Experimental report

25/02/2022

Proposal:	**9-10-1617**	**Council:**	10/2019
Title:	Electroresponsive structuring of non-halogenated ionic liquids on cobalt: A mimic for passive tribological films		
Research area:	Engineering		

This proposal is a new proposal

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Samples:
Propylene Carbonate
1-d13-hexyl-3-d6-methylimidazolium bisorthoborate
1,2-Propylene-d6 carbonate
1-d21-decyl-3-d6-methylimidazolium bisorthoborate

Instrument	Requested days	Allocated days	From	To
SUPERADAM	5	4	18/05/2021	22/05/2021

Abstract:

Over the last 2 years we have studied the electroresponsivity of ionic liquids (ILs) and their solutions at gold electrodes on a range of tribologically interesting ILs, to test the nature of their electroresponsivestructure (ERS). The decision to change to cobalt is twofold: 1) the thin oxide layer is more representative of the oxide layers found on the meal surfaces (e.g., steel) in contacts; 2) we can compare directly to confinement experiments performed with the ATLAS device at EC-Lyon where we prepare Co surfaces with approximately 5 Å roughness. This application introduces a new French team to the neutron reflectance (NR) community who are also strategically located to take advantage and collaborate.

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Polarized neutron reflectivity (PNR) measurements were performed for the first time on halogen-free phosphonium orthorborate ionic liquid (IL) additives in hybrid and bio-based oils at metal-oxide interfaces. Metal substrates are native passive oxide layers, including iron and steel substrate, a comparison was also made with an iron substrate coated with silica. In total, 6 systems of ILs dispersed in a bio-based or hybrid (isoparaffins/bio-based) oil were studied as a function of applied potential. The bio-based oil was 2-Ethylhexy Laurate (2-EHL), and isoparaffins oil was BIO-2130 offered by Nynaa AB, Sweden. The molecular structures of the IL ions and hydrogenated solvent are shown in Fig. 1.

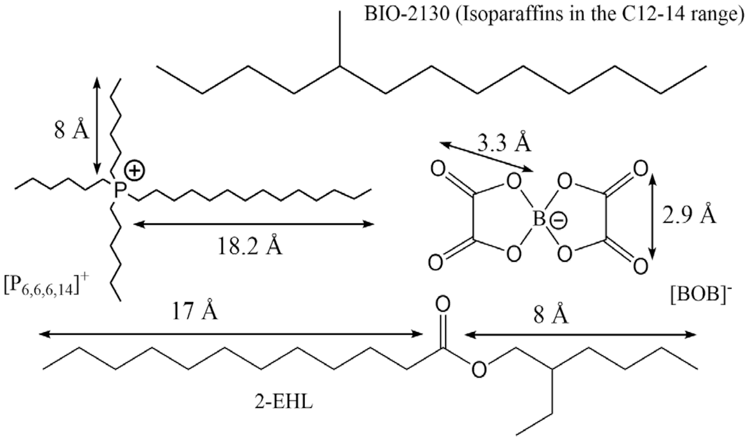

Figure 1. Molecular structures and dimensions of IL ions and solvent, 2-EHL and BIO 2130.

For metal-oxide interfaces, 4 potentials were studied (open circuit potential, -1, 0, and +0.25). The potentials were chosen to be within the anticipated electrochemical windows of the ILs. The order of the potentials was deliberately chosen to test the reversibility of the electro-induced changes. All reflectivity measurements were collected after a 30 minutes stabilization at the applied potential. During this time and NR measurements, the current across the cell was monitored. For all the IL mixtures, the current across the cell reached a plateau within the stabilization time, suggesting all charge transfer triggered by the applied potentials occurred during this time and equilibrium was reached. The external magnetic field was applied to the sample cell during the PNR measurements. To highlight any changes in the interfacial IL layers, the scattering length density (SLD) of the bulk IL-oil solution was matched to that of the substrate by adding the appropriate ratio of hydrogenated and deuterated analogues 2-EHL (~d40; 98%D). The latter of which was provided by the National Deuteration Facility, Australia. The hydrogenated and deuterated 2-EHL, as well as BIO-2130, were used as received. The ILs were purified under a high vacuum and elevated temperature (60 ℃) for 72 hours to reduce the concentration of residual water.

A complete analysis of the results is still ongoing. However, below we detail some of our initial findings. As an example, asymmetry plots $\Delta I=[I^V(Q)-I^0(Q)]/ [I^V(Q)+I^0(Q)]$ highlighting the changes in the Kiessig fringes arising from the metal-oxide/IL interface are plotted as a function of bias voltage ($I^V(Q)$) with respect to 0 V or open circuit potential (OCP) ($I^0(Q)$). The IL/2-EHL mixtures are shown in Fig. 2. Overall, a potential response could be identified for PNR with both up and down spins. However, down-spin (du) measurements revealed a greater response at low Q. Asymmetry plots of iron oxide (divided by 0 V) and iron silica (divided by OCP) showed a more significant response to bias voltages than steel (divided by OCP). Conversely, the asymmetry plots for up-spin (uu) measurements showed a clear periodic signal at the steel surface.

Meanwhile, we also tested 6 wt% [P6,6,6,14][BOB] in the hybrid oils, 2-EHL with 20 mol% BIO-2130, on the iron oxide interface at different applied potentials. More details will be represented in the continuation experiment report for proposal CRG-282.

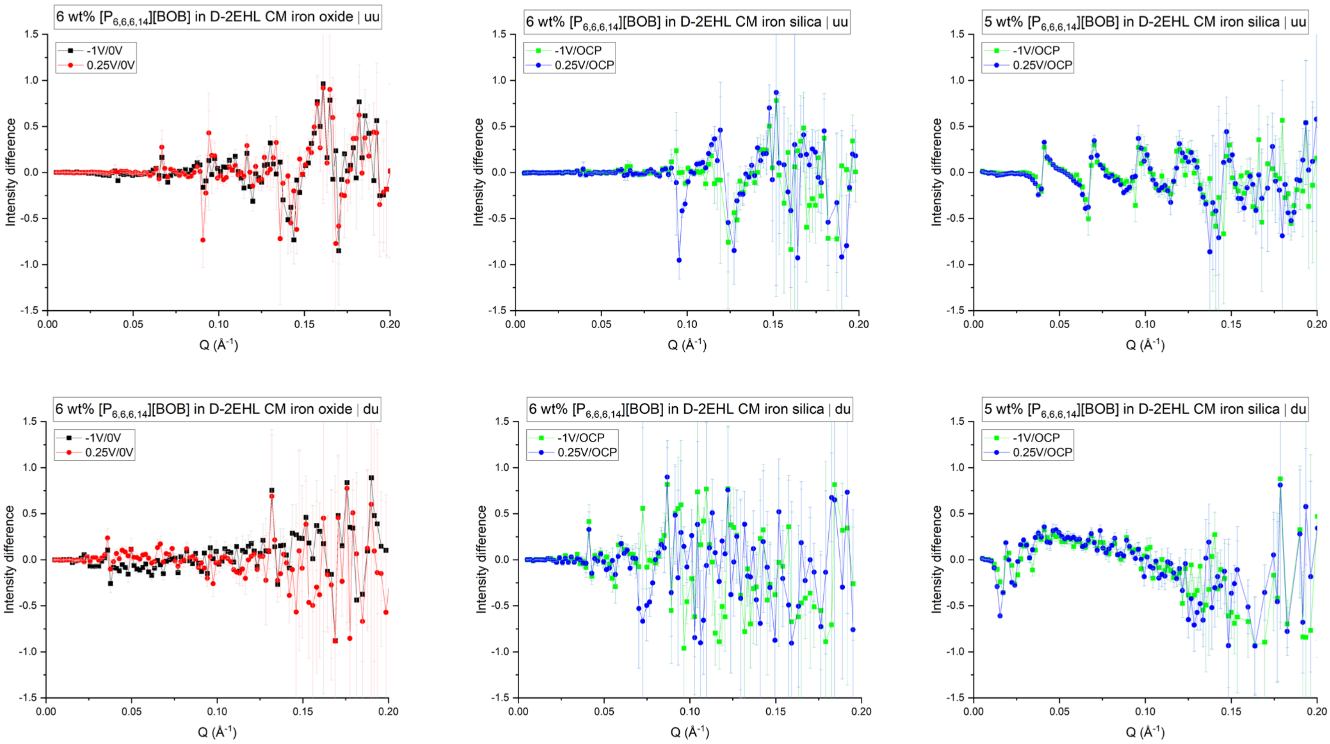

Figure 2. Asymmetry plots of PNR relectivity curves measured at different metal oxide interfaces in IL/2-EHL mixtures at different applied potentials. The potentials were applied in the order presented in the figure legend.

Overall, these results will help us unravel and understand the PNR measurements on tribologically relevant metal-oxide interfaces in novel bio-based oil-IL mixtures as a function of applied potential. It is hoped that such studies will provide valuable mechanistic understanding to tribotronic tests with such non-halogenated ILs and their additive oils on metal oxide surface at KTH.