Experimental report

02/09/2015

Proposal: 9-10-1351 **Council:** 4/2014

Title: Adsorbed Surfactant at the Solid/Liquid Interface Under Applied Shear

Research area: Chemistry

This proposal is a new proposal

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Samples: Al2O3
AOT (surfactant)

Instrument	Requested days	Allocated days	From	To
FIGARO	2	2	11/09/2014	13/09/2014

Abstract:

In this proposal we aim to investigate the effect of an applied shear to adsorbed surfactant layers at the solid/liquid interface. This is a continuation of preliminary measurements taken on FIGARO which prove that a loss of order can be clearly observed. Here we aim to carry out a focussed study into the breakdown mechanism of this industrially relevant system.

Adsorbed Surfactant under Shear at the Solid/Liquid Interface

The two experiments 9-10-1351 and 9-10-1352 were carried out consecutively on the FIGARO reflectometer with a rheometer in-situ. The aim of these experiments was to fully characterise the behaviour of adsorbed AOT surfactant multilayers at the alumina-water interface under applied steady and dynamic shear rates. This experimental set-up enables the molecular scale adsorption to be measured simultaneously with the bulk rheological properties. This was a continuation of experiment 9-10-1335 in which the relatively complicated set-up was optimised.

Experimental Set-up:

A photograph of the experimental set-up is shown in Figure 1. The alumina crystal is clamped in place on the rheometer sample stage and acts as the 'plate' of a cone-plate rheology geometry. The surfactant solution was loaded onto the crystal and the cone was lowered into place. A solvent trap was used to try and minimise evaporation and H/D exchange. The neutron beam was reflected up through the alumina crystal to the solid-liquid interface. Two angles of 0.375 and 1.8^{o} were used to generate the full reflectivity profile. The sample stage was set to a constant temperature of 12^{o}C, which was monitored using a thermocouple between the crystal and aluminium mount. The sample averaged 18^{o}C throughout the experiment.

The rheometer used was an Anton Paar MCR501 Physica, with a Ti cone attachment of angle 1.0^{o}.

Improvements to set-up:

During the initial measurements of experiment 9-10-1335 there were significant issues with H-D exchange/evaporation from the relatively open sample set-up. Therefore an aluminium sample clamp and o-ring were added to generate a sample well for the liquid. This was slightly larger than the cone diameter to maintain free rotation. The liquid well reduced the air-liquid surface area and enabled the sample to be overfilled. However, this may affect the rheology measurements so additional off-line measurements were taken with the 'correct' volume of liquid for comparison.

This sample-well reduced the previous issues, but did not remove them completely. However the effect on the reflectivity data was restricted to near the critical edge and did not affect the data at higher Q. The exception was in the measurement of the bare alumina crystal in D_2O where there is very little contrast variation. In this case the reflectivity data could not be fit to a simple model.

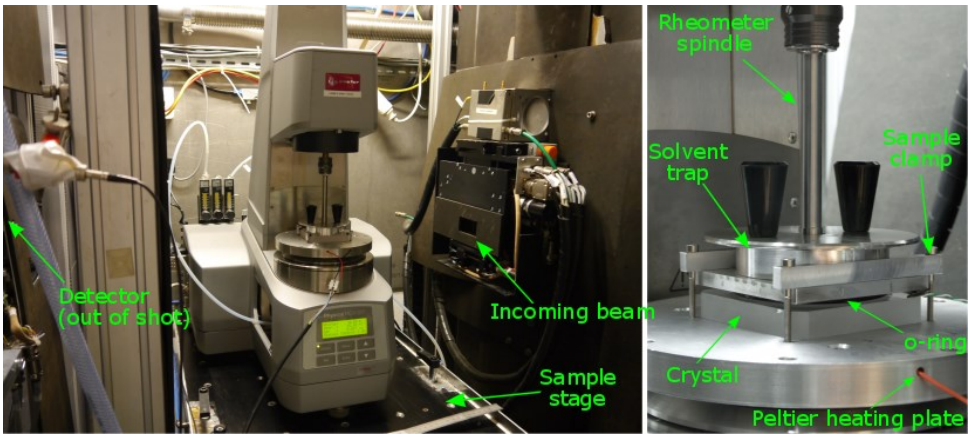

Figure 1: Photograph of the rheometer set-up on the FIGARO sample stage. Right picture shows a close-up of the sample, including the o-ring implemented during this experiment.

Results:

This experiment considered the behaviour at higher concentrations of AOT (2wt%), where multi-layers are present at the interface. These are identified by Bragg peaks within the specular reflection, which are accompanied by significant off-specular scattering. The off-specular scatter is indicative of correlated undulations within the planes of the multilayers. The higher angle of 1.8° provided the Q-range for two orders of Bragg peak around 0.03 and 0.06Å^{-1} respectively. This angle was measured as a series of 5 minute runs under a range of applied shear rates.

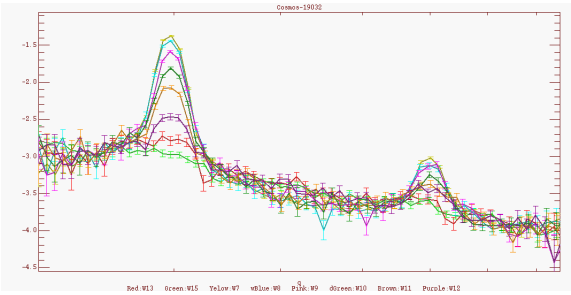

Figure 3: Series of reflectivity profiles under an applied steady shear of 1s^{-1}, with the data sets in 5 min intervals.

The first AOT bilayer adsorbed onto the alumina surface did not change under all applied shear rates. This was easily identified by a relatively large Kiessig fringe in the specular data and indicates that the applied shear conditions were insufficient to disrupt this initial layer. However, significant changes to the multilayers were observed, with loss of the Bragg peaks. Figure 2 shows an example set of peaks under steady shear.

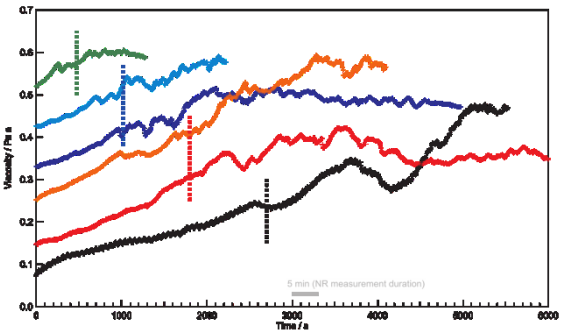

Figure 3: Variation in viscosity with time under applied steady shear rates from 0.5s^{-1} to 2s^{-1}. Vertical dashed lines indicate approx. time of Bragg peak loss in reflectivity.

To characterise these changes, a Gaussian fit to the Bragg peak was used to capture the position, width and height. These fits suggest that the position and therefore interlayer spacing does not change under applied shear, but the peaks become shorter and wider. This predominantly indicates a reduction in the number of ordered layers within the multilayer stack. Under steady shear the peaks are lost completely, but under a dynamic shear some order is retained.

Figure 3 shows example rheology data under steady shear, with the vertical dashed lines indicating the approximate position where the Bragg peaks were lost within the specular reflection. There appears to be a change in the rheology corresponding to the observed loss of surface multilayers, with the data becoming much noisier. This suggests that this is a change to the bulk liquid.

Two GISANS measurements were carried out before and after application of a steady shear, with the resultant scatter shown in Figure 4. This indicates a powder pattern in the data from the in-plane correlation of multilayers before shear is applied, which is lost after shear has been applied and in good agreement with the specular and rheology observations.

In summary, we are very pleased with these results and plan further shear based measurements to extend and develop this work.

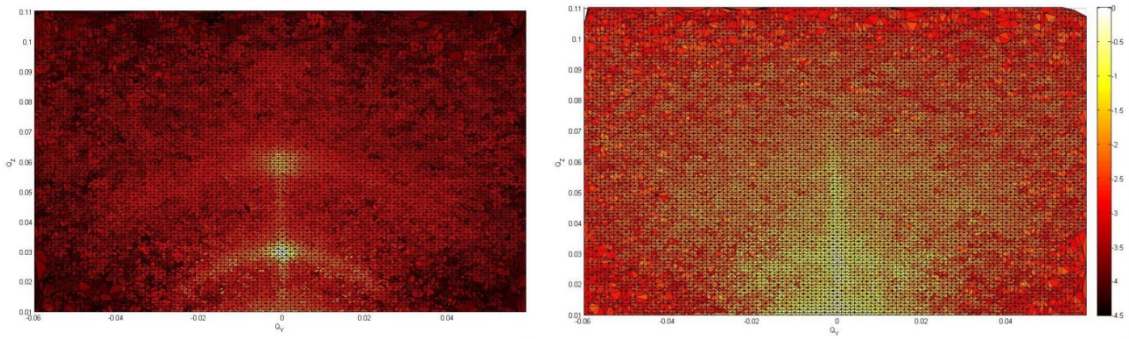

Figure 4: GISANS measurement of 2wt% AOT in D_2O on alumina, before and after application of 2s^{-1} steady shear.