



Experiment title: Formation mechanisms for the self-assembly of surfactant-templated silica from acidic solutions.	Experiment number: CH-1182
Beamline: BM26B	Date of experiment: from: 26/11/01 to: 1/12/01
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Report:

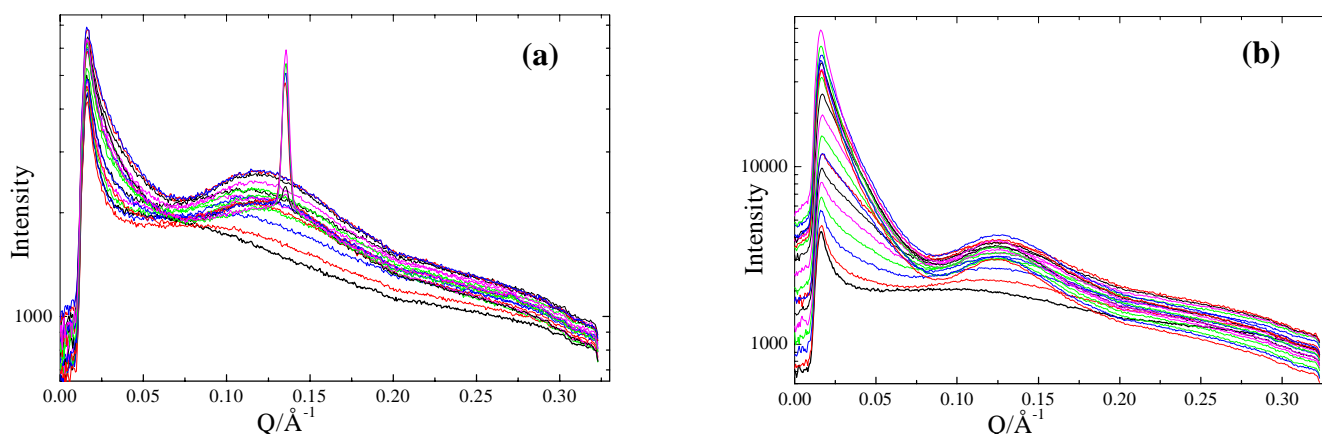
This experiment was a continuation of a previous experiment (SC740) in which the development of mesophase surfactant-templated silicates in acidic solution was observed. Surfactant-templated silicates are composed of surfactant micelles encased in a silicate framework. Under some synthesis conditions the micelles order into hexagonal or cubic phases equivalent to surfactant liquid crystalline phases in water.¹ Under other conditions, wormlike phases are formed. In acid catalysed syntheses the structures formed are well-defined not only on the nanometer length scale, but also on much larger length scales, forming solid thin films across the entire area of solution, or monodisperse spheres, ropes or faceted “single crystals” of mesophase silica-surfactant composite.² The formation mechanisms both at the mesoscale and for larger scale structures are not well understood. We have studied the time evolution of solution structures in several areas of the phase diagram in order to determine the differences between formation mechanisms at the nanoscale which drive the formation of the various macroscale morphologies.

From time-resolved reflectivity experiments with 1 minute time resolution carried out on Troika II³ we have observed two distinct mechanisms for film formation at different concentrations of the silica source, TMOS.⁴ At higher TMOS concentrations, film growth occurs at the surface of solution, and the nucleation and growth of ordered mesophase domains can be observed. At lower TMOS concentrations however, film growth appears to be bulk-driven, with preformed mesophase particles packing together at the interface; no evolution in mesophase structure or domain size in the film is observed. Our experiment on BM26B was therefore concerned with mapping the solution-phase evolution of structure in order to confirm and extend our results from the reflectivity experiments.

We carried out time resolved SAXS experiments on solutions containing molar ratios of surfactant : water : HCl : TMOS, of $1.52 \times 10^{-3} : 1 : 3.63 \times 10^{-3} : X$ where X varies between 0.005 and 0.02. We varied the surfactant used by changing both the surfactant headgroup – from cetyltrimethylammonium (CTA) to cetylpyridinium (Cp) – and by changing the anion from bromide to chloride. Finally we varied the acid concentration from 0.2M to 0.6M, since for 0.6M HCl all surfactants produced highly ordered mesostructured films in the reflectivity experiments, whereas at 0.2M HCl, only films templated with surfactants containing bromide anions produced ordered mesostructures. Films containing the chloride surfactants at 0.2M HCl did not develop sharp diffraction peaks, although a broad correlation bump was observed. SAXS measurements were taken at 5 min intervals, every 10 min. To maximise use of the beam time, two samples were mounted at once and measurements taken by swapping between them every 5 min. As structure development takes place over several hours this did not entail a significant loss of time resolution. Scattering patterns were measured until precipitate formed in solution – this precipitate occurs simultaneously with film formation and was taken to mark the end of observable structure development in solution.

The SAXS experiments showed clear differences between the solution phase structure development for different TMOS concentrations. At lower TMOS concentrations, we observed development of a broad correlation peak, which then decreased in intensity again, followed by the development of two or three orders of diffraction corresponding to formation of particles containing a hexagonal mesophase (see Figure 1a). In solutions at higher TMOS concentration, the correlation peak appeared in the subphase solution, but no diffraction peak was observed, even when precipitate was present in the capillary (Figure 1b). Changing the surfactant headgroup and counterion altered the time required for the precipitate to form, and also altered the mechanism between the two observed for different TMOS concentrations. In some cases the diffraction peaks grew in on top of the correlation peak, indicating the presence of both free micelles and mesostructured particles in solution. SANS results with much lower time resolution have suggested an ellipse to cylinder transition in this system,⁵ and modelling of this X-ray data with much better time resolution is currently proceeding.

Figure 1: SAXS patterns taken from solutions containing (a) CTABr/TMOS=0.277 (b) CTABr/TMOS=0.093. Patterns are shown at 45 min intervals, so that the trends in structure development are easier to see.



References

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