



	<b>Experiment title:</b> <b>In-plane structural study of liquid and liquid-liquid interface</b>	<b>Experiment number:</b> SC -1243
<b>Beamline:</b> BM32	<b>Date of experiment:</b> from: 2-07-2003                      to: 7-07-2003	<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:

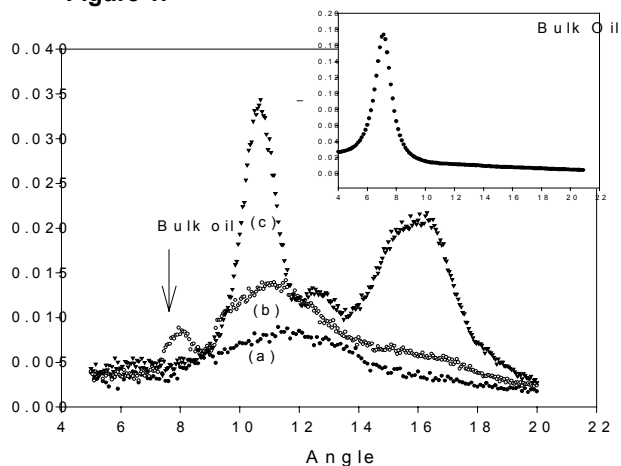
Despite the importance of the interface between water and oil in a vast number of physical and biological applications, it is only recently that real progress has been made in performing detailed studies resolving the structure of the interfacial region at the sub-molecular level. A range of experimental methods, both spectroscopic and structure determining, are now available and are currently at a stage in their development that enables a deeper insight into the structure at liquid-liquid interfaces and permits the origin of the structure at such interfaces to be probed. The oil-water interface is of special interest as determination of the structure allows a deeper understanding of the hydrophobic effect. Specifically, the issue regarding how water molecules organise themselves in proximity of a non-polar, hydrophobic species can be addressed.

In our previous experiment SC-1023, the main result of which is shown in Fig. 1, the in-plane scattering pattern obtained emanating from the interface between a water subphase and vapour saturated with cyclohexane. The change in scattering with time as a wetting film of cyclohexane is developed is evident. The amorphous scattering peak obtained from scattering from an air-water surface is shown, displaying a typical broad amorphous peak at 11.3 °. However, the scattering patterns differ significantly from those of the surface of water when in the presence of a cyclohexane-saturated vapour and/or a wetting film of cyclohexane. The main peak at 11.3 ° remains common to all patterns, but for the system containing cyclohexane the peak at 11.3 ° becomes more prominent and a smaller, second peak at 17.0 ° emerges as a thin film is condensed on the surface. As a thin layer of cyclohexane is formed the second peak (17.0 °) moves to slightly lower angle (15.9 °) which subsequently splits, resulting in a third peak at 12.5 °. The enhanced scattering and subsequent reduction in the peak half width at 11.3 ° and 17.0 ° are indicative of increasing ordering of the water molecules at the oil-water interface. A draft paper on this work is to be submitted soon.

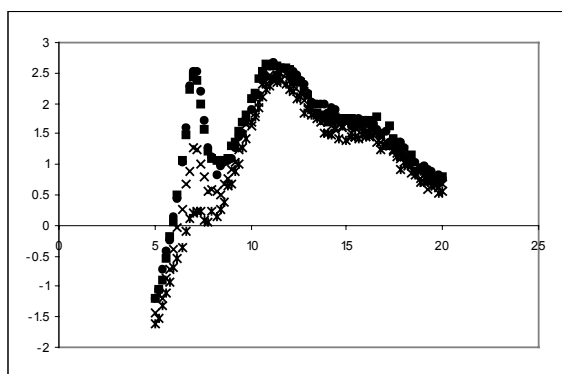
These results were broadly confirmed in our current experiment (SC-1243). On this occasion we had improved control of oil layer and were able to refine our procedure and check the reproducibility of the measurements. This was deemed necessary before moving on to our proposed next stage of resolving the structure of lipid, surfactant and polymer films at oil-water interfaces. Fig. 2 shows how the amorphous peak of water behaves as a condensed oil film gradually drains from the surface over a period of several hours. The peak at 7.5 ° is the amorphous oil peak and its intensity is a measure of the thickness of the oil film. As is shown, the intensity of this peak decreases with time as the condensed oil film drains. The structural evolution of the water amorphous peak was followed as the oil layer thinned [Fig. 2]. The main result here is that the peak at 17.0 ° is enhanced relative to that observed for the air-water interface and that the structure of the water beneath the oil peak is stable. Interesting features in the amorphous water peak appear, however, when the oil film becomes thin. Fig. 3 shows the evolution of several peaks under such conditions. This result is consistent with the results reported from SC-1023. It is unclear whether the enhanced ordering is a consequence of the presence of an ultrathin oil film or whether it arises as part of the dewetting process [cyclohexane wets water when the film is thick but doesn't wet when the film is thin]. Further experiments are necessary to clarify this.

We were also able to as part of this experiment compare the amorphous surface structure of  $H_2O$  and  $D_2O$  at several temperatures [shown in Fig. 4 for  $H_2O$ ]. The comparison of surface structure of  $H_2O$  and  $D_2O$  are very important in the field of the contrast variation deployed extensively in neutron reflectivity experiments. Isotopic substitution is carried out under the assumption that the structure of the system remains the same (and same surface structure for  $H_2O$  and  $D_2O$  are assumed) after the substitution. However, our results here indicate that this assumption may not be totally justified. The in-plane data suggest a more order structure for the surface of  $D_2O$  than that for  $H_2O$  and further that the order increases as the temperature is reduced towards the bulk freezing point. This is not unexpected due to the different nucleus resonance from these two species. This result is significant and warrants further study.

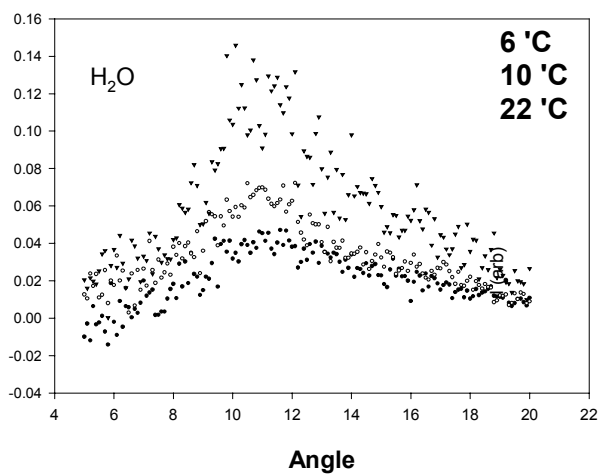
**Figure 1.**



**Figure 2.**



**Figure 4.**



**Figure 3.**

