



	Experiment title: Molecular criteria for aqueous boundary lubrication: <i>An XRR study of surfactant layer structures at mica-water interface</i>	Experiment number: SC-2575
Beamline: BM28	Date of experiment: from: 27 Nov 2008 to: 01 Dec 2008	Date of report: Feb 2009
Shifts: 15	Local contact(s): Dr. Laurence Bouchenoire	<i>Received at ESRF:</i>

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Report:

This has been a very successful and highly productive experiment in several aspects, as summarised below.

- 1) The measurements were carried out by using two liquid cells that house the samples. We designed and constructed the cells and the main body for which is shown in Fig. 2. They have been used for previous measurements (at ID10B) and will be used for future related measurements, and could also be adapted to neutron reflectometry experiments.

We carried out three different sets of experiments.

- 2) We studied the salt (NaNO_3) effect on the adsorption of three surfactants on mica: one hydrogenated gemini $((\text{C}_{12}\text{TAB})_2\text{-H}_{12})$ and two semifluorinated gemini F-spacer surfactants $((\text{C}_{12}\text{TAB})_2\text{-H}_{4}\text{F}_{4}\text{H}_{4})$ and $((\text{C}_{12}\text{TAB})_2\text{-H}_{3}\text{F}_{6}\text{H}_{3})$. As we increased the concentration of salt solution (20, 50, 100 and 200 mM) added to the surfactant solutions, by keeping the same surfactant concentration at 0.1 cmc, we found that the thickness and the density of the bilayer increased.
- 3) The second system we studied is the competitive adsorption between hydrogenated and semifluorinated single chain surfactants. We looked at three surfactants mixtures: C16TAB-F4H11(d)TAB, C16TAB-F5H10TAB and C18TAB-F8H6(d)TAB. We kept the total concentration

of surfactants mixture at 1 cmc, while varying the composition. We started with a composition of 100% hydrogenated surfactant and as we gradually add the semifluorinated surfactant we believe that they displace the hydrogenated surfactants as they adsorb more strongly.

- 4) Finally we looked at the interaction between three components: a polymer, Polyethyleneimine (PEI), a perfluorinated surfactant, Cesium Perfluorononanoate (CsPFN) and a salt, NaNO_3 . The effects of varying surfactant and salt concentrations were studied in the following sequence: i) 100 ppm PEI was adsorbed on mica. ii) 50 ppm PEI in water was injected in the liquid cell. iii) A mixture of 50 ppm PEI and CsPFN was added in different steps with increasing surfactant concentrations. iv) 50 mM NaNO_3 solution was added to the mixture varying the CsPFN concentration v) CsPFN concentration was kept constant and NaNO_3 concentration varied. vi) The system was rinsed and the sequence repeated from step iv). We found a quite dramatic response of the layer structure to the change in the solution conditions. Some reflectivity curves, for this system, are shown in Fig. 1. Distinct Keissig fringes are evident, and both the reflectivity and the fringe spacing vary as the concentration of the surfactant increases from 0.1 cmc to 1 cmc and as the 50 mM salt solution is added to the PEI-CsPFN mixture. We also observe some Bragg peaks, either due to multilayer formation or to liquid crystal formation of the CsPFN surfactant below its Krafft temperature. This is an interesting observation, and we would like investigate this effect further in possible future experiments.
- 5) We found that our local contact, Dr Bouchenoire, extremely knowledgeable and helpful. The beam alignment was non-trivial due our gently curved mica surface geometry. Dr Bouchenoire was very careful and patient with us.
- 6) Overall, we anticipate 3 manuscripts to be submitted as a result of every single set of experiment.
- 7) We find the analysis of the XRR data from mica non-trivial and are in the process of seeking help from several collaborators.

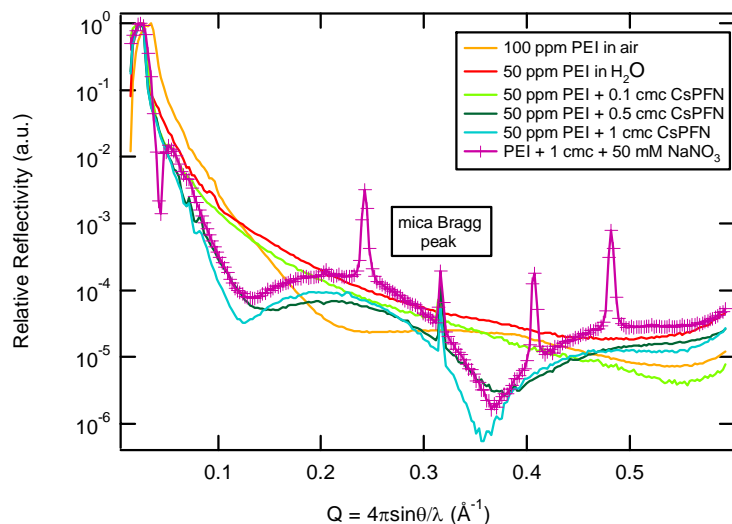


Fig. 1. Example XRR curves from the three component system in Study 3): polymer PEI, surfactant CsPFN and NaNO_3 salt solution on mica.

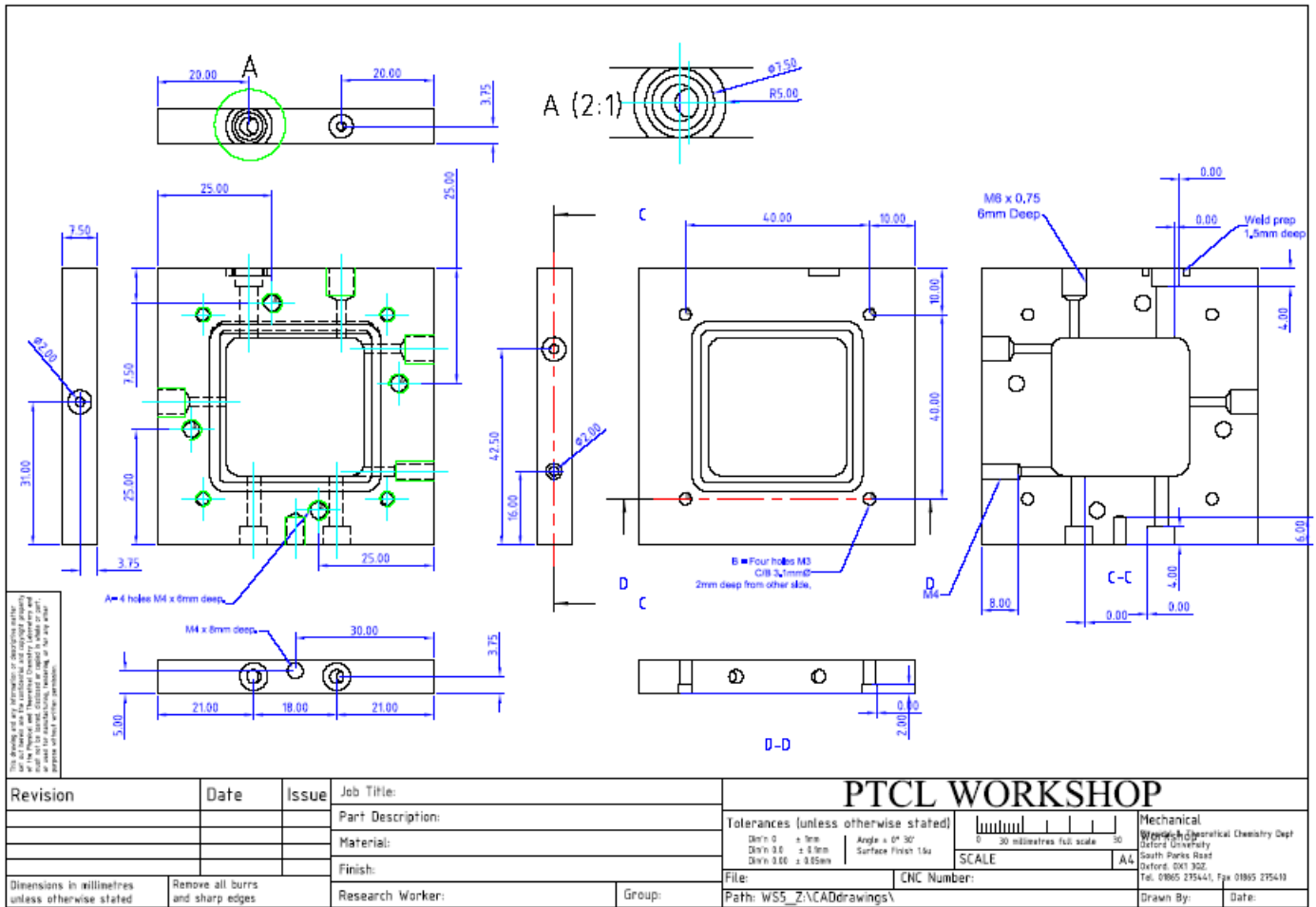


Fig. 2. Mechanical drawing for the main body of a liquid cell designed for BM28 beam line.