



	Experiment title: Formation of Free-standing Solid Polyelectrolyte-Surfactant Mesostructured Films at the Air-Solution Interface	Experiment number: CH-1747
Beamline: ID10B	Date of experiment: from: 10 th to: 16 th November 2004	Date of report: 24 January 2005
Shifts: 18	Local contact(s): Dr Leide Cavalcanti	<i>Received at ESRF:</i>
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Report:

In this experiment thin films of a neutral polyelectrolyte (polyethylenimine – PEI) and a cationic surfactant (hexadecyltrimethylammonium bromide – C₁₆TAB) that form at the air-solution interface were examined using Grazing Incidence X-ray Diffraction (GIXD) and specular reflectivity on the Troika II beamline. Film formation between polyelectrolytes and surfactants is often achieved through a layer-by-layer deposition on a solid substrate. These films however are self-supporting, clearly visible to the naked eye and form spontaneously at the air-solution interface from the polyelectrolyte-surfactant solutions. This experiment follows up our preliminary experiments, in which it was shown that the micron thick films contain a well-ordered mesostructure formed from organised surfactant micelle arrays surrounded by the polyelectrolyte.¹

For these films we have previously demonstrated that the primary interaction is that of a neutral polymer with a cationic surfactant, however in the pH range used, the polymer in the films still carries a small net positive charge. We have shown that by manipulating the degree of charging it is possible to modify the ordering in the film.² A preliminary experiment performed at the ESRF also showed a pattern of diffraction spots, indicating that the ordering in these films is that of a hexagonal array of cylindrical micelles oriented with the long axis of the cylinder lying parallel to the air-solution interface.

In this experiment two polymer molecular weights (MW~ 750,000 – long and 2,000 – short) were used at various concentrations to determine the effect of both the polymer MW and concentration dependence of these films. Brewster angle micrographs indicate that films formed by long PEI are much thicker and have smoother surfaces than those prepared using short PEI. The C₁₆TAB concentration was constant at 0.04M, while the concentration of the PEI (expressed as molar concentration of monomer units, so that the two molecular weights can be directly compared) was varied from 1.4M to 0.088M. The effect of the charge on the polyelectrolyte on the structure of the films was also examined for a range of polyelectrolyte concentrations by adding 0.1 M sodium hydroxide to the solutions, which decreases the

charge on the polymer to approximately zero. We also studied the effect of changing the humidity of the atmosphere above the films on the mesostructural ordering.

Preliminary analysis of the data (Figure 1) indicates that there is a strong polymer MW dependence for nanoscale ordering in these films. Those films prepared with long PEI are less ordered (generally exhibiting only a single powder ring in the diffraction pattern) than those prepared using short PEI. There is also an increase in the level of observed order for both molecular weights as the concentration of polymer (at constant surfactant concentration) is decreased. There appears to be an optimum concentration of PEI around 0.175M for the short polyelectrolyte, since beyond this point the ordering decreases again, however we did not go low enough in polymer concentration to observe this for long PEI – for this molecular weight ordering was still improving at 0.088M PEI, the lowest concentration measured. Consistent with the fact that the primary interaction between the polymer and surfactant is a neutral/cationic interaction the order of the films improves upon the addition of sodium hydroxide to the films. The removal of residual charge from the polyelectrolyte allows the charged surfactant micelles to form a more ordered array within the film.

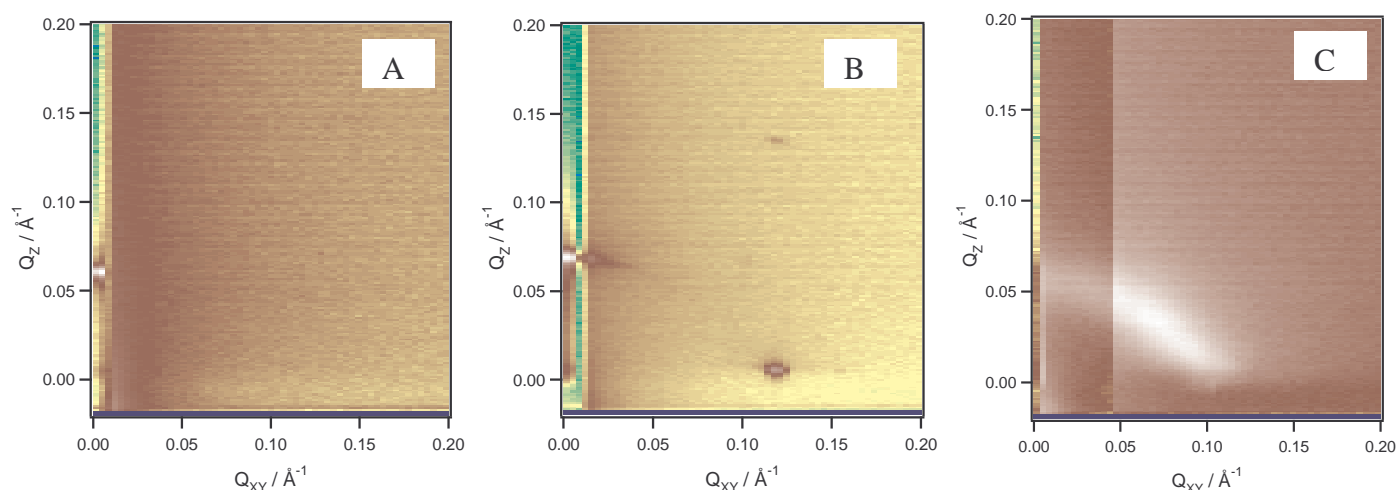


Figure 1: GIXD patterns of short PEI (0.088M) and C₁₆TAB (a) without added NaOH, (b) with added NaOH, and (c) long PEI and C₁₆TAB without added NaOH. No absorber correction has been made to the patterns.

Experiments on the effect of the humidity of the atmosphere above the films showed that ordering in the films is directly related to the humidity. At high humidities the sharp diffraction peaks observed in specular reflectivity patterns gradually disappear over ~1 hour, leaving a pattern characteristic of the air-water interface of a surfactant only solution. Reducing the humidity to ambient (~21% RH) caused the diffraction peaks to re-form within minutes. Evaporation must obviously therefore play an important role in forming and maintaining the ordered films at the interface.

References:

- (1) Edler, K. J.; Goldar, A.; Brennan, T.; Roser, S. J. *Chem. Comm.* **2003**, 1724.
- (2) O'Driscoll, B. M. D.; Milsom, E.; Fernandez-Martin, C.; White, L.; Roser, S. J.; Edler, K. J. *Macromolecules* **2005**, in preparation.