



<b>Experiment title:</b> In-plane structural study of liquid/liquid interface		<b>Experiment number:</b> SC -713
<b>Beamline:</b> BM32	<b>Date of experiment:</b> from: 5-07-2000 to:10-07-2000	<b>Date of report:</b> 23-08-2000
<b>Shifts:</b> 15	<b>Local contact(s):</b> Francois Rieutord	<i>Received at ESRF:</i>

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**Report:**

Recent measurements of aqueous surfaces and interfaces using sum-frequency spectroscopy (SFS) have revealed interesting ordering behaviour of water molecules. Evidence has been found suggesting that the structure of water is more ice-like (extensively hydrogen-bonded) at a bare oil/water interface than at its free surface. However, the presence of a charged monolayer at the free surface (as at the oil/water interface) leads to a field-induced alignment of water molecules in the sub-monolayer region. This alignment extends several nanometres into the bulk and appears to be ice-like in structure. Although the origin of these two ordering phenomena are different (hydrophobic effect *versus* electrostatic interactions) their manifestation, at least as far as the SFS spectra are concerned, is similar. Surface diffuse x-ray scattering measurements from the free surface of aqueous ionic surfactant solutions is a reasonable starting point for investigating the contribution to the x-ray scattering made by the ordered water. Extending the measurements to liquid/liquid interfaces is the broader outlook of these experiments.

In experiment SC-713 we have made in-plane x-ray scattering measurements from the free surface of an aqueous solution of the cationic surfactant cetyltrimmonium bromide ( $C_{16}TAB$ ). The solutions have a concentration  $\sim 0.5\text{mM} < \text{cmc}$ . The measurements were performed with an in-plane scattering vector range associated with the amorphous scattering peak of water and with x-rays with an incidence energy of 20 keV. In diffuse surface scattering experiments this amorphous peak arises from scattering associated with the path of the evanescent wave through the surface and immediate sub-surface fluid. Fig. 1 shows the surface scattering intensity as a function of in-plane scattering angle for scattering from the free surface of pure water. Fig. 2 shows an analogous spectrum for transmission through bulk water. Exchanging the pure water for a surfactant solution results in two features. First, the shape of the spectrum changes, which is most likely attributable to the change in scattering from capillary waves due to the lowering of the surface tension. Second, transient Bragg diffraction peaks are observed in the spectrum (Fig. 3). The temporal nature of the Bragg peaks is depicted in Fig. 4 for measurements made with the detector located at  $10.25^\circ$ . Similar plots are

found for other detector angles. Fig. 5 shows the analogous plot for transmission through the bulk solution; note that in scattering terms the origin of the Bragg peaks is apparently surface specific.

The origin of the 'crystals' which give rise to these Bragg peaks is now a point of further investigation. The measurements were performed at room temperature, which is coincidentally very close to the Krafft point for the  $C_{16}$ TAB solution. The Krafft point ( $T_k$ ) is the temperature at which the solubility limit of the surfactant in solution equals the critical micelle concentration. However, despite  $c < c_{mc}$  for these measurements, the fluctuations associated with the phase transition may still be present. If this is the case, the observations suggest that the crystals forming near  $T_k$  are either very surface active or possibly a pre-transitional crystallisation has taken place.

We now return to the issue of the water distribution. Addition of salt (0.1 M NaCl) to the solution should effectively screen the electrostatic interaction between the surfactant head groups and the surface water molecules. Fig.6 (ignoring the Bragg peak) shows that the addition of salt does in fact change the shape of the amorphous peak of water. However, this may be due either to water redistribution or possibly to a change in the distribution of surfactant molecules in the surface monolayer. Further work is necessary to resolve this.

Clearly this experiment has generated several issues that need to be resolved. Controlled experiments (embracing a temperature and composition range) on a surfactant exhibiting an experimentally convenient  $T_k$  should aid the understanding of the phenomenology associated with a Krafft point (i.e. continue studying CTAB since much complementary structural information is available from neutron reflection experiments). Similarly, experiments using a surfactant (e.g. sodium dodecyl sulphate) far away from a Krafft point would consolidate this information. In terms of the influence of charged headgroups on the arrangement of water near a surface, then experiments involving non-ionic surfactants and ionic surfactants with different concentrations ( $c < c_{mc}$ ) would be useful.

