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Report:

In contrast to solids liquids are thought not to possess regular periodic atomic and molecular arrangements. The structure of liquids is normally characterised by ordering at short molecular separations but on the whole liquids lack any long range order which characterises a solid. Recent measurements of aqueous surfaces and interfaces at ambient temperature and pressure 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.

In this experiment we have investigated the grazing-incidence scattering of 20 keV X-rays from the surface of water in the presence of a thin oil (cyclohexane) layer and in its free state in the absence of any oil. A temperature-controlled sample environment was constructed and commissioned for this experiment. This new sample environment allowed for an accurate control of both water sub phase temperature and that of the oil vapour. This arrangement allowed condensation of a very thin oil layer on the surface of water. Further to the measurement of scattering from the free water surface and the oil-water surface scattering from the surface of bulk oil has also been measured as a reference, and the structure peak of the oil has been thus determined.

Figure (1a). The water structure peak is shown and as expected it has the characteristic of a very broad amorphous peak, however it does have some finer structures (Figure 1b) which could be the contribution from ordering at the surface of pure water itself. However, owing to domination of bulk scattering this remains inconclusive.

Figure (2). When the oil layer is thin (<< 1000 Å) we see that the intensity of the first water peak increases by a factor of 4 and the peak splits and a second distinct structure peak appears at higher angle (~ 16 º). This is indicative of an increase in ordering of the surface water molecules.

Figure (3). When the oil layer is relatively thick we observe a contribution from the structure peak of the oil with, however, much reduced intensity than that of bulk oil (Figure 3 insert). In addition the contribution due to the water structure is also present probably arising from the penetration of a refracted beam into the bulk water as the condition for total reflection is no longer satisfied.

The intermediate transitions from the profiles shown in Figures (2) to (3) were also observed and the peaks evolution were measured but not shown here. The water peak in the absence of oil is broad. The full width at half-height (Δk) (where $k = \frac{4\pi \sin\theta}{\lambda}$) for both profiles Figure 1a and Figure 2 are 0.81 and 0.26 Å^{-1} respectively. This gives an indication of characteristic range of structure of disorder $R = 2\pi / \Delta k \sim 7.8$ and 24 Å for pure water and oil vapour/water interface. There is overwhelming evidence for increasing ordering of water molecules at the oil/water interface. Further analysis is in progress. The intensity distribution $I(k)$ will be normalised to the structure factor $S(k)$, also taking into account the changes in the beam foot-print. The reduced distribution function, $G(r)$, will then be

obtained and the coordination number determined from the total radial distribution function. Hence a full structural detail of the surface of water in the presence of oil can be deduced. A draft paper on this work is also in preparation.