	Experiment title: Effects of polymer branching and hydrophobic species in formation of polymer-surfactant films	Experiment number: SC-2706
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Shifts: 18	Local contact(s): Dr Armajeet Singh	
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Report:

This experiment aimed to investigate the effect of incorporation of hydrophobic and slightly amphiphilic species in to the surfactant within polymer-surfactant films. Our group is currently investigating the design, formation and characterisation of surfactant templated polymer-surfactant films that form spontaneously at the air-water interface upon mixing of aqueous polymer and surfactant solutions. This method of structured film formation offers a compelling alternative to more labour intensive methods such as layer-by-layer deposition or spin coating.

Our initial film forming system comprised of mixtures of cationic surfactant hexadecyltrimethylammonium bromide (CTAB) and polyethylenimine (PEI). We found it possible to cross-link the PEI within the films using ethylene glycol diglycidyl ether (EGDGE) to enable robust film removal and determined that the film structure was 2D hexagonal close packed (CH2281 Dec 06)¹. More recent experiments showed that it was possible to form films from mixtures of cationic surfactant CTAB and the anionic surfactant sodium dodecyl sulfate (SDS) and a wider variety of biocompatible polymers such as polyacrylamide (PAAM). In these experiments we found it possible to achieve continuous 3D cubic structures by variation of the surfactant ratios (and therefore surfactant micelle curvature) and electrostatic architecture of the polymer (SC2452, Jul 08)².

We have begun investigating the incorporation of hydrophobic and slightly amphiphilic species into the hydrophobic core of the surfactant micelles in the polymer-surfactant as we intend to utilise our film forming systems as a drug delivery system. Hydrophobic species are good analogues for drug molecules due to the similar partitioning between micelle and water phases exhibited by both kinds of molecule. Our initial experiments in this area consisted of incorporating species such as benzene, decane, cyclohexane and cyclohexanol into CTAB/PEI films. It was found that films with decane incorporated exhibited a micellar cubic phase whereas films with cyclohexane or cyclohexanol incorporated exhibited a more ordered 2D close packed hexagonal phase when compared to films comprised of just CTAB and PEI (CH2281, Dec 06)³. As we found it possible to form and rationally characterise films of different structures in earlier experiments though adjustment of the surfactant micelle

curvature (SC2452, Jul 08)² we have extended our studies on the encapsulation of hydrophobic species with these surfactants, chosen for their ability to form micelles with different surface curvature to that exhibited by CTAB; ie hexadecyltriethylammonium bromide (CTEAB) which exhibits greater surface curvature and didodecyltrimethylammonium bromide (DDAB) which exhibits less micelle surface curvature. The molecules chosen as hydrophobic and slightly amphiphilic were cyclohexane and cyclohexanol respectively.

We studied films formed from CTEAB, mixed DDAB/CTAB in the molar ratio 1:2 and DDAB with PEI, choosing these surfactant combinations to achieve a range of surfactant micelle curvatures. Surfactant concentration was kept constant at 0.05M and PEI concentration at 1.5% wt. Each film was investigated using x-ray reflectivity and grazing incidence x-ray diffraction (GIXD). Exact determination of the phase exhibited by each film forming system is on-going. However it can be seen that the addition of hydrophobic species into the hydrophobic core of the surfactant micelles has a direct effect on the mesophase of the films. For example CTEAB/PEI films exhibit a possible cubic phase (Fig 1A) with long range order evident from the periodic nature of the intensities in the GIXD. The addition of cyclohexane reduces the long range order but a different (also possibly cubic) phase exists in the CTEAB/PEI film (Fig 1B). With DDAB/PEI films a possible 2D hexagonal phase exists (Fig 1C) and the addition of cyclohexane has less of an effect on the mesostructure although changes are also evident in the GIXD (Fig 1D).

We originally intended to also investigate incorporation of the hydrophobic dye Nile Red into the films and the effect of other polymers on the film mesostructure. However, due to time constraints this was not possible as this experiment given block allocation with SC-2707, as requested by the review panel.

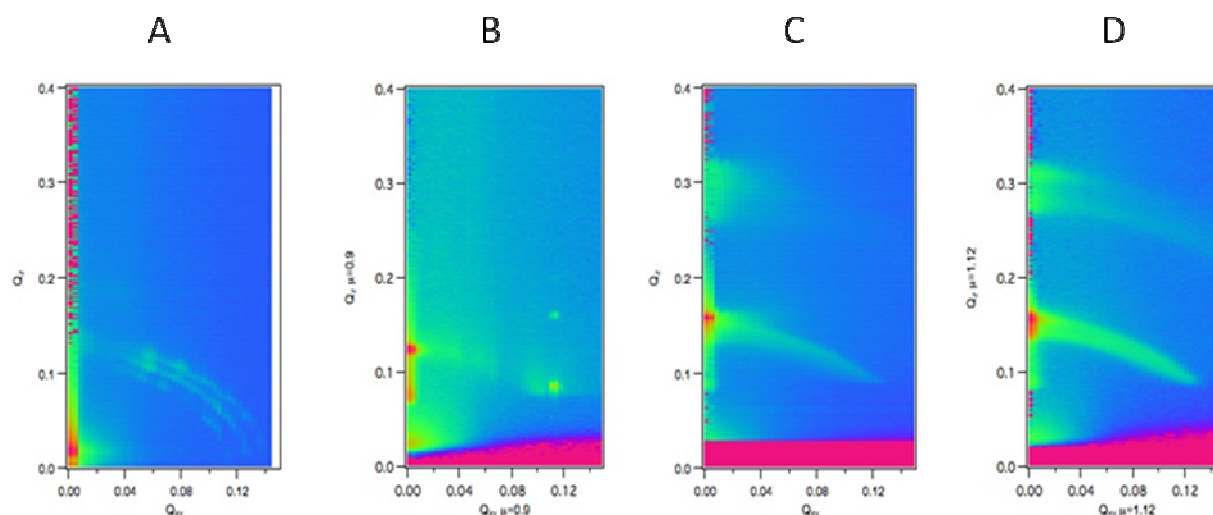


Fig 1. GIXD of films. CTEAB 0.05M PEI 1.5% wt exhibiting a cubic phase (A), CTEAB 0.05M PEI 1.5% wt with cyclohexanol exhibiting a different (cubic) phase (B), DDAB 0.05M PEI 1.5% wt exhibiting a possible 2D hexagonal phase (C) and DDAB 0.05M PEI 1.5% wt with cyclohexanol exhibiting a possible 2D hexagonal phase with higher order peaks more prominent (D)

References:

1. O'Driscoll, B. M. D., Fernandez-Martin, C., Wilson, R. D., Knott, J., Roser, S. J. and Edler, K. J., *Langmuir*, 2007, 23, 4589-4598.
2. Edler, K. J., Wasbrough, M.J., Holdaway, J.A. and O' Driscoll, B.M.D., *Langmuir*, 2008, 25, 4047-4055.
3. O'Driscoll, Benjamin M. D., Hawley, Adrian M. and Edler, Karen J., *J. Colloid Interface Sci.*, 2008, 317, 585-592.