Experimental report

22/06/2020

Proposal:	**6-03-442**	**Council:**	10/2018
Title:	Electroresponsive structuring of halogen-free ionic liquids in a polar solvent: Effect of anion		
Research area:	Chemistry		

This proposal is a new proposal

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Local contacts:	Alexei VOROBIEV

Samples:	[P6614] [BMB] d4-propylene carbonate [P6614] [BOB] Propylene Carbonate

Instrument	Requested days	Allocated days	From	To
SUPERADAM	6	4	23/01/2020	27/01/2020

Abstract:

This proposal addresses a sustainability challenge in the design of next generation of machinery. In particular, we are aiming at developing active lubrication technology to enable on-line control of friction and wear. The technology is based on using ionic liquids as additives to oils. Since ionic liquids are composed of cations and anions it may be possible to selectively attract to a charged surface positive or negative ions and as the result control the friction properties. Neutron scattering data are necessary to provide a coherent picture of interfacial assembly at charged surfaces. Our findings will be of importance not only in tribology but also for other interface intensive applications such as batteries and solar cells.

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Instrument: SuperADAM

Local contact: Alexei Vorobiev

Dates scheduled: 23rd – 27th January 2020

A total of 3 halogen-free phosphonium orthoborate ionic liquids (ILs) dispersed in polar solvent, propylene carbonate (PC) were studied at a gold electrode interface as a function of applied potential. For all systems, 4 potentials were studied (0, -1, +0.25 and -1.5 V). 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 minute stabilisation at the applied potential. In order to highlight any changes in the interfacial IL layers the scattering length density (SLD) of the bulk IL-PC solution was contrast matched to that of the gold (4.56×10^{-6} Å^{-2}; the bulk IL SLDs range from 0.44 to 0.77×10^{-2} Å^{-2}), by adding the appropriate volume of hydrogenated and deuterated analogues of the solvent, PC.

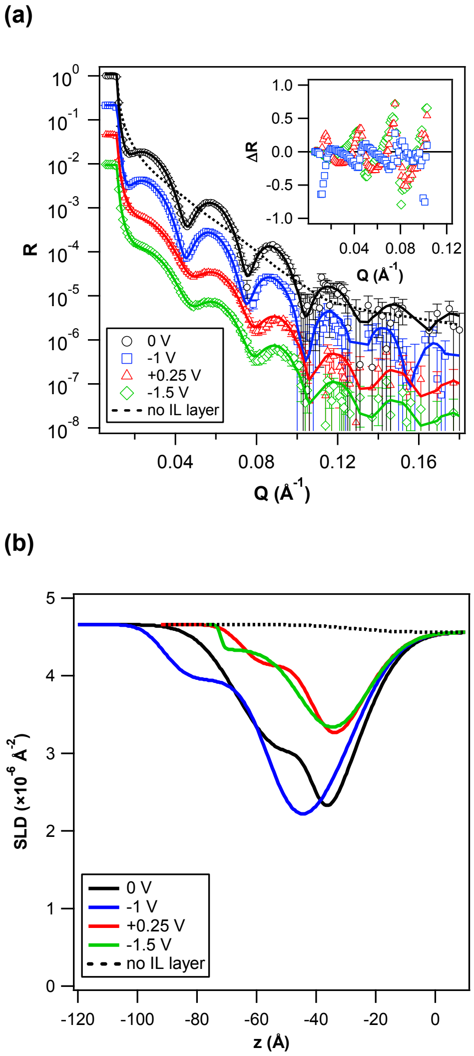

Figure 1. (a) Normalised reflectivity *R* for a 2 mol% solution of the DIL $[P_{8,8,8}\text{-}C_{12}\text{-}P_{8,8,8}][BOB]_2$ in PC at a gold electrode for different applied potentials. The inset shows corresponding asymmetry plots $\Delta R = [R^{+V}(Q)\text{-}R^{-V}(Q)]/[[R^{+V}(Q)+R^{-V}(Q)]$ highlighting the changes in the reflectivity curves between with respect to 0 V. The order of the potentials in the legend reflects the order the potentials were applied. **(b)** Variation in solution SLD from at the gold electrode interface (z = 0) into the bulk solution (z = ∞) for each potential corresponding to best-fits to the reflectivity curves shown as the solid lines in (a). The best-fits to the data were determined using a logarithmic figure of merit (FOM) in GenX.

The 3 ILs studied were synthesised at Stockholm University (SU), Sweden. The ILs studied all shared the same orthoborate anion, bis(oxalato)borate ([BOB]), but had three different phosphonium cations of different size and number of molecular charges were investigated. More specifically, two ILs were dicationic phosphonium ionic liquids with two different tri(alkyl)phosphonium cationic *headgroups* coupled with a alkane *linker* of equal chain length, namely 1,12-dodecanediylbis(tributyl)-phosphonium dibis(oxalato)borate ($[P_{4,4,4}\text{-}C_{12}\text{-}P_{4,4,4}][BOB]_2$) and 1,12-dodecanediylbis(trioctyl)phosphonium dibis(oxalato)borate ($[P_{8,8,8}\text{-}C_{12}\text{-}P_{8,8,8}][BOB]_2$). The third IL was a monocationic phosphonium with the same phosphonium *headgroup* as the ($[P_{4,4,4}\text{-}C_{12}\text{-}P_{4,4,4}][BOB]_2$ DIL, but with a single long alkane chain: tributyl(tetradecyl)phosphonium bis(oxalato)borate ($[P_{4,4,4,14}][BOB]$). All ILs were synthesised according to literature procedures by alkylating the corresponding trialkylphosphine using the mono- or dibromoalkane. This process was then followed by a metathesis in water using Na[BOB] followed by an extraction using ethyl acetate. Before use, the ILs were dried in a vacuum oven for 72 hrs at a maximum temperature of 60°C.

In contrast to traditional monocationic ionic liquids with a single cation, dicationic ionic liquids (DILs) (sometimes referred to as geminal ILs) are known to often exhibit higher thermal stabilities, viscosities, and densities. Furthermore, as their alkane linker chain can be considered as an additional structural moiety, offering more variation in terms of tuning of their physicochemical properties compared to their monocationic analogues and increasing their miscibility with different fluids. A full analysis of the results is still ongoing, however below we detail some of our findings and initial attempts to fit the data. The results from this study are anticipated to lead to a novel publication on dicationic ILs, which are still relatively new materials, whose interfacial behaviours is still largely unknown.

To investigate the effect of the cation *headgroup* size on the structuring of tetra(alkyl)phosphonium DILs, the electroresponsive structuring (ERS) of [P$_{4,4,4}$-C$_{12}$-P$_{4,4,4}$][BOB]$_2$ and [P$_{8,8,8}$-C$_{12}$-P$_{8,8,8}$][BOB]$_2$ DIL, were compared for the same bulk IL concentration (2 mol%) in PC. The reflectivity profiles for 2 mol% [P$_{8,8,8}$-C$_{12}$-P$_{8,8,8}$][BOB]$_2$ in PC at different potentials are shown in Fig. 1a. Clear variations in the amplitudes and periodicities of the Kiessig fringes in the reflectivity curves were observed in response to applied potentials, suggesting SLD and thickness changes in the interfacial region. The asymmetry plots in the Fig. 1a inset show these changes with respect to the reflectivity initially measured for 0 V. From the asymmetry curves it can be seen that after applying the positive (+0.25 V) potential the changes in the reflectivity are almost equal and opposite that observed for the first negative potential (-1 V), suggesting these changes were reversible. However, for the second negative potential (-1.5 V), the asymmetry curves reveal the changes in reflectivity induced by the positive potential were not fully reversed. Best-fits to the reflectivity curves are also shown in Fig. 1a.

The corresponding SLD profiles obtained from these fits are shown in Fig. 1b. For all potentials a 2 layer model provided a significantly better fit than a 1 layer model, the addition of subsequent layers was found to not lead to any notable improvement in the fits. The SLD profile at 0 V reveals an initial interfacial region of an inner layer with notably lower SLD than the bulk solution (which was contrast matched to the gold SLD) and thicker outer layer of higher SLD. After applying -1 V, the SLD profiles suggest thickness of the inner layer increases and the SLD decreases. These thickness changes are then reversed at +0.25 V and the SLDs of the layers are significantly higher than that at the other potentials. The calculated SLDs of the IL component ions (estimated from the bulk IL density) are -0.26×10^{-2} Å^{-2} for the [P$_{8,8,8}$-C$_{12}$-P$_{8,8,8}$]$^{2+}$ cation and 3.02×10^{-2} Å^{-2} for the [BOB]$^-$ anion. The longest and shortest axes of cation are ~38 Å and 20 Å, respectively, whilst the anion is much smaller, approx. ~3 × 7 Å. The observed changes in the thicknesses and SLDs of the inner and outer layers therefore suggest: 1) an initial preference at the gold interface of the cation; 2) there is a reversible orientation change in the cation at the gold interface, whereby the cations longer axis in parallel to the interface towards positive potentials and is perpendicular at the negative potential; 3) significantly less cations are at the interface at the positive potential; and 4) the changes induced by the positive potential are not fully reversed on applying a second, larger negative bias.

Figure 2 shows the reflectivities and asymmetry plots at different applied potentials for the other DIL ([P$_{4,4,4}$-C$_{12}$-P$_{4,4,4}$][BOB]$_2$) and monocationic IL ([P$_{4,4,4,14}$][BOB]). It can be seen that the changes induced by the applied potentials are notably less remarkable than observed for [P$_{8,8,8}$-C$_{12}$-P$_{8,8,8}$][BOB]$_2$. Our initial analysis of the reflectivity curves (not shown here) suggests that [P$_{4,4,4}$-C$_{12}$-P$_{4,4,4}$][BOB]$_2$ and [P$_{4,4,4,14}$][BOB] form significantly thinner adsorbed boundary films at the gold interface. Furthermore, there is no indication that any large thickness changes with applied potential.

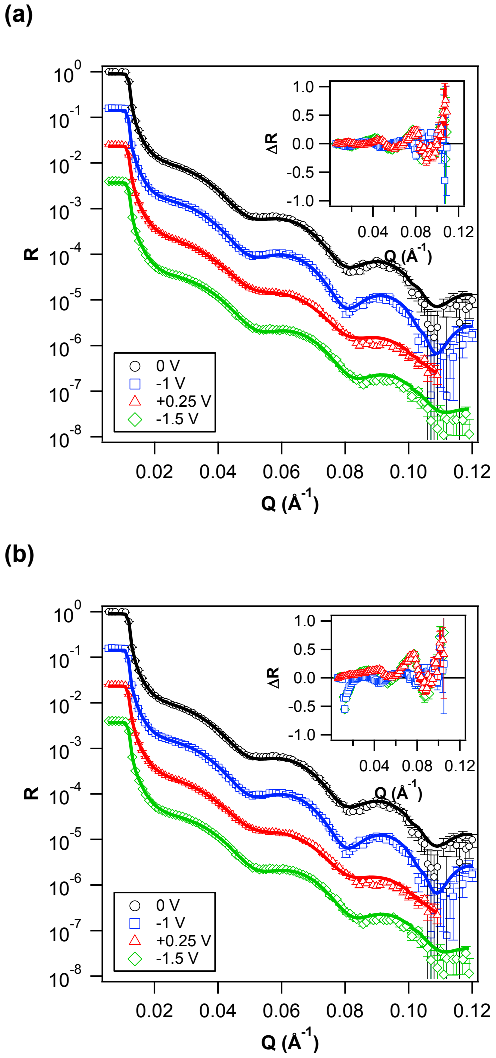

Figure 2. Normalised reflectivity *R* for a 2 mol% solution of the **(a)** DIL [P$_{4,4,4}$-C$_{12}$-P$_{4,4,4}$][BOB]$_2$ and **(b)** (mono) IL [P$_{4,4,4,14}$][BOB] in PC at a gold electrode for different applied potentials. The inset shows corresponding asymmetry plots $\Delta R = [R^{+V}(Q)-R^{-V}(Q)]/[[R^{+V}(Q)+R^{-V}(Q)]$ highlighting the changes in the reflectivity curves between with respect to 0 V. The order of the potentials in the legend reflects the order the potentials were applied.

In conclusion, we believe these results are the first of their kind in their attempt to unravel and understand the electroactive behaviours of DILs as a function of their molecular architecture. The results suggest the choice of the tri(alkyl)phosphonium headgroup plays a large role in determining the interfacial adsorption structures of the ILs at electrode surfaces and reveal a possible mechanism for controlling the orientations of dicationic ions at charged interfaces.