ESRF	**Experiment title:** **Structural control of mesophase silica-surfactant films**	**Experiment number**: CH-1120
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Report:

This experiment is a continuation of a series of experiments studying the growth thin films of mesophase silica at the solution/air interface. These films grow from dilute solutions of surfactant, a silica source (tetramethoxysilane) and HCl as a catalyst. Previous experiments have looked in detail at the nucleation and growth of surfactant-templated silica films using cetyltrimethylammonium bromide (CTAB) as the templating surfactant, discovering a concentration dependent formation mechanism. In the current experiment, we have studied the effect of altering either the counteranion (from bromide to chloride ie CTAB to CTACl), the effect of changing the structure of the headgroup of the surfactant (from cetyltrimethylammonium to cetylpyridinium ie CTAB to CpBr) and finally the effect of mixtures of either the anion or the headgroup on the growth kinetics and resultant film structure. We also measured the grazing incidence diffraction patterns in the x-y plane for several films *in situ* after they had grown. GID measurements were taken both for angles above the critical angle where the penetration of the X-ray beam is small, and at a higher angle in order to compare surface structures with those found deeper in the film.

Using the off-specular reflectivity measurement outlined in previous reports we can collect kinetic data for structure development in the z-direction with extremely high (1 minute) time resolution from these syntheses.[1] Changing the counter anion of the surfactant from Br^- to Cl^- caused a marked slow down in the induction period required before film formation occurs. At low HCl concentrations, the mesophase in the surfactant templated films was much less well organised for the CTACl surfactant than for CTAB equivalent,

however raising the HCl concentration improved the mesophase ordering (see Fig 1). Changing the headgroup from the quaternary ammonium to the pyridinium cation resulted in an increase in the rate of film formation while retaining good mesophse order. At low acid concentrations the CpBr had a tendancy to co-crystallise at the surface of the solution, forming patterned regions of two dimensional lamellar surfactant crystals phase separated from, but connected to the silica-surfactant film.

A grazing incidence X-ray diffraction pattern from the interior of a mesophase silica film templated with CTAB is shown in Figure 2. This pattern shows the structure in the depths of the film which has distinct differences from the structure observed at the air-film surface. At the air surface, well-defined diffraction spots indicate a single domain hexagonal film. A shift in d-spacing from the hexagonally ordered peaks visible in the higher angle pattern occurs, indicating that the drier surface, close to the air interface has undergone a distortion from true hexagonal packing. Also an intriguing vertical feature with a *ca* 100Å repeat distance appears in the pattern from the bulk film which does not appear at the surface.[2] Work is continuing to determine the origin of this feature.

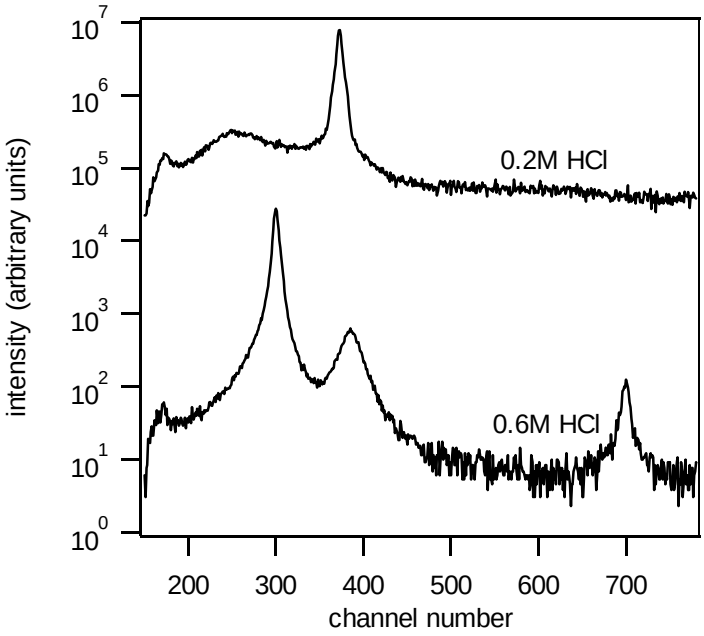

Figure 1: *Initial and final off-specular scattering pattern showing structure in the z-direction from a film templated with CpCl at 0.6M HCl and 0.2M HCl. The sharp peak in the 0.2M pattern is the specular reflection peak from the interface. It is also obeserved at the same channel position in the the final pattern from the 0.6M solution, however it has broadened and decreased in intensity indicating significant surface roughening occuring along with development of mesostructure peaks.*

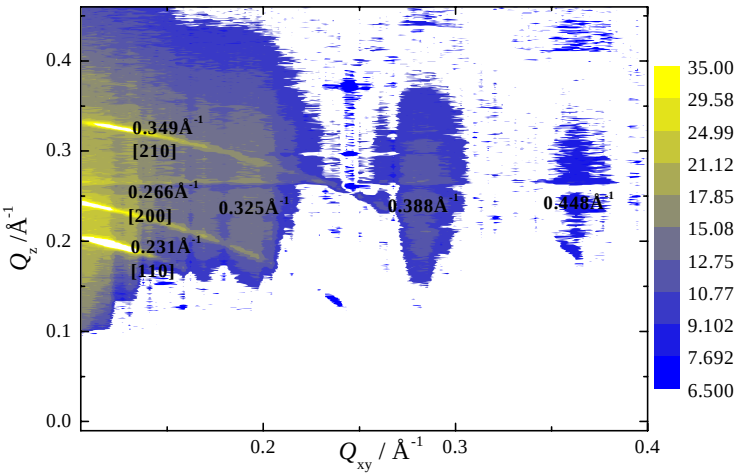

Figure 2: *GIXD pattern taken from a mesophase silica-surfactant film templated with CTAB, incident angle 1.27° showing the vertical features with a 100Å repeat distance. Peaks have been indexed to the hexagonal lattice.*

References:

(1) Edler, K. J.; Goldar, A.; Hughes, A. V.; Roser, S. J.; Mann, S. "Structural studies on surfactant templated silica films grown at the air/water interface" *Microporous Mesoporous Mater.* **2001**, *44-45*, 661-670.

(2) Brennan, T.; Edler, K. J.; Roser, S. J.; Mann, S. "Characterisation of the structure of mesporous thin films grown at the air/water interface using x-ray techniques" *in preparation* **2002**.