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Report:

Recently sum-frequency spectroscopy (SFS) measurements from aqueous surfaces have revealed ordering behaviour of water molecules, suggesting the structure of water molecules at the air–water interface to be partially ice-like (~ 10%). This ordered structure is enhanced in the presence of an oil phase (hydrophobic effect) and ionic surfactant (dipolar ordering).

In our recent two experiments (SC-713 and SC-847) we have studied:

(i) The water ordering enhancement by an adsorbed Gibbs film of cationic surfactant molecules. We have measured in-plane X-ray scattering (using an incidence energy of 20 keV) from the free surface of an aqueous solution of the cationic surfactant cetyltrimethylammonium bromide (C_{16}TAB). The solutions have a concentration $c \sim 0.5$ mM < critical micelle concentration. We principally observe an amorphous scattering peak, which arises from scattering associated with the path of the evanescent wave through the surface and immediate sub-surface of water fluid (Fig. 1). After the addition of surfactant solution, however, the shape of the scattering pattern changes and is most likely attributable to the change in scattering from capillary waves due to the lowering of the surface tension. Second, more important features observed were the transient, intense Bragg diffraction peaks (Fig. 2). The temporal nature of these Bragg peaks were measured as a function of time.

(ii) In our most recent experiment, we have used a temperature-controlled vapour-tight cell. We measured the in-plane scattering from a pure water-vapour interface over a range of fine angular steps on two occasions. We observed two or more small Bragg peaks superimposed on the water amorphous peaks. Again we find all but one (at ~ 13°) of the observed peaks to be transient (Fig. 3). These peaks were enhanced on the introduction of oil vapour in to the sample cell (Fig. 4 & 5). These peaks are assigned indices assuming a hexagonal structure although a combination of hexagonal and cubic structure may be a more appropriate. A more in-depth analysis is currently under way. We have taken the normal precaution of measuring the transmission through our windows and also the empty cell in addition to the bulk scattering from the sub-phase. These indicated that the ordered structures observed were a surface phenomenon. We have also carried out a height scan (Fig. 6) with the detector located at 10.25° (the position of the amorphous peak). This height

scan suggested, due to the size of our cell (80 mm in diameter), the contribution of the surface scattering on top of the amorphous scattering varied depending where the sample is placed with reference to this height scan. This is due to the shallow angle (~ 0.03°) used in these experiments and the beam clipping part of the water meniscus. To overcome this we need to increase the available sample footprint area presented to the beam by designing a larger sample trough. PTFE will be used as the material for construction to aid meniscus presentation and to prevent creeping of the meniscus with time.

The fact these results suggest small amount of order on surface of pure water which has not been observed before and their subsequent enhancement by the addition of oil are extremely exciting and deserve a further and urgent continuation experiment.