ESRF	**Experiment title:** In-plane structural study of the liquid/liquid interface	**Experiment number**: SI-452
Beamline: ID10-B	**Date of experiment**: from: 09/06/99 to: 15/06/99	**Date of report**: 18/08/99
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Report:

Introduction: The sum frequency spectroscopy measurements by Richmond and co-workers have revealed some interesting structural features at liquid/liquid interfaces [1]. In particular evidence has been found suggesting the structure of water is very different at its free surface than at an interface with an insoluble liquid phase, e.g., CCl_4. It is found that the tetrahedral ordering of the water is more pronounced at the liquid/liquid (CCl_4/H_2O) interface, suggesting extensive hydrogen bonding and an 'ice-like' structure. Furthermore, the addition of ionic surfactants (e.g., sodium dodecyl sulphate) to the aqueous phase results in a charging of the interface leading to field-induced alignment of water molecules (observed as an increase of ice-like structure) which can be varied by:

(a) Surface concentration: the ordering increases with increasing surface charge up to an optimum surface coverage.

(b) Ionic strength: the ordering decreases with increasing ionic.

The aim of this current experiment was to assess the capability of in-plane diffraction/surface diffuse scattering to study the (possible) ice-like structure at liquid/liquid interfaces with and without the presence of surfactants.

Experimental: We examined two systems with Gibbs amphiphilic layers:

1. Sodium dodecyl sulphate, SDS, (0.5 mM) at the carbon tetrachloride/water interface;
2. Cetyl tri-ammonium bromide, CTAB, (0.6 mM) at the hexane/water interface.

The bare interfaces were studied first, followed by addition of the aqueous surfactant solution. For 2., NaCl (0.1 M) was further added.

In both systems grazing angles of incidence of ca. 0.025º were necessary. In this experiment we have used hard X-rays (24keV, from a C(111) monochromator) for the first time on the Troïka II beamline. In-plane scans (δ-scans) were performed and the scattered radiation was detected using a NaI scintillator detector with Soller entrance slits. With such a geometry only the in-plane component of the momentum transfer is scanned.

In these experiments it is necessary to correct for the bulk scattering from the incidence medium. Accordingly, scattering from the bulk incidence phases was measured by lowering the sample by 1mm and repeating the scans.

Difficulties and possible solutions: Surface diffuse scattering experiments from liquid/liquid interfaces have only recently been accomplished [2]. We encountered several difficulties which restricted the quality of the measured data. Small shifts in the synchrotron beam orbit meant that the beam profile (and hence relative scattering intensity) and alignment were not as constant as desired throughout a given experiment (this may be the penalty to be paid for operating at such shallow incidence angles.) Also, in total reflection geometry the scattering intensity was down by a factor of 3-4. Although there was a proportion of the beam transmitted straight through the sample the loss of intensity could also be attributable to an unstable liquid/liquid interface. For present purposes, we have accounted for the proportion of missing beam by normalising the data with respect to the alignment scans. Improved slit design and sample cell design may go some way to reducing these problems.

Improvements to the sample cell could also be made to suppress any possible long-wavelength vibrational modes at the interface by reducing the depth of liquid and following Schlossman *et al*. [3] and using angled windows to reduce meniscus problems. Steps could also be taken to reduce the background scatter [4].

Results and discussion: Despite the experimental difficulties expressed above the initial results show promise. In Figure 1 we show the change in shape of the amorphous peak for system 1. This peak is generally attributed to scattering from the bulk fluid visited by the evanescent wave. However, there are distinct changes in the shape of this peak that can be attributed to either enhanced ice-like ordering or else the presence of the surfactant. Additional reflectivity experiments (γ scans) would help clarify this situation. In Figure 2 we show the scattering spectra from system 2. The data for the surfactant-bearing solutions are noisy but display two features worth further investigation. First, there are some oscillations in the salt-containing system spectrum and, second, there is a relatively sharp peak displayed by the CTAB system without added salt. Following the logic of the SFS results [1], this peak could be a signature of ice-like ordering since it corresponds to a periodicity of ≈10Å; however, any changes to the monolayer structure upon addition of salt also needs to be clarified.

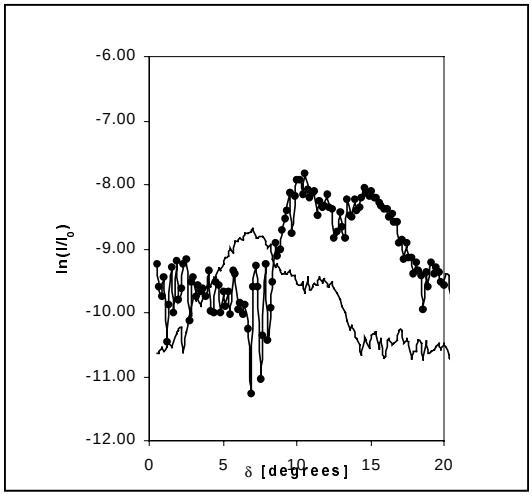

Figure 1. Carbon tetrachloride/water interface: ● bare interface; - with SDS.

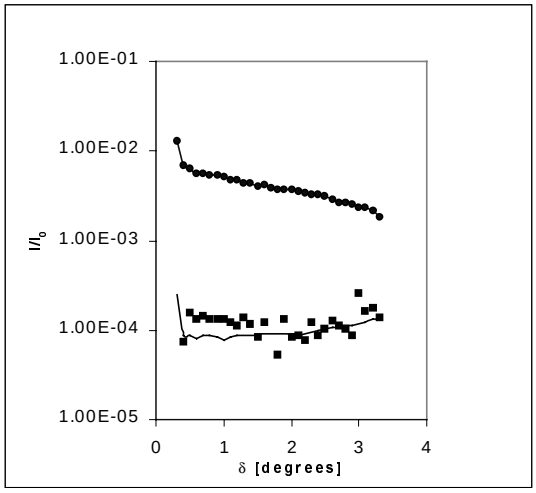

Figure 2. Hexane/water interface: ● bare interface; ■ with CTAB; - with CTAB and NaCl.

References

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[2] C. Fradin *et al*. *Langmuir* (1998) **14**, 7327.
[3] M.L. Schlossman et al. *Synchrotron Radiation News* (1999) **12**(2), 53.
[4] C. Fradin *et al*. *Physica* (1998) **B248**, 310