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Report:

The aim of these experiments is to study the growth of surfactant templated silica composites in acidic solutions in order to discover the solution processes that lead to the development of particular macroscopic morphologies. These materials are formed by the polymerization of silica around surfactant micelles in solution to form composite solids containing a channel system that has the dimensions and connectivity of a surfactant liquid crystalline phase.[1] They have many potential applications: as thin films or monoliths for filtration, as high surface area spheres, powders and "single crystals" with applications in chromatographic separations, as heterogeneous catalyst supports and in nanotechnology. We are, in particular, interested in the solution processes which occur in the subphase during formation of thin films of these composites. As a result of experiments using cationic cetyltrimethylammonium bromide (CTAB) as the templating surfactant we put forward a model of silica-surfactant interaction that suggested the polymerising silicate in this acidic system acts in a similar fashion to a branched polyelectrolyte interacting with surfactant micelles.[2] Mesostructured film formation occurs at the surface of these solution for a wide range of concentrations, however the mesostructure development follows either a surface-driven or a bulk-driven pathway.[3] Under a narrow range of concentrations corresponding to bulk-driven film formation, mesostructured particles formed in the subphase of this solution, characterised by the development of sharp diffraction peaks in SAXS or SANS patterns.[4] At concentrations outside this range, only elongated silica-coated micelles were observed in solution. This behaviour is similar to coacervate formation observed in polyelectrolyte-surfactant systems.

This experiment studied two directions derived from this previous work. We studied first the replacment of the cationic CTAB with increasing amounts of the nonionic surfactant polyoxyethylene (10) cetyl ether (Brij 56) which is known to form mixed micelles with CTAB in order to observe the effect of changing the charge on the micelle. These experiments showed rapid development of silica coated micelles in solution, but no development of sharp diffraction peaks for the range of concentrations investigated, suggesting film formation in these systems is largely surface-driven at the chosen acid
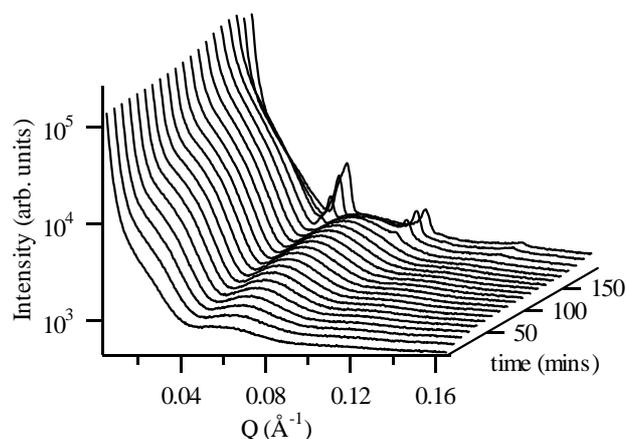
concentration of 0.2M HCl. Previous experiments on BM26B at 0.6M HCl using Brij 56 alone showed development of sharp diffraction peaks in solution, indicating a strong effect of pH which will be the focus of future experiments and also the subject of a reflectivity experiment on ID10B in November this year.

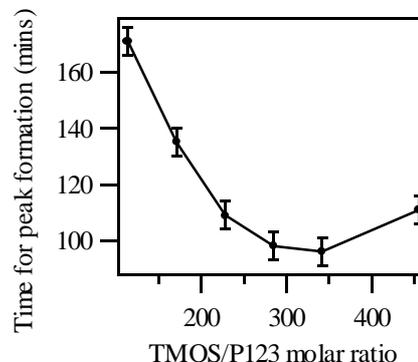The second direction of study, on the use of Pluronic P123 triblock copolymer, itself a polyelectrolyte, as the surfactant template $(EO)_{20}$-$(PO)_{70}$-$(EO)_{20}$, gave more interesting patterns and the reactions proceded more quickly making it possible to collect a detailed set of data. In these solutions well-ordered mesophases developed in the subphase over a wide range of silica:surfactant ratios, even though homogeneous film formation in this system is observed in only a small range of concentrations. The solutions initially show a broad correlation peak characteristic of scattering from micellar solutions centred around 0.063 Å^{-1}, and sharp diffraction peaks grow in around 0.050 Å^{-1} after the end of the induction

Figure 1: Development of diffraction peaks in a solution containing molar ratios of P123: water: HCl: TMOS of 0.95×10^{-4}: 1 :3.6×10^{-3}: 0.011.

period (Fig. 1). The d-spacing of the first order peak increases slightly with increasing silica:surfactant ratio. The mesophases can be indexed as lamellar or hexagonal phases, depending on the concentration of TMOS and P123 present in the solution. The lamellar phase was only observed for a relatively high absolute surfactant concentration, at low silica:surfactant ratios. In most cases the hexagonal phase was formed, with frequently only the 100, 110 and 210 peaks present, with the 200 peak missing, indicating a relatively thick silica wall, developing in these materials.[5] Overall the peak development was faster for *lower* absolute P123 concentrations. And, interestingly, similar to the CTAB-TMOS system, the length of the time for diffraction peak development shows a horse-shoe shaped dependence on silica-surfactant molar ratio (Fig. 2). This suggests that although in this case the dominant

Figure 2 Time for formation of diffraction peaks at a constant P123 concentration of 5.5×10^{-3}M.

interactions between template and silicate are not electrostatic and the mesostructure formed does not easily segregate into films , similar factors must govern the self-assembly processes producing ordered mesostructures in this system as for TMOS-CTAB.

References:

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