ESRF	**Experiment title:** Electronic Double Layer Structures in Alkylimidazolium Ionic Liquids at the Sapphire (0001) Interface	**Experiment number:** SC-3716
Beamline: ID03	**Date of experiment:** from: 09/12/2013 to: 09/16/2013	**Date of report:** February 25, 2014
Shifts: 12	**Local contact(s):** Francesco Carlà	*Received at ESRF:*

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Report:

The stated aim of experiment SC-3716 was the investigation of interfacial layering of alkylimidazolium ionic liquids and its dependance on the size and geometry of the ions. Therefore, X-ray reflectivity measurements were performed at the buried sapphire/liquid interface on ESRF beamline ID03.
Data was obtained by putting bulk liquid samples on top of a smooth (rms roughness $\sigma \approx 2\,\text{Å}$), clean sapphire (0001) substrate inside a custom built sample cell and measuring the reflected signal from the solid/liquid interface. The X-ray beam enters the cell from the side through a polished sapphire window, impinges the interface and leaves the cell through a second window after a transmission length of about 5 mm through the liquid. The recorded signal thus is a superposition of specular reflection from the interface and bulk liquid scattering. Using the 516×516 pixel MAXIPIX detector at ID03 we were able to record both reflectivity and background signal simultaneously in one run.
Using this setup, reflectivity curves of all four different combinations of 1-ethyl-3-methylimidazolum [EMIM] and 1-decyl-3-methylimidazolium [DMIM] cations with bis(trifluoromethylsulfonyl)imide [NTf2] and tris(pentafluoroethyl)trifluorophosphate [FAP] anions were taken (cf. fig. 1).
Figure 2 (a) depicts the reflectivity data for [EMIM][NTF2] together with the best matching fit, while 2 (d) shows the resulting scattering length density (SLD, prodcut of electron density and classical electron radius) profile where the cation contribution is indicated by a red line, the anion contribution by a blue one. In comparison with figures 2 (b-c) and (e-f) – showing alternative models –, it is obvious that the

measurment confirms that there is alternating cation/anion layering with a periodicity of D=7.5 Å(which closely matches the diameter of a cation-anion-pair [1]) and an excess of cations at the interface. An increased density of anions or so-called checkerboard layering with an equal number of anions and cations in each layer can be ruled out. For all cases, we use a modifified version of the "distorted crystal" model for describing the contributions to the scattering length density [2, 3]. Fitting the experimental data with a simple single- or bilayer density model does not describe the curve properly.

Fig. 1

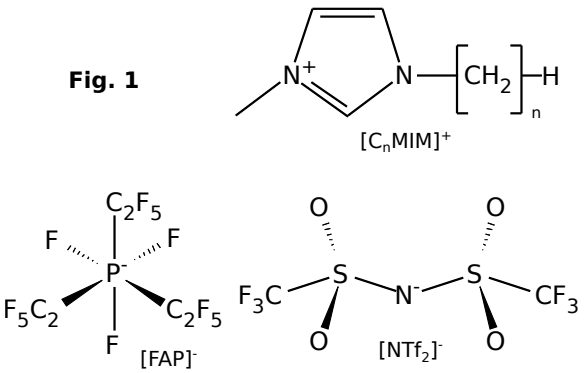
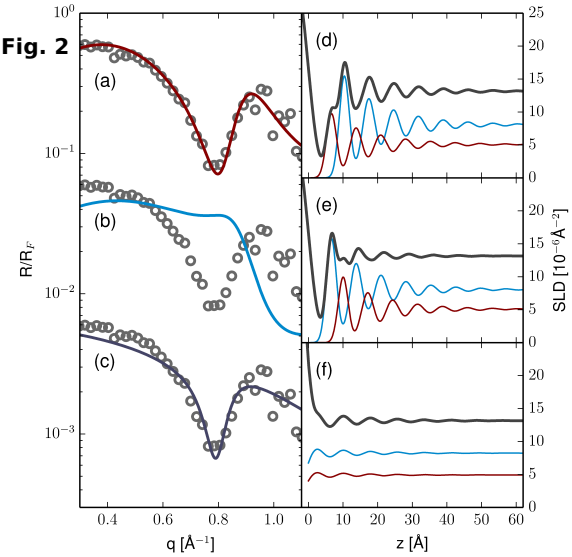


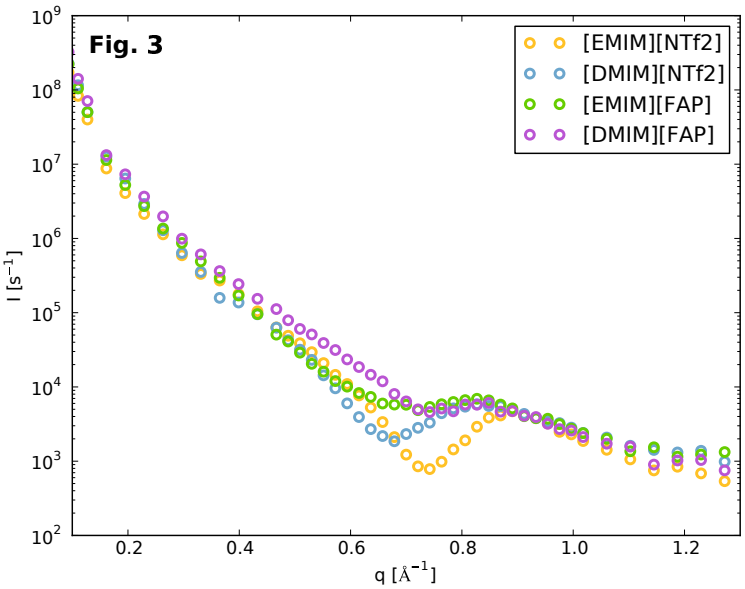
Fig. 2



These results match the findings of our previous experiments, as well as other studies on this or similiar systems using various surface sensitive techniques [3, 4, 5]. Figure 3 shows a comparison of [EMIM][NTf2] with the other liquids used in this experiment. Substituting [EMIM] with the [DMIM] results in a significant shift of the featured dip towards smaller q – indicating increased layer thickness – as well as a reduced dip amplitude, giving a hint towards weaker layering than with the short-chained cation. Ionic Liquids based on the [FAP] anion appear to exhibit even weaker layering in general. Intrestingly, in this case longer alkyl chains seem to lead to more compact layering.

While the results give clear evidence of interface-induced alternating cation/anion layering of both [NTf2]- and [FAP]-based alkylimidazolium ionic liquids, the detailed analysis of the experimental data – including comparison with MD simulations – is still a work in progress.

In addition to these studies we have examined the stability of the observed layering phenomena under the application of shear forces. This was achieved by pumping the liquid through a narrow channel (crosssection 5×0.5 mm^2) along the sapphire substrate and perpendicular to the X-ray beam. Using our gear pump with this setup, shear rates of up to $\dot{\gamma} = 4.4 \cdot 10^4$ s^{-1} could be achieved. For the studied liquids, no significant changes to the layering properties was observed, even at the highest flow rates, which is a clear indication for tightly bound structures in all four cases.



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