Experimental Report

21/01/2014

Proposal:	**9-10-1335**	**Council:**	10/2012
Title:	Metal/Liquid Interface Under Shear		

This proposal is a new proposal

Researh Area: Chemistry

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Samples: copper coated silicon with hexadecanoic acid adsorbed from dodecane
dodecane (d- 26)

Instrument	Req. Days	All. Days	From	To
FIGARO	2	2	01/07/2013	03/07/2013

Abstract:

This proposal aims to directly study a molecular adsorbate layer at a metal/liquid interface under well-defined shear conditions.

EXPERIMENTAL REPORT: 9-10-1335

Adsorbed Surfactant under Shear at the Solid/Liquid Interface

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The effect of shear on the adsorbed surfactant sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) was investigated at the alumina/water interface via simultaneous rheology and neutron reflectometry. The rheometer and reflectometer were successfully coupled and changes in the surfactant structure at the surface were observed. This experiment focussed on establishing a reliable experimental method, which provides an excellent basis for further research.

INTRODUCTION

There are many industrial applications which use organic additives to manipulate the surface properties of a material, from lubricant or anti-corrosion additives, through to hydrophobic coatings. Many of these scenarios work under dynamic conditions with a flowing liquid, yet much of the research is carried out under static conditions. There has, however, been significant investigation into the effect of an applied shear on the phases formed in the bulk surfactant solution. Within this work we aimed to test a new experimental set-up on FIGARO which allows the simultaneous measurement of rheology and neutron reflectometry, providing the frame-work for more detailed experiments into the effect of an applied shear on adsorbed layers at the solid/liquid interface.

EXPERIMENTAL SET-UP

An Anton Paar Physica 501 rheometer was placed on the sample bench of FIGARO as shown in Figure 1. The neutron beam was reflected up through the crystal to the solid/liquid interface, taking advantage of the vertical range of the FIGARO detector. A Ti cone attachment was used to provide an even shear rate across the full diameter of the sample. A solvent trap was used to minimise evaporation and H/D exchange of the surfactant solution. A pulse sent from the FIGARO computer was used to trigger changes in the rheometer settings.

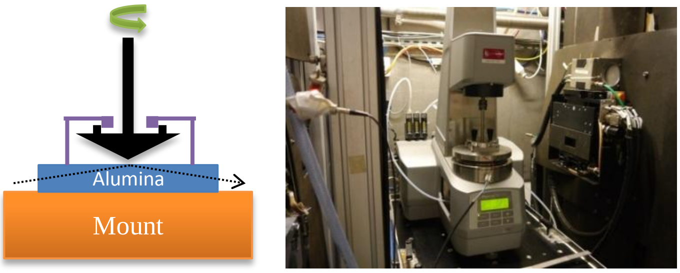

FIGURE 1: SCHEMATIC AND PHOTO OF THE RHEOMETER SET-UP ON FIGARO.

Al_2O_3 was used as the solid phase within this work due to its excellent neutron transmission and high SLD (5.7e-6Å^{-2}). This provides an excellent contrast to the hydrogenated surfactant (~1e-6Å^{-2}) in D_2O (6.35e-6Å^{-2}). It is also possible to polish alumina to a very low roughness, providing a good surface for reflection.

Two concentrations of AOT were used in this experiment: 2.5 mM (CMC) and 2 wt%, which are known to form a single bilayer, and a series of ordered lamellar bilayers, respectively on alumina. This provides two length-scales of order to probe under increasing shear stresses.

RESULTS AND DISCUSSION

The crystal was initially characterised in 3 water contrasts: H_2O, D_2O and HDO. Fitting of this data showed a clean crystal with a very low surface roughness. A solution at the CMC concentration of AOT was added and the resulting bilayer characterised, in good agreement with previous work. This was then tested under a series of applied steady and then oscillatory shear rates up to 500s^{-1} and 200% at 100Hz respectively. In both cases there was no significant change in the reflectivity at high Q values, but a small drop in scattered intensity was observed around the critical edge (Figure 2). This change provided the first major challenge of this coupled experimental set-up. Following a series of tests both with and without an applied shear stress, it was found that this change was independent of the applied shear rate. Instead this drop was due to either evaporation of the liquid sample or H-D exchange with water vapour in the air due to the relatively open nature of the sample set-up. Both of these scenarios lead to regions of the illuminated sample having a lower bulk solution SLD, causing a loss of the critical edge. This effect is particularly significant for the D_2O/Al_2O_3 system due to the very similar SLDs of the two bulk phases, and resulting low critical edge in Q. Further tests indicated that this was an evaporation problem which was successfully minimised through use of the solvent trap, control of the temperature and open dishes of D_2O within the instrument block.

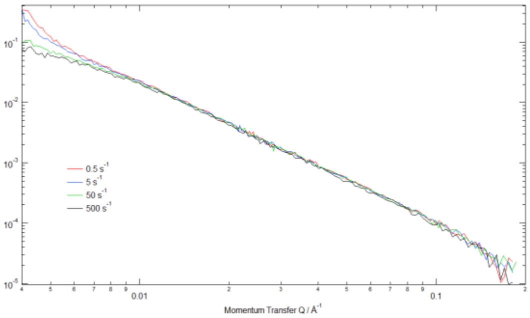

FIGURE 2: REFLECTIVITY DATA OF 2.5mM AOT UNDER STEADY SHEAR SHOWING STEADY LOSS OF CRITICAL EDGE.

In addition, due to the horizontal geometry, the incoming neutron beam is significantly affected by gravity whose effect varies with wavelength. Therefore the beam footprint was reduced and the aligned height shifted to maximise the central illuminated area. This effect is greatest at smaller angles, so combined with the evaporation tests only the higher angle of 1.8° was used for the subsequent shear runs.

The AOT bilayer structure was unaffected by the applied shear rates. Therefore, the concentration was increased to 2wt% AOT; longer range order is observed at this higher concentration, and a 'thicker' layer can be thought to exist at the surface. The unsheared surfactant shows a bilayer adsorbed at the alumina surface and repeating bilayer lamellae parallel to the surface. This high degree of positional order is shown by 3 orders of Bragg peak within the reflectivity data, and significant off-specular scattering on the 2D detector. In the limited remaining time a quick series of steady and then oscillatory shear rates were applied to the sample with changes in order monitored using the well-defined first and second Bragg peaks. A single angle of 1.8° was again used to minimise the effects of evaporation.

At low shear rates there appeared to be some shear ordering – although there was insufficient time to explore this fully. This was followed by a plateau of no change as the shear rate was increased, before a steady loss of ordered lamellar at higher rates. Figure 3 shows an example of the Bragg peak changes observed under steady shear as the longest range order was lost. This was accompanied by a loss of off-specular scattering. Using an adaptation of the Scherrer equation, the number of ordered layers was estimated from the width and position of the peaks. Figure 4 shows how this number changed on application of an oscillatory shear. Each data point is a separate FIGARO run and the dashed lines indicate when the applied shear rate was increased. Unfortunately there was insufficient time to fully equilibrate the structure at each applied shear rate, but the results were very successful in showing that there is a loss of order on applied increasing shear. Our preliminary analysis suggests there was a drop in the number of ordered lamellar layers, which was successfully observed using this technique.

We are pleased to have established the key experimental approaches which enable the combination of rheology and reflectivity. We now plan to exploit this success to further understand the structure and chemical origin of critical shear rates required and mechanisms involved.

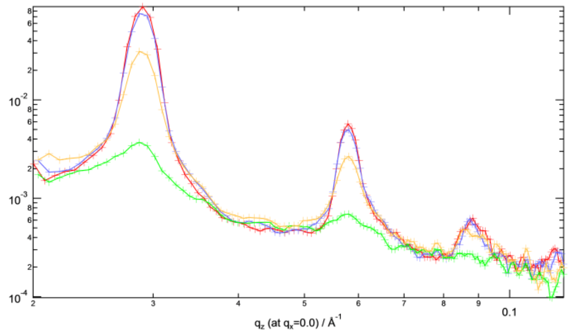

FIGURE 3: SPECULAR REFLECTIVITY CURVES OF 2WT% AOT UNDER A STEADY SHEAR RATE OF $5s^{-1}$, SHOWING LOSS OF BRAGG PEAKS WITH TIME.

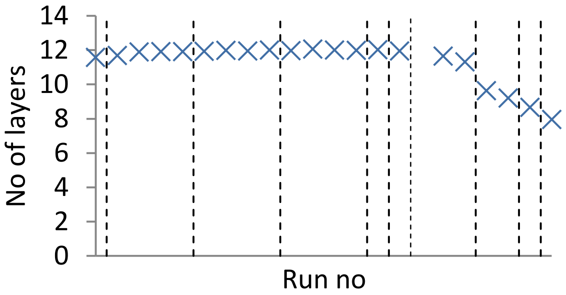

FIGURE 4: CHANGE IN THE CALCULATED NUMBER OF ORDERED LAYERS AT THE SURFACE UNDER OSCILLATORY SHEAR. EACH DATA POINT IS A FIGARO RUN AND EACH DASHED LINE SHOWS A CHANGE IN SHEAR CONDITIONS.