ESRF	**Experiment title:** Silica as a polyelectrolyte – Effects of ionic strength and micelle charge on surfactant-templated film formation	**Experiment number**: CH-1553
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Names and affiliations of applicants (* indicates experimentalists):

*Dr. Karen J. Edler (Chemistry Department, University of Bath)

*Dr. Stephen J. Roser (Chemistry Department, University of Bath)

*Ms Cristina Fernandez-Martin (Chemistry Department, University of Bath)

*Mr Roland D. Wilson (Chemistry Department, University of Bath)

Report:

This experiment is part of a series of experiments which we are carrying out in order to understand the formation mechanisms in surfactant-templated inorganic materials. From our earlier experiments on silica film formation in these systems we have been able to propose a detailed mechanism for the self-assembly process. Our suggested mechanism of film formation implies that the polymerising silica acts as a branched polyelectrolyte during the self-assembly process, and in this experiment we wished to test this theory by investigating the effects of using mixed micelles to vary the charge density per micelle and by changing the micellar charge by addition of salts. Both systems were initially studied using Brewster angle microscopy (a technique with micron scale resolution) to determine film formation times. The experiments on ID10B enable us to study formation of the mesoscale structure within the films, and its evolution with time, with 60s time resolution.

In the current set of experiments we began with investigation of mixed micellar systems using dilute acidic solutions of the cationic surfactant cetyltrimethylammonium bromide (CTAB), and the nonionic surfactant octaethyleneglycol hexadecylether (OEGC) at three different molar ratios (0.3, 0.4 and 0.5 OEGC/CTAB). These surfactants are known to mix ideally in micelles. Tetramethoxysilane was used as the silicate source, at three molar ratios of silica: total surfactant (10.82, 7.25, 3.61). As before we see two different mechanisms of film growth. After the induction period the film mesostructure either develops rapidly showing sharp peaks which grow in intensity, but have constant width, or slowly developing a broad bump in the position of the first order peak which gradually increases in intensity and either decreases in width to form a diffraction peak or a sharp peak eventually grows in on top of the broad peak. Interestingly in this set of samples, in cases where the film develops through rapid growth of sharp peaks, the time for diffraction peaks to appear proved to be 2-3 hours faster than was required for a macroscopic film to appear at the air-solution interface in preliminary Brewster angle microscopy (BAM) experiments. On the other hand where the film mesostructure develops slowly from a broad bump, the broad

feature appears around the same time as a film was observed in the BAM measurements but the time until sharp peaks form is 2-3 hours longer. This data implies that these films templated by mixed micelles form at the surface some time before the well-defined mesostructure develops. Since this slow growth and ordering mechanism occurred more frequently in the solutions we studied, we ran out of time to study salt effects, preferring to collect a complete data set for the mixed micelle system.

In the mixed micelle solutions rapid development of sharp peaks was observed for the lowest silica concentration at all OEGC/CTAB ratios, and at the intermediate silica concentrations, for the highest OEGC/CTAB ratio. The slower development of the mesostructure from broad peaks occurred for high silica concentrations and lower OEGC/CTAB ratios. The sharp peak development implies that film growth is driven by aggregation at the surface of mesostructured particles which formed initially in the bulk solution, while the broad bump implies film growth through aggregation of individual silica-coated micelles at the solution-air interface, in line with our previous results.[1] Thus it seems that for highly charged micelles, silica concentration has the most important effect on growth mechanism. However as the micelles become less charged through incorporation of nonionic surfactant, film growth switches from bulk driven to surface driven at intermediate silica concentrations. In solutions containing only noninonic micelles, the mechanism is bulk-driven at all three silica concentrations.

This sensitivity of the mechanism towards micelle surface charge, suggests that the interaction between silica polymer and surfactant is at least in part electrostatic, and similar to polyelectrolyte-surfactant interactions. When the charge on the micelle is reduced, the formation of phase separated particles in solution occurs at lower TMOS concentrations implying less silica polymer is required to enable the silica-surfactant complexes to collapse together into particles. For films which grow through the surface driven mechanism, when the micelles have a lower surface charge, a film is visible at the surface for some time before the well-ordered mesostructure develops. Micelles with a lower surface charge will have a shorter range electrostatic force driving ordering so possibly in this case the mesostructure does not order until the entangled micelles are drawn close together by continuing silica polymerisation and dehydration of the film at the interface. However these effects do not explain the return to the bulk-driven mechanism for the fully nonionic surfactant system, and we are continuing to work to understand the interactions during formation of these films.
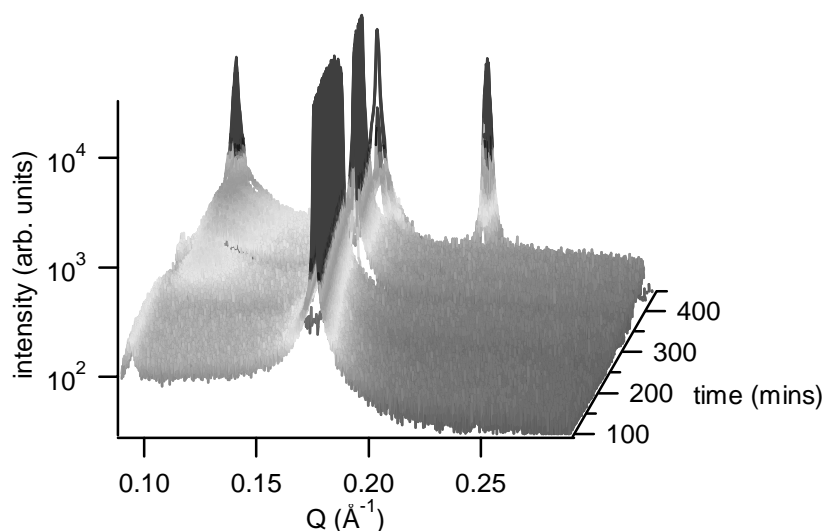

Fig 1: Development of diffraction peaks on either side of the initial specular peak for a solution containing 0.3 OEGC/CTAB, 0.54M TMOS in 0.2M HCl. A broad bump forms in the position of the first order diffraction peak prior to the appearance of the sharp diffraction peaks indicating formation of an ordered mesophase.

References:

(1)   Brennan, T.; Hughes, A. V.; Roser, S. J.; Mann, S.; Edler, K. J. *Langmuir* 2002, *18*, 9838-9844.