

	Experiment title: Behavior of Interfacial Multilayer Structures in Ionic Liquids under Shear	Experiment number: SC-3596
Beamline: ID03	Date of experiment: from: 05/07/2013 to: 05/10/2013	Date of report: August 8, 2013
Shifts: 9	Local contact(s): Francesco Carlà	<i>Received at ESRF:</i>
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Report:

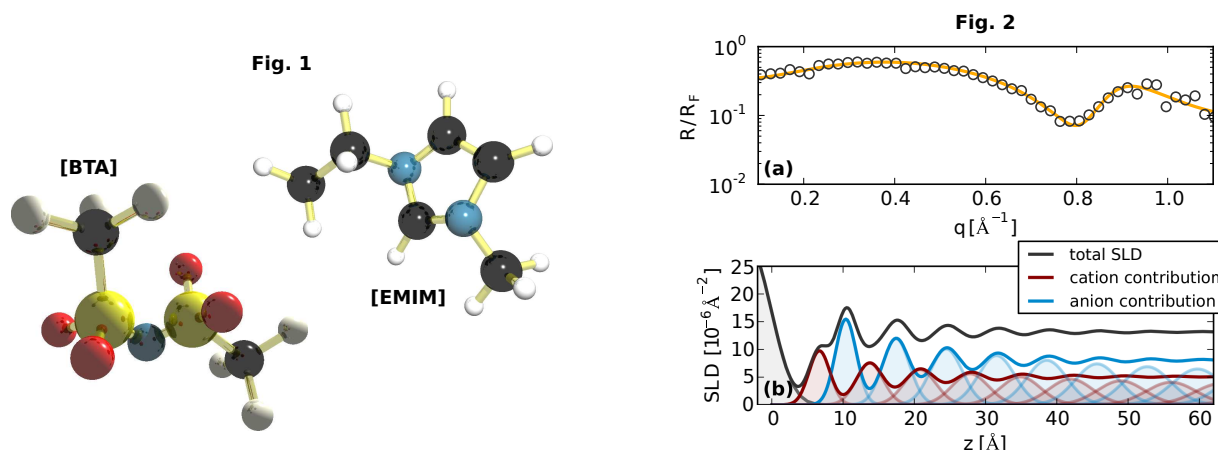
During experiment SC-3596 we have investigated interfacial layering properties of the 1-ethyl-3-methylimidazolium–bis(trifluoromethylsulfonyl)imide ([EMIM][BTA]) ionic liquid (cf. fig. 1) via X-ray reflectivity measurements at the buried sapphire/liquid interface. From our previous experiments with [EMIM][BTA] we know that the molecules can be dissociated by high-intensity X-ray irradiation which is a hindrance for the desired layering.

Before the actual reflectivity experiments we have thus determined the influence of the X-ray beam at ID03 by watching the characteristic dip at $q \approx 0.8 \text{ \AA}^{-1}$ in figure 2 (a) disappear over time. As a result, after careful alignment of several spots on the interface, the whole system was moved laterally (perpendicular to the beam) at a pace of 0.5 mm per data point with a counting time of five seconds during measurements. In between separate scans, the sample chamber was flushed with fresh which has been found to restore initial conditions as subsequent scans match each other very well.

The buried interface between liquid and substrate is accessed by transmission through the liquid (pathlength of about 5 mm). As a consequence, the signal recorded in reflecting geometry, at $\theta_{\text{out}} = \theta_{\text{in}}$, is a superposition of specular reflectivity and bulk liquid scattering. With the 516×516 pixel MAXIPIX detector, we were able to record reflectivity and structure factor signal simultaneously in one run.

Figure 2 (a) shows background corrected, normalized reflectivity data – divided by the Fresnel reflectivity of a single sharp interface – of [EMIM][BTA] on sapphire with the best matching fit. The corresponding scattering length density (SLD) profile, which is

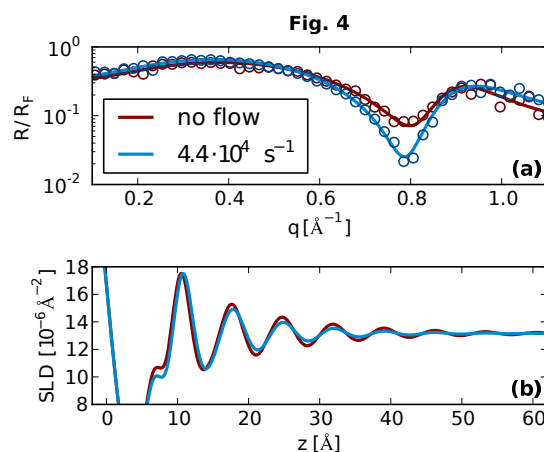
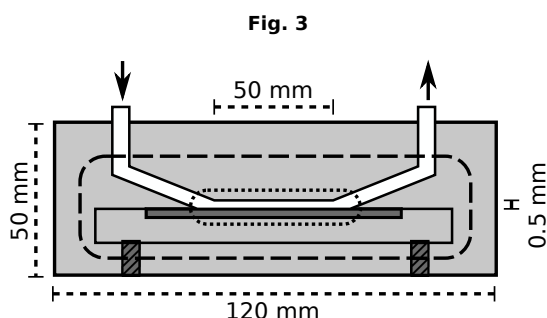
proportional to the electron number density ρ_e , is depicted in figure 2 (b). The prominent dip at $q \approx 0.8 \text{ \AA}^{-1}$ in the reflectivity curve cannot be described properly using a simple single- or bilayer model for the fit. Instead, we use a "distorted crystal" model – modified for a two-component liquid – in the fitting process [1, 2]. [EMIM]- and [BTA]-layers are each described by a series of gaussian functions that are blurred with distance from the interface to match the bulk liquid density. The substrate features a constant scattering length density with an erf-like decay to account for roughness at the interface.



The result is clear evidence of interface-induced alternating cation/anion layering of [EMIM][BTA], starting with the [EMIM]-cation (similar size, less electrons; lower scattering length density) at the substrate. This is in good agreement with the results of AFM studies of [EMIM][BTA] at the Au(111) interface [3] and other reflectivity experiments on similar ionic liquids [2, 4], all revealing alternating monolayers with a cation enrichment close to the interface. Moreover, the double layer thickness of 7.1 \AA is close to the bulk liquid Ion-Pair diameter $D = 7.5 \text{ \AA}$, calculated according to the method described in [5].

For the second half of the experiment, we applied shear forces to the layering at the interface in the direction perpendicular to the X-ray beam. This was achieved using our custom made flow cell, a gear pump and 100 ml of [EMIM][BTA]. The flow cell features a small channel with a cross section of $5 \times 0.5 \text{ mm}^2$ (h×v) along the substrate (cf. fig. 3). The gear pump setup reaches a flow rate of 0.55 l/min or an average speed of $\bar{v} 3.6 \text{ m/s}$ inside the cell's channel. Assuming a parabolic velocity profile, due to the liquids Newtonian behavior, the shear rate at the interface can be calculated as $\dot{\gamma} = 6\bar{v}/d = 4.4 \cdot 10^4 \text{ s}^{-1}$, where d denotes the channel's height.

Figure 4 depicts the direct comparison between the data shown in figure 2 and the reflectivity curve of a measurement at $\dot{\gamma} = 4.4 \cdot 10^4 \text{ s}^{-1}$ with the corresponding fits and models. In the normalized reflectivity, the dip at $q \approx 0.8 \text{ \AA}^{-1}$ stays at its position and becomes more pronounced while the rest of the q -Range remains relatively unchanged. For the actual layering this means a small decrease in double layer thickness ($D = 6.9 \text{ \AA}$) and slightly less defined layering, especially from the fourth layer from the interface towards the bulk liquid. Moreover, with $\dot{\gamma} = 4.4 \cdot 10^4 \text{ s}^{-1}$ lateral translation of the sample – as it was done for the static measurements – is no longer required. Measurements with and without simultaneous translation are identical within the errorbars. This implies that while strong layering is observed at the ionic liquid/sapphire interface, either ion exchange, even in the innermost



layers, must be possible to remove dissociated molecules with new ones provided by the flow or the whole layer system is not tightly bound to the interface but moves along it with the flow of the bulk liquid. While none of these cases, nor a combination of both, can directly be ruled out from the data of this experiment, the small but nonetheless measurable decrease in double layer thickness when shear is applied might give a hint towards lateral movement within the layered system as the rod-like [BTA]-anions and the alkyl chains of the [EMIM]-cations might align more parallel to the direction of flow.

References

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