ESRF

Experiment title: AMPHIPHILIC MONOLAYERS AT SUBMERGED OIL/WATER INTERFACES.

Experiment number: SC-314

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Report:

This experiment was part of an investigation of the statistical and elastic properties of two-dimensional organic monomolecular films down to very short in-plane length-scales. During experiments SC-15 (6-11 October 1994), SC54 (11-16 April 1995), and SC-98 (4-9 October 1996) an experimentalmethod was developped to measure the height-height correlation function (or capillary-wave spectrum) of the liquid/air interface down to molecular scales. This method was successfully applied during experiments SC-234 (11-16 December 1996) and SC-298 (20-24 February 1997). It therefore appeared possible to extend such measurements to Water/oil interfaces which are most important because of their practical applications, and also because the very low surface tensions that can be achieved would allow one to observe interesting phenomena beyond the simple capillary effects over a larger wave-vector range. The aim of experiment SC-314 was to attack this very interesting but also more difficult problem.

This experiment was different from the previous ones and implied the use of a new dedicated two-barrier Langmuir trough made of glass (lower part containing water) and teflon (upper part containing oil) to avoid leaking, equipped with very thin ($50\mu m$) teflon windows for the x-ray beam. The trough was 2cm wide in order to limit the background due to bulk scattering along the beam-path in the oil (hexadecane) that we expected to be the main difficulty of the experiment. We chose to spent two days (5-7 April 1997) to test the new cell and measure the background.
It appeared that the cell width was much too small to get any reflection from the interface because of the meniscus curvature and of the small angle of incidence (the critical angle of reflection for the water/hexadecane interface is 0.5mrad or $0.03°$). Subsequent tests showed that the optimal cell width at such small angles of incidence was 7cm and a new cell was built for the June experiment. The energy was fixed at 18keV (λ = 0.068nm) were the transmission of the 7cm wide film of hexadecane is $\approx$ 0.26.

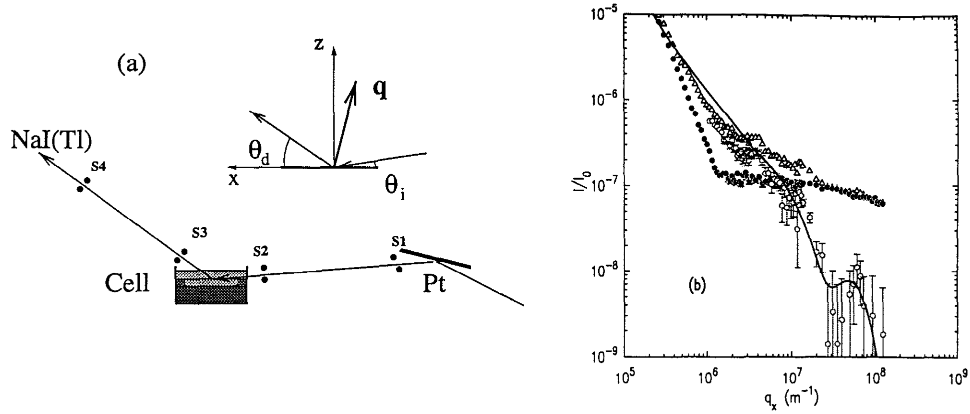

Figure *1*: (a) Schematics of the experiment. (b) Diffuse scattering of a DPPC film (surface tension $\gamma = 10mN/m$) at the water/hexadecane interface. The scan is a detector scan in the plane of incidence. The signal is represented by triangles, the background by filled circles, Signal - Backgrounds by empty circles. The continuous line is calculted using electronic densities similar to those of compressed films at the water/air interface.

The intensity scattered by an interfacial film is (this is in fact an over-simplified expression):

$$I \propto F(q_z) \times < z(q_{xy}) z(-q_{xy}) > \qquad (1)$$

where $F(q_z)$ gives account of the normal structure of the inter-facial film (q_z is the normal wave-vector transfer) and $< z(q_{xy}) z(-q_{xy}) >$ is the capillary wave spectrum (q_{xy} is the normal wave-vector transfer). If q_z is varied during a scan, as for detector scans in the plane of incidence with fixed grazing angle of incidence, oscillations in $F(q_z)$ due to interferences between the beams reflected at the water/film and film/oil interfaces provide direct evidence that scattering by film fluctuations are actually observed. If q_z is kept constant, as for detector scans in the plane of the sample, the scattered intensity is directly proportional to the capillary wave spectrum.
We chose to fix the grazing angle of incidence (using a platinum coated glass mirror) below the critical angle for total external reflection of the hexadecane/water interface because this allows the measurement (and subtraction) of the background by simply lowering the trough and performing the same scan. Using a fixed angle of incidence has the advantage of saving much alignment time (nevertheless over 2 days) as compared to the installation of the crystal beam-deflector necessary for reflectivity experiments, without preventing one from determining the structure normal to the interface which can be obtained from detector scans in the plane of incidence.
The detector used throughout the experiment was a NaI(T1) scintillator. The intensity of the $15\mu m \times 300\mu m$ was approximately 3 x $10^6 ct/s$. Note that the machine mode was the so-called 16 bunch mode which is not the most appropriate for such flux-demanding experiments.
We first performed detector scans in the plane of incidence (Fig. la). The amphiphile used was the phospholipid di-palmitoyl-phospshatidyl-choline (DPPC) which forms very stable films at the water/oil interface and can therefore be compressed to high pressures (i.e. low surface tensions), thus giving rise to a large diffuse scattering. The preliminary analysis of the results of Fig. lb (surface tension $\gamma = 10mN/m$) shows that the fluctuations of amphiphilic films at the oil water interface could be measured up to wave-vectors $\approx 10^8 m^{-1}$. As expected, the background is very large (and could only be reduced by reducing the cell width) but the subtraction procedure is efficient and reliable enough to allow the measurement of very small signal to background ratios. The structural parameters used to analyse the data of Fig. lb are equal to those of compressed DPPC films at the water/air interface. The analysis of the diffuse scattering in the plane of the sample has not yet been performed.

As a conclusion, the results obtained in this first experiment are very encouraging and one can be confident that further improvement of the experimental cell and experimental procedure should make this technique a standard and powerful tool of analysis for liquid/liquid interfaces.