



	Experiment title: Encapsulation of hydrophobic material in mesostructured polyelectrolyte-surfactant films	Experiment number: CH-2281
Beamline: ID10b	Date of experiment: from: 13/12/06 to: 18/12/06	Date of report: 18/1/07
Shifts: 15	Local contact(s): Oleg Kononov	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Karen Edler - University of Bath, UK* Benjamin O'Driscoll - University of Bath, UK* Adrian Hawley - University of Bath, UK*		

Report:

We are studying the formation of novel polyelectrolyte-surfactant films at the air-solution interface in order to understand why they form, and to investigate possible applications of these films in encapsulation and release systems. In a previous neutron reflectometry experiment we observed that the addition of hydrocarbons to cetyltrimethylammonium bromide (CTAB)/polyethylenimine (PEI) aqueous solutions (which spontaneously form films at the air/water interface) resulted in a number of interesting changes in the film structure. These changes suggested that hydrocarbons are incorporated into the hydrophobic region of the CTAB micelle and therefore into the film, however despite this positive result many questions remained regarding the magnitude and exact nature of the structural changes observed in the films.

For this experiment we therefore chose to examine the structural changes in films of CTAB with 25,000 Da (medium, M-)PEI and 2,000 Da (short, S-)PEI upon the addition of the hydrocarbons: benzene, decane, cyclohexane and cyclohexanol. Relating to our earlier experiments we chose to use hydrocarbon contents (as a volume % of the micelle core) of 27, 30, 30 & 30% respectively. The CTAB concentration was 0.037M and the PEI concentration 15 g/L. For each film a reflectivity

pattern was initially taken, followed by grazing incidence diffraction at an incident angle of 0.13° and at the angle of the first order diffraction peak measured in the reflectivity pattern. This probes further into the film, and allows us to compare surface structures with those deeper in the developing films.

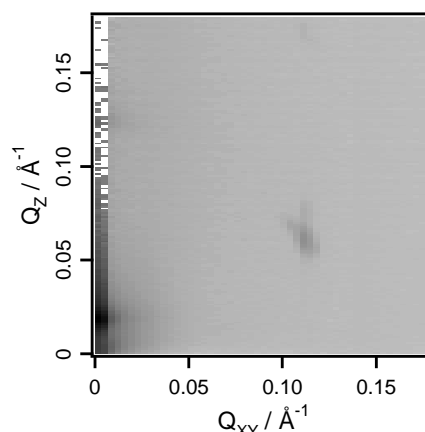


Figure 1. GID pattern of the CTAB: S-PEI: Cyclohexane Film (incident angle = 0.13°)

The addition of benzene, cyclohexane or cyclohexanol to either the M-PEI or S-PEI did not result in any significant changes to the ordering of the sample. For the S-PEI films the principle feature in the grazing incidence diffraction (GID) patterns is a single spot, which corresponds to an ordered and aligned 2D hexagonal phase (Figure

1). For the M-PEI films a hexagonal phase is also observed however in these films the GID pattern shows only a single diffraction ring, indicating the presence of an ordered but non-aligned phase.

Notably for the S-PEI film, without added hydrocarbon the structure in the films disappears with time, but this is not always the case when a hydrocarbon was present. For the S-PEI: cyclohexanol film in particular, good structure is maintained in the film throughout the experiment; suggesting that this film is thicker and more stable than the hydrocarbon-free film. In this case therefore incorporation of the hydrocarbon enhances the properties of the film.

The most significant changes were observed when n-decane was added to the systems. With M-PEI there was a distinct broadening of the diffraction ring observed in the GID pattern. This would usually indicate a loss of ordering within the film, however for film with S-PEI the initially broad diffraction ring resolved into the three rings of the Pm3n cubic phase in the second GID pattern recorded at higher incident angle (Figure 2).

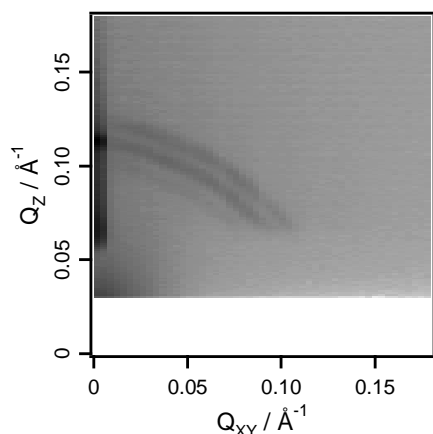


Figure 1. GID pattern of the CTAB: S-PEI: Decane Film (incident angle = 0.80°)

Cubic phases have previously been observed to form in these film when very thick films are formed. Here however it appears that the micelles preferentially form spherical micelles in the film when decane is incorporated, as the lattice spacing determined for this sample was 126 \AA , approx. 10 \AA greater than previously observed for cubic phases in these films, suggesting that the micelles are swollen with hydrocarbon. An increase in volume in the micelle core, without altering the headgroup charge, is expected to cause micelles with higher curvature to form, thus the cubic phase present in these films is consistent with incorporation of hydrocarbon inside the micelles.

In this experiment measurements were also performed on a number of cationic surfactant-polymer films. We previously observed that highly structured films were formed using an over-positive CTAB/sodium dodecyl sulphate (SDS) vesicles and polyacrylamide (PAAm),¹ and we wished to examine these films further.

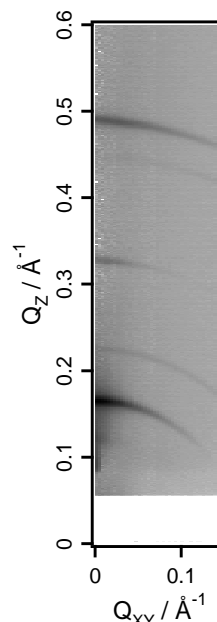


Figure 3. GID pattern of the 0.03M DMHA, 0.02M SDS, 1 wt% PAAm, 0.01M NaBr film (incident angle 1.16°)

One of the more interesting results obtained was the ability to maintain this high-level of (non-aligned lamellar) ordering, while replacing the CTAB with dimethylhexadecylamine hydrobromide (DMHA) (Figure 3). Unlike CTAB, DMHA does not carry a permanent positive charge and as such is far less toxic and that ability to use this as a substitute makes the eventual application of this research far more likely. Encapsulation in these cationic films was also investigated and the results similarly suggested that hydrocarbons can be incorporated into the hydrophobic regions of the surfactant phase without significantly affecting the structure of the films. Further work will study the release of hydrophobic species from the films triggered by changes in pH and salt content of the subphase.

References

- (1) O'Driscoll, B. M. D.; Nickels, E. A.; Edler, K. J. *Chem. Commun.* **2007**, DOI: 10.1039/b614224a