pack into cone-like structures and form micellar solutions. Double-tailed surfactants (e.g. phospholipids) pack into more cylindrical structures, and form vesicles and lamellae. It has been shown that mixtures of cetyl trimethylammonium tosylate (CTAT), a cationic surfactant, and sodium dodecyl benzene sulfonate (SDBS), an anionic surfactant, form vesicles when mixed in aqueous solution, although the pure components form micelles in water.¹⁰ This unique phase behavior is due to the formation of a neutral dimer complex of the cationic and anionic species that resembles a double-tailed surfactant, which is expected to form bilayers. In much the same way, the polyanionic silicate species assembles several CTAB cations to form a neutral complex that resembles a multi-tailed surfactant, and is thus expected to form higher order aggregates such as lamellar phases and hexagonal phases.
References


11. The authors would like to thank A. Firouzi and D. Kumar for sample preparation, A. Firouzi and B.F. Chmelka for $^2$H NMR spectroscopy and analysis, and G. Stucky for useful discussions.