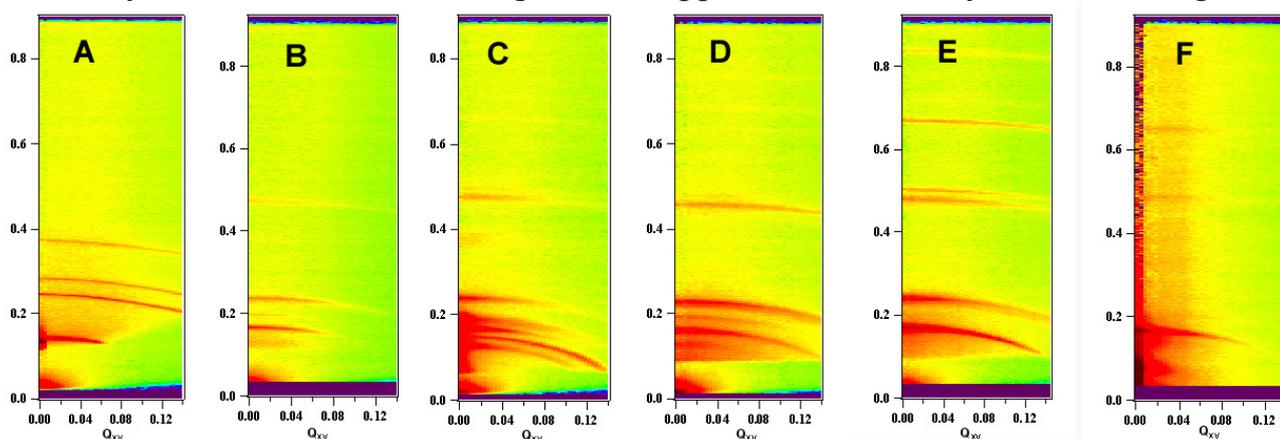




	<b>Experiment title:</b> Polyelectrolyte-surfactant films as templates for inorganic oxides	<b>Experiment number:</b> CH-3068
<b>Beamline:</b> ID10B	<b>Date of experiment:</b> from: 23 June 10                      to: 29 June 10	<b>Date of report:</b> 6/8/2010
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr Alexei Vorobiev	<i>Received at ESRF:</i>
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### Report:

In this work, we continue our investigations into polymer-surfactant complex templated inorganic films at the air/water interface. Our group has extensively researched the self-assembly of silica-surfactant films at the air-solution interface.<sup>1-3</sup> Recently, we have also been studying mesostructured polymer-surfactant films formed at the air-solution interface which were inspired by our silica-surfactant work.<sup>4</sup> We have found two classes of polymer-surfactant film, the first, cationic surfactants with polyethylenimine (PEI) produces optically clear, thinner membranes,<sup>5</sup> however if cat-anionic surfactant mixtures are used, thick, opaque films form with a wide range of polymers, making this a more versatile system.<sup>6</sup> Previously we mineralised PEI/cetyltrimethylammonium bromide (CTAB) films to make highly ordered 2D hexagonal silica films at the air-solution interface. These can be pulled off the interface as a self-supporting film and are stable to calcination or template removal by washing.<sup>7</sup> We have also now made silica films at the solution interface templated on cat-anionic CTAB/sodium dodecylsulphate (SDS) mixtures with various polymers. The inorganic species deposit in polymer hydrogel regions of the film, around arrays of ordered micelles. This work provides an easy way to introduce a polymer into the inorganic film to make it robust and mechanically strong, but also to incorporate polymer into the silica wall to enhance its functionality which could be advantageous for applications in catalysis and sensing.

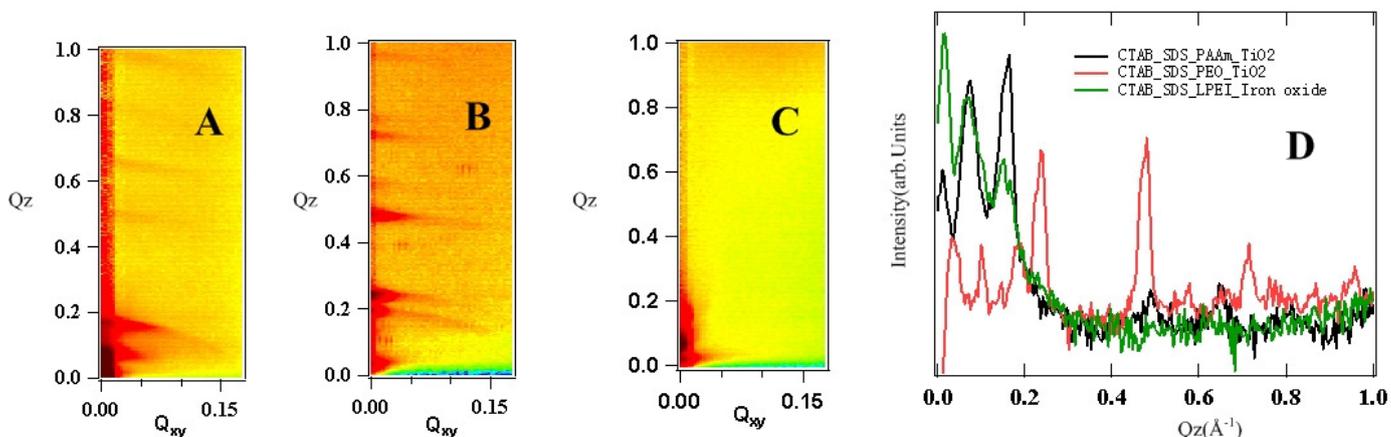


**Figure 1** Typical GID patterns collected on interfacial CTAB/SDS-polyelectrolyte-silica films. (CTAB:SDS molar ratios and polymer concentrations in g/l are: A: CTAB:SDS=8 20SPEI, B: CTAB:SDS=4 10SPEI, C: CTAB:SDS=4 40SPEI, D: CTAB:SDS=4 10LPEI, E: CTAB:SDS=2 20LPEI, F: CTAB:SDS=2 30PAAm)

In this experiment ID10B (Trokia II) was used to measure time-resolved off-specular reflectivity of films growing at the air/water interface. Once the films were formed, we carried out reflectivity and grazing incidence X-ray diffraction (GIXD) measurements on the mature inorganic films to obtain structural details of the phases within the films. CTAB/SDS mixtures with polyethylenimine (PEI), polyacrylamide (PAAm) or polyethylene oxide (PEO) were used as co-templates, three inorganic precursors (tetramethoxysilane (TMOS), titanium butoxide (TiB) and ferric chloride ( $\text{FeCl}_2$ )) were used as mineralising agents. CTAB:SDS surfactant ratios ranged from 1:2 – 1:8, and polymer concentrations varied from 10g/l - 40g/l.

The results indicate that the chemical nature of the polymer, its solution concentration and the cat-anionic molar ratio have strong effects on the phase behaviour in the silica films. GID patterns in Fig 1 show typical structures, assigned as (from A to F) 2D hexagonal,  $Pn\bar{3}m$ ,  $Fm\bar{3}m$ ,  $Pn\bar{3}m$ ,  $Im\bar{3}m$  and lamellar mesophases. Changes in micelle interfacial curvature with reagent concentration are thought to be responsible for the observed transitions in polymer-silica film mesophases.<sup>8</sup>

The mineralization has also been extended to titania and iron oxide films. Figure 2A & B show typical GID patterns collected for CTAB/SDS-PAAm-titania and CTAB/SDS-PEO-titania films respectively. Titania with PAAm, Fig 2A has two distinct peaks at  $0.075\text{\AA}^{-1}$  &  $0.160\text{\AA}^{-1}$  suggesting a lamellar phase (Fig 2D black line), while titania films made with PEO display a cubic structure, the first few peaks at  $0.101\text{\AA}^{-1}$ ,  $0.148\text{\AA}^{-1}$  &  $0.180\text{\AA}^{-1}$  are assigned as the (110), (200) and (211) reflections of the  $Im\bar{3}m$  space group, with a d-spacing of  $62.2\text{\AA}$  (Fig. 2D red line). GID patterns of iron oxide films display two peaks at  $0.073\text{\AA}^{-1}$  and  $0.149\text{\AA}^{-1}$ , typical of a lamellar phase with d-spacing of  $86.0\text{\AA}$ . This corresponds well to SAXS data from dry surfactant-polyelectrolyte-iron oxide films after recovery from the solution interface.



**Figure 2** Typical GID patterns collected on air/water interfacial CTAB/SDS-polyelectrolyte-inorganic films. (The molar ratios and polymer concentrations in g/l are as follows: titania A: CTAB:SDS=4 1.25wt% PAAm B: CTAB:SDS=8 2.5wt% PEO, iron oxide, SDS 0.02M 20LPEI, pH=12) D is the line profile at  $Q_{xy}=0.007\text{\AA}^{-1}$  from GIXD patterns A,B and C respectively.

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