Experimental report

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Proposal: **9-10-1544**

Council: 4/2018

Title: Adsorbed molecular layer of phenolon iron under pressure

Research area: Chemistry

This proposal is a new proposal

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Samples:
silica block with Fe layer
nonyl phenol in dodecane

Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	2	2	26/08/2020	28/08/2020

Abstract:

Here we aim to directly observe and structurally characterise the molecular layer of an important alkyl phenol, 4 nonyl phenol, on the surface of iron oxide adsorbed from oil (dodecane) under pressure conditions which are more typical of the commercial environment. We will use the technique of neutron reflection to obtain this structural information that cannot be obtained by any other means.

Experimental report:

9-10-1544 : Adsorbed molecular layer of phenol on iron under pressure

Summary

This was our first experiment using the high pressure neutron reflection cell on Figaro. In summary we achieved much of what we set out to do and identified the key chemical and physical constraints on the experimental approach. The technical details of the pressure cell meant we had to change our approach somewhat and, as discussed below, we were not able to observe adsorption of a molecular layer, as indicated by initial ‘home based experiments’. However, we were able to track pressure and temperature driven freezing of the solvent and additive separately and obtained some initial indications of important kinetic effects and were very pleased to see surface freezing of the additive. This experiment will provide a firm foundation for future experiments.

Background

There is an increasing need to characterize adsorbed layers under extreme conditions of temperature and pressure relevant for applications such as lubrication and wear prevention. Here we made our first experiment to use a high pressure neutron reflection cell to characterize the changes in molecular adsorption with pressure (and temperature).

Experimental Details

The experiment exploited one of two pressure cells for reflection on Figaro at ILL. There is a small volume cell (I) that can go to higher pressures than a larger volume cell (II). However, the technical details of the seals in the cell I prevent us from using simple hydrocarbon solvents (the seals would dissolve). Hence, we were required to use the larger volume cell II. In addition, the larger volume cell enabled us to see a wider Q-range required to characterize the likely position in Q-space of the adsorbed layer. We are in discussions with our local contact to see if we might be able to adopt more chemically resistant seals in the future, which will facilitate a wider range of samples to be studied.

The requirement to use such a large sample volume has had a knock-on effect for the samples we were able to use for this experiment. Because we wanted to use h- and d- contrast to highlight the adsorbed layer, we had to make sure we could obtain enough of the h-/ d-solvent and h-/d-additive to fill the cell (and usually a bit more to allow for spills/ re-fills etc.). Hence, we initially made preliminary measurements using cheaper additive/solvent combination (stearic acid /cyclohexane) to ensure the experiment worked well. We will then progress to using the additive/solvent system we ultimately want to study.

In preparing for the experiment, we have also made a lot more calculations and off-line experimental measurements to make sure we picked the ‘best’ system and conditions for this initial study. For example, we wanted to do our best to impose concentration conditions such that when we increased the pressure we would see changes over the limited pressure range available. In making these deliberations, we noticed that that there is likely to be a related behaviour on cooling the system to increasing the pressure (both will be expected to lead to more freezing and more adsorption). Hence, we decided to do a cooling experiment to locate the bulk freezing point. This also dictated the use of cyclohexane which has a convenient freezing point (6C) as solvent. We then did the pressure dependent measurement adjacent to this temperature point where we believe we would be most likely to see pressure induced changes.

We had also made new very accurate density measurements to characterize the partial molar volume changes of the systems, which also gave us some indication of what effect increasing pressure might have for this particular additive/solvent mixture (increased pressure should lead to more adsorption).

The aim is to ultimately investigate the adsorption of additives on Fe2O3 substrates. In these neutron reflection studies, these are made as Fe2O3 deposited thin films on very flat Silicon blocks. Hence in this initial experiment, we began with a bare silicon substrate with a view to adding a Fe2O3 (the Fe2O3 layer gives very large fringes that can obscure adsorbed monolayer features). A whole series of additional lab-based experiments were made to confirm and characterize the adsorption isotherms of the systems on silicon/silica so that we could optimize the use of the neutron time.

Summary of results and initial interpretation

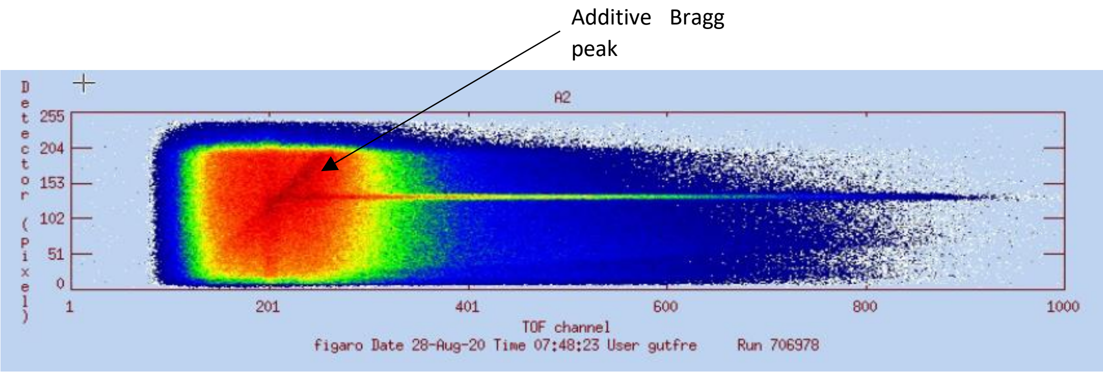
NOTE: We are most grateful to Philipp Gutfreund, the beam line scientist, and colleagues who kindly ran this experiment for us during the COVID period when we were unable to attend in person.

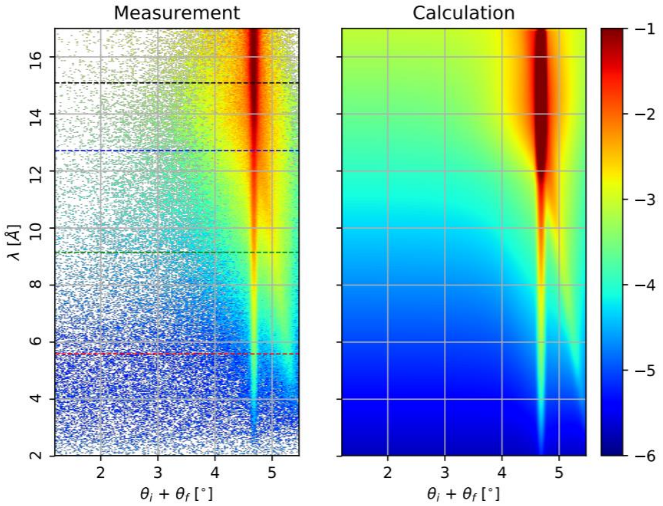
The experimental system worked well.

We were able to perform useful characterisation of the pure solvent freezing under increased pressure and/or reduced temperature. This was most evident in the position of the critical edge reflecting the density changes on freezing (6% change in mass density). We were not able to observe solid cyclohexane diffraction peaks in the accessible Q-range used.

Similarly, we were also able to characterise the behaviour of the additive and its pressure and temperature driven freezing. Importantly we could observe the low Q diffraction peak from the solid additive. This means we can identify separately solvent and additive freezing as we go through the liquidus and solidus. The observation of these peaks indicates that the additive crystallites are oriented with their long axis perpendicular to the interface. Peak width analysis indicates an interface excess of stearic acid to the equivalent of 26 monolayers upon freezing of 8 mM solution and up to 47 monolayers in 50 mM solution. Approximately 5-10% of the surface is covered with crystallites.

The in-plane size of the crystallites reduces from 600 nm at ambient pressure to below 50 nm at 390 bar upon freezing. So it seems that upon freezing at higher pressure and thus higher temperature the adsorbed amount is actually, and unexpectedly, reduced.


Additive Bragg peak



Off-specular signal used to calculate the in-plane crystalline sizes

Interestingly there was also some evidence of kinetic barriers. The rate of pressure increase was relatively high and occasionally we appeared to trap the sample in a non-crystalline state (weaker diffraction peaks) than if we took pains to ‘anneal’ the sample. These are only initial studies and more significant study will be required. However, this is a particularly important aspect as there is other evidence in lubricated bearings that there is glass formation, rather than crystallization, due to non-equilibrium. Unfortunately, despite very good evidence from lab based adsorption isotherm data which reliably demonstrated good adsorption, there was no evidence of a sufficiently dense adsorbed layer to change the reflection data in the pressure cell. There may be some adsorption but not of a dense phase – there were no changes in this respect with P and T, as we had hoped for.

There are a number of possible causes which include (i) there may have been depletion of additive on the walls of the cell such that there was not enough to complete the surface layer. Additional higher concentration measurements confirmed that this was not the case. In addition, the appearance of the additive diffraction clearly indicates the sample is still in the cell, close to the surface. (ii) water may be an issue: as usual, the substrates were cleaned in conc nitric and rinsed with ultrapure water. Usually air drying is sufficient to prevent water remaining in the cell and out competing the additive. However, there may have been a little left. We tried to check this by fitting of the reflectivity data from the pure solvent. Indeed, there was no indication of a low SLD region at the surface that would have indicated water being present. However, a single monolayer or bilayer of water would be difficult to see. We also rinsed the cell with dry solvent to try and remove any water. (iii) other competing impurity. In the same way that water might outcompete the additive, other ‘dirt’/impurity might also remove the additive of interest. However, as discussed above there was no sign of any adsorbed impurity evident in the reflection from the ‘clean’ solid/liquid interface.

Summary

This was the first time our group has used this high pressure reflection cell. We successfully characterized the clean solid/liquid interface and could follow the pressure and temperature driven freezing of both the solvent and the additive. We have successfully identified key temperature and pressure driven formation of additive crystallization how much and some indication of the crystal phase formed. Some initial evidence of important kinetic behaviour was obtained but, unfortunately, we were not able to follow the adsorbed layer behaviour but were very pleased to see surface freezing of the additive of interest.