Experimental report

25/09/2019

Proposal: 9-12-553 **Council:** 10/2018

Title: Organic Friction Modifier Film Structure at the iron oxide/dodecane Interface

Research area: Engineering

This proposal is a new proposal

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Samples: dodecane-d26
Glycerol monooleate

Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	3	2	24/07/2019	26/07/2019

Abstract:

Lubrication ensures the reliable operation of combustion engines whilst also offering a reduction in emissions and fuel consumption. Organic Friction Modifiers (OFMs) are a common class of friction-reducing additives included in engine lubricants and are known to adsorb at metal surfaces. However, the exact mechanism by which OFMs operate has yet to be defined. To understand how these additives function, a novel tribometer rig has been developed which enables neutron reflectivity experiments to be carried out at elevated temperatures and pressures, whilst the surface is sheared. In this set of experiments, we will measure the thickness of the film formed by glycerol monooleate molecules on iron oxide surfaces as a function of concentration and shear.

Experimental Aim:

There were two main aims for this experiment. As the tribometer had not been used on FIGARO before, the primary aim was to setup the tribometer rig on the beamline and ensure reflectivity could be measured. Our other aim was to characterise the conformation of the adsorbed film formed by glycerol monooleate at the iron oxide/dodecane interface under static and sheared conditions using a combination of the tribometer and a solid/liquid cell. This work was carried out at ambient temperature and pressure, and the concentration of glycerol mono oleate used in the tribometer was set at 15 mM which is an approximately 12.5 times greater than the CMC. The concentration of glycerol monooleate used in the solid/liquid cell was varied from below to above the CMC to establish how the adsorbed film structure changes with concentration.

Experimental Report:

Two silicon substrates, sputter coated with iron, were used in this experiment. They are referred to as S1 and S2. Initially, the reflectivity was measured in an air/solid geometry at room temperature using two scattering angles, 0.646° and 3°, with a usable wavelength range of 2-20 Å and a dQ/Q FWHM resolution of approximately 6.9 %. Following this, both substrates were characterised in solid/liquid cells with dodecane-h_{26} and dodecane-d_{26} with two scattering angles, 0.646° and 3.2°. S1 was then placed in the tribometer and S2 was used in the solid/liquid cell for the remainder of the experiment. All data was reduced using a combination of COSMOS and Mantid.

Solid/Liquid Cell Experiments

In the solid/liquid cell, S2 was loaded with a solution of 0.5 mM GMO in dodecane-d_{26} and the reflectivity measured. After, a 5 ml aliquot of solvent was pushed into the cell in order to measure the reflectivity after washing the surface with excess solvent. Following this, solutions of 3 and 15 mM GMO in dodecane-d_{26} were successively pushed into the cell and their reflectivity measured. After collecting the reflectivity of the 15 mM GMO solution, another 5 ml aliquot of solvent was pushed into the cell and the surface was characterised again. The cell was then washed with excess dodecane-h_{26}, and solutions of 0.5, 3 and 15 mM GMO in dodecane-h_{26} and dodecane-h_{26}/d_{26} (65:35) were successively loaded into the cell and their

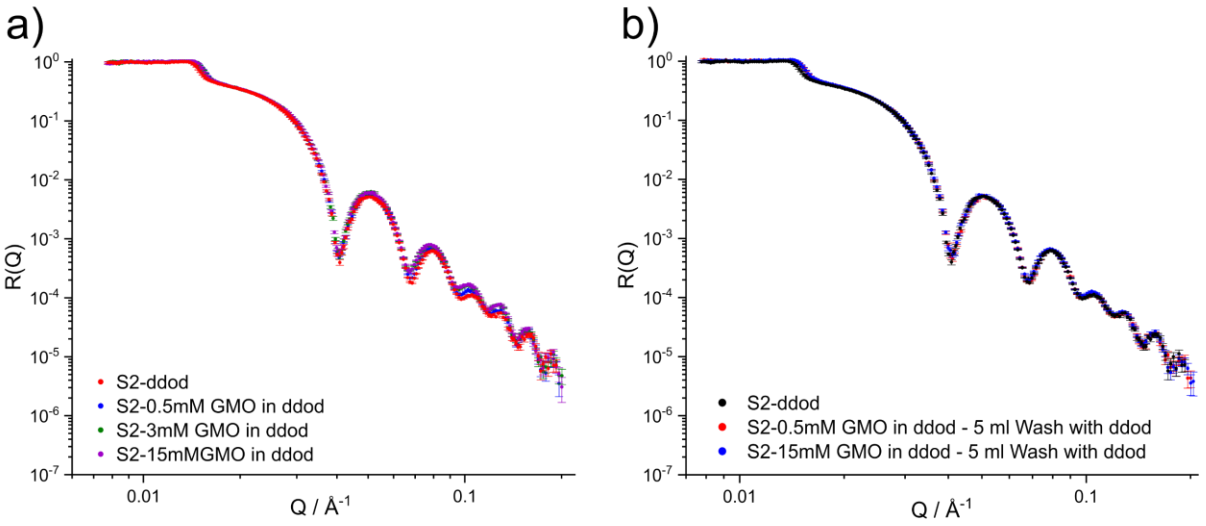

Figure 1 – a) Reflectivity profiles collected with solutions of varying GMO concentrations in dodecane-d_{26} against S2. b) Reflectivity of S2 washed with dodecane-d_{26} after being exposed to solutions of 0.5 and 15 mMol dm^{-3} GMO in dodecane-d_{26}.

corresponding reflectivity's measured. Hence three solvent contrasts per GMO concentration were collected. Exemplar reflectivity profiles of GMO in dodecane-d_{26} are shown in Figure 1a.

The Q value at the critical edge in the profiles collected with dodecane-d_{26} is approximately 0.0142 $Å^{-1}$, suggesting the solvent deuteration was not 100 %. The Q value of the critical edge in the profile collected with neat dodecane-d_{26} is slightly lower than the rest of the profiles as some remaining dodecane-h_{26} had remained in the cell after flushing. The Kiessig fringes in the profiles mainly arise from the sputtered iron layer, with a spacing that corresponds to an approximate iron layer thickness of 200 Å. There are small differences between the reflectivity profiles collected with the GMO solutions and the profile collected with the blank solvent system, and the differences become more pronounced as the GMO concentration increases. These changes are caused by the spontaneous adsorption of GMO at the interface from solution, which results in a change in total thickness and scattering length density across the interface. This agrees with the shifts in fringe spacing and fringe amplitude. However, it is noted that these differences are only slight, and the relatively large shifts expected when an additional layer with a low SLD (GMO ~ 0.21 x 10^{-6} $Å^{-2}$) is included at the interface is not observed. This is akin with previous neutron reflectometry results collected on these systems. We believe the reason for the similar profiles for the solvent system and the GMO systems is due to the contamination of the interface when in the solvent. The similar fringe amplitude between the solvent and GMO profiles suggest the contaminant layer has a SLD around 0. Possible contaminants could be water or non-deuterated organic material, which are both plausible considering the hygroscopic nature and purity of the solvent used. No significant difference is found for the profiles collected in dodecane-h_{26} or the dodecane-h_{26}/d_{26} (65:35) solvent system. This is thought to be due to the low contrast between the solvent and the SLD of the GMO layer. The profiles collected after pushing through the extra 5 ml of solvent in the 0.5 and 15 mM GMO systems shows the removal of the features ascribed to the GMO layer. The profiles become very similar to the solvent blank profile, suggesting the majority of the adsorbed GMO layer is physisorbed at the interface.

Tribometer Experiments

After S1 was initially loaded into the tribometer, the roller was set at 0.2 mm from the substrate surface using the laser displacement sensors. The oil bath was then charged with 10 ml of dodecane-d_{26}. Reflectivity profiles were then collected when the tribometer was static and when under shear with shear rates of 6.4 x 10^2 s^{-1}, 2.5 x 10^3 s^{-1} and 3.8 x 10^3 s^{-1}. These profiles were collected with two scattering angles of 0.646° and 3.808° with a usable wavelength of 2-20 Å on the first angle and 2-30 Å on the second angle. The heights of slits 2 and 3 were both set at 0.26 mm for the first angle and were set at 1.8 and 2.038 mm for the second angle respectively. The widths of slit 2 and 3 set at 60 and 25 mm respectively.

The unstitched reflectivity profiles collected under static and sheared conditions are shown in Figure 2a. Comparing the individual angle profiles shows there is no change in the first minima with shear, but a clear change in both minima at Q = 0.04 and 0.07 $Å^{-1}$ that increases with shear for the second angle. The reason why this is only apparent in the second angle is not clear, but this leads to poor overlap between the first and second angles. The difference at certain Q values may suggest a gravitational effect on the reflectivity but it is unclear if this is the case.

Following these results, the height of slits 2 and 3 were reduced to 0.13 mm for the first angle and 0.9 mm and 1.137 mm for the second angle. By changing the sample stage height by 10 mm either up or down from the aligned position, it was possible to scan across the surface of the sample in three positions. Two profiles were collected with dodecane-d_{26} at shear rates of 6.4 x 10^2 s^{-1} and 3.8 x 10^3 s^{-1}. No significant difference is seen between the different positions

in the reflectivity profiles, suggesting that the sample was homogeneous across the surface. It is noted that the overlap between the first and second angle has significantly improved compared to the profiles collected with larger slit heights. However, it appears the overlap between angles at higher shear rates is poorer than at lower shear rates. A slight change with shear is still apparent, which is the case for both angles. This is consistent with previous data collected on INTER, ISIS, UK. It is postulated that the difference with shear arises from the expulsion of air at the interface as more solvent is entrained at the interface with greater angular velocities.

The solvent in the oil bath was then replaced with solutions of 0.5 and 15 mM GMO in dodecane-d_{26} successively. The tribometer was run at two shear rates, 6.4 x 10^2 s^{-1} and 3.8 x 10^3 s^{-1}, for both solutions and the reflectivity profiles collected. These are displayed in Figure 2b. The profiles display similar angle overlaps and decreases in fringe minima to those seen in the profiles collected with solvent. Curiously, when comparing the reflectivity profiles collected with GMO and those collected with solely dodecane-d_{26} at 6.4 x 10^2 s^{-1} there is only a small difference between the profiles, and this becomes even smaller when the shear rate is increased to 3.8 x 10^3 s^{-1}. It is expected that the difference between the profiles would be similar to those at the same GMO concentrations in the solid/liquid cells and previously collected data with the tribometer on INTER has indeed shown this to be the case. It is not clear why a larger difference is not observed or why increasing the shear rate decreases the differences. One postulate would be the removal of the GMO layer with shear, but this isn't consistent with previous data collected at similar shear rates with GMO. Another possibility that could explain the former observation is that the smaller slit settings are not optimal. As seen in Figure 1, the differences between the profiles collected with neat solvent and GMO solutions are most observable between Q = 0.07–0.1 $Å^{-1}$. Similar differences can be seen in the tribometer data, but they of much lower intensity. This suggests that a GMO layer is present, and that some other effect has altered the reflected intensity at this Q range. When using the larger slit settings, it was apparent that the first fringe was affected by something altering with shear. It is possible that whatever caused this is still affecting the reflectivity but at a different Q range when the slit settings are reduced. Work is on-going to establish the cause of the mentioned changes when using the tribometer.

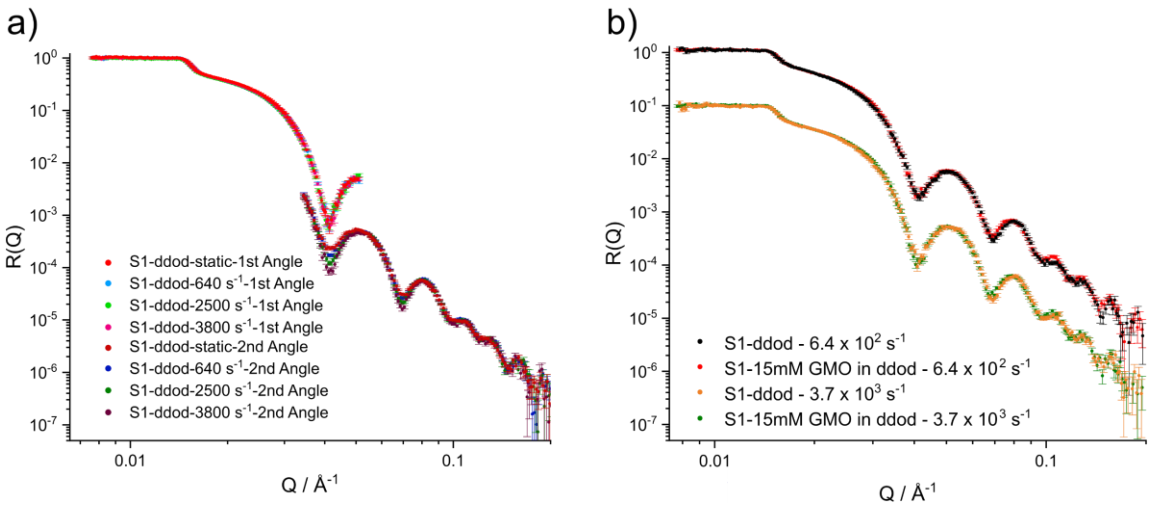

Figure 2 – a) Unstitched reflectivity profiles of dodecane-d_{26} entrained against the Fe coated Si blocks in the tribometer at four different shear rates. Changes with shear are only visible in the second angle. The second angle profiles are offset by 10^{-1} in the vertical axis. b) Reflectivity of dodecane and 15 mM GMO in dodecane at two shear rates. The profiles collected at the same shear rates are overlaid and the higher shear rates are offset by 10^{-1} in the vertical axis.