	Experiment title: Molecular Scale Structure of Ionic Liquid-Aqueous Solution Interfaces	Experiment number: SC-3780
Beamline: ID15A	Date of experiment: from: 06/11/2013 to: 09/11/2013	Date of report: 01/03/2014
Shifts: 9	Local contact(s): HONKIMÄKI Veijo	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): MEZGER Markus* HOU Binyang* REICHERT Harald* MARS Julian* WU Xilin*		

Report:

During our ESRF experiments on the project “Molecular Scale Structure of Ionic Liquid-Aqueous Solution Interfaces” we employed x-ray reflectivity (XRR) to study the free surface and the liquid-liquid interface between ionic liquids (ILs) and water.

In collaboration with Oleg Konovalov (ID10B) we investigated the structure of 1-methyl-3-docosylimidazolium bis(trifluoromethyl-sulfonyl)imide ($[C_{22}mim]^+[TFSI]^-$) at the free surface (Fig. 1). As the temperature decreases, close to the bulk melting point two Bragg-like peaks emerge. The peak positions (first order peak at 1.7 nm^{-1} , second order peak at 3.4 nm^{-1}) suggest the formation of a surface crystalline structure (surface freezing) with a layer spacing of $\sim 3.7 \text{ nm}$. This interpretation was confirmed by a quantitative analysis using a modified distorted crystal model (solid black lines). At the highest temperature (92°C) the experimental XRR pattern is perfectly reproduced without adding a crystalline layer to the model profile. In contrast, the XRR data obtained at 68.8°C could not be adequately reproduced without accounting for the formation of a crystalline layer at the free surface.

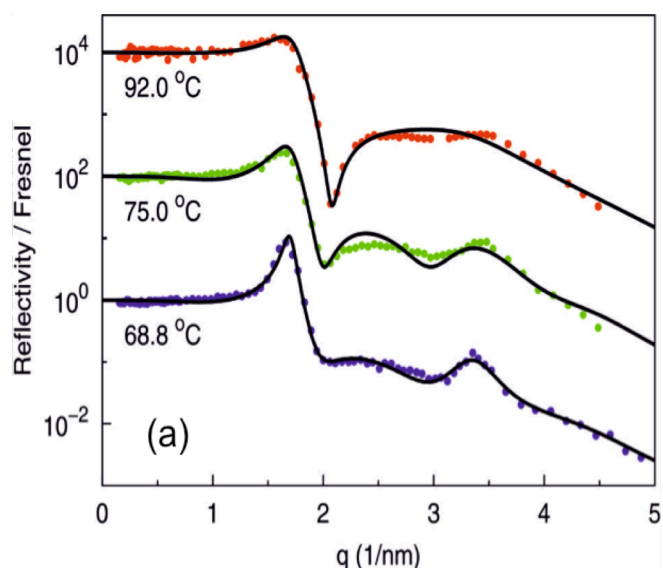


Figure 1: (a) Measured (symbols) and model fitted (lines) temperature dependent x-ray reflectivity of the free surface of $[C_{22}mim]^+[TFSI]^-$ normalized to the Fresnel reflectivity (data from ID10B). Curves are vertically shifted for clarity.

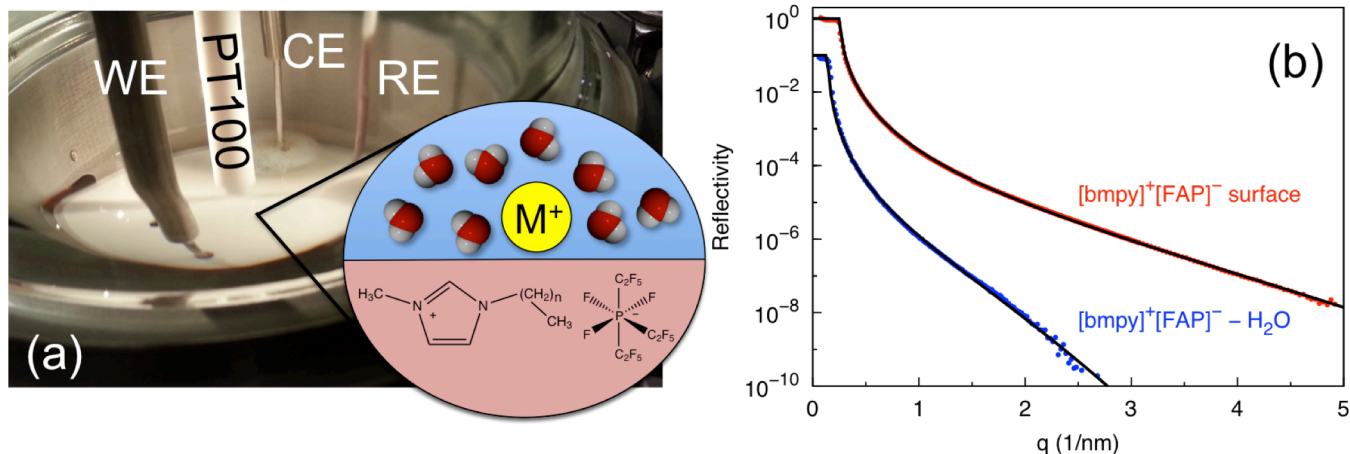


Figure 2: (a) Photo of the liquid-liquid cell for in-situ x-ray reflectivity experiments under applied electric potential. Temperature sensor (PT100); platinum working electrode (WE); platinum counter electrode (CE); Ag/AgCl reference electrode (RE). (b) X-ray reflectivity of $[bmpy]^+[FAP]^-$ at the free surface (red symbols) and at the buried IL-water interface (blue symbols, data from ID15A). Calculated patterns (black lines) are obtained by parameter refinement assuming a single liquid interface with capillary wave roughness. Curves are vertically shifted for clarity.

XRR experiments on deeply buried IL-water interfaces were performed at the high-energy micro diffraction (HEMD) instrument at ID15A. For these experiments we developed a new modular sample cell allowing temperature dependent XRR measurements at liquid-liquid interfaces under electrochemical control (Fig. 2a). Using this setup we could reproduce the XRR data on the free surface of $[C_{22}mim]^+[TFSI]^-$. However, for this IL, experiments on the buried IL-water interface turned out to be rather difficult. The relatively low interfacial tension and the high melting point of $[C_{22}mim]^+[TFSI]^-$ (68°C) as well as the similar mass density of the IL and water precluded the preparation of a stable liquid-liquid interface. Therefore, $[bmpy]^+[FAP]^-$ (mass density 1.58 g/cm^3 , melting point 4°C) was selected for experiments at the IL-water interface. The experimentally obtained XRR data from the free surface (Fig. 2b; red symbols) is perfectly reproduced by a model comprised of a single surface with capillary wave roughness (black line). XRD on bulk samples showed that in this IL the typical nearest intermolecular distance between anions is approx. 8 \AA , i.e. much smaller than that of $[C_{22}mim]^+[TFSI]^-$. Therefore, the characteristic features that contain information related to the molecular arrangement of anions and cations near the interface appear at momentum transfers above 5 nm^{-1} . Figure 2 shows the XRR measurements of the $[bmpy]^+[FAP]^-$ -water interface together with the calculated curve, assuming a single liquid-liquid interface (black line). In contrast to the data obtained from the free surface, deviations between the experimental curve and the calculated pattern were observed around approx. 2 nm^{-1} , indicating the presence of a more complex interfacial structure.

To investigate the influence of an external electrical potential on the interfacial structure, the XRR signal at a constant angle of $2\theta = 0.2^\circ$ was recorded during cyclic voltammetry (Fig. 3). The data show clear modulations of the reflected intensity $I(t)$ with the applied electric potential $U(t)$. More experiments, carried out at different scattering angles, as well as XRR curves vs. incident angle at fixed potentials will be necessary to elucidate whether the observed modulations originate from changes in the capillary wave spectrum or are caused by adsorption and desorption of ions at the IL-water interface.

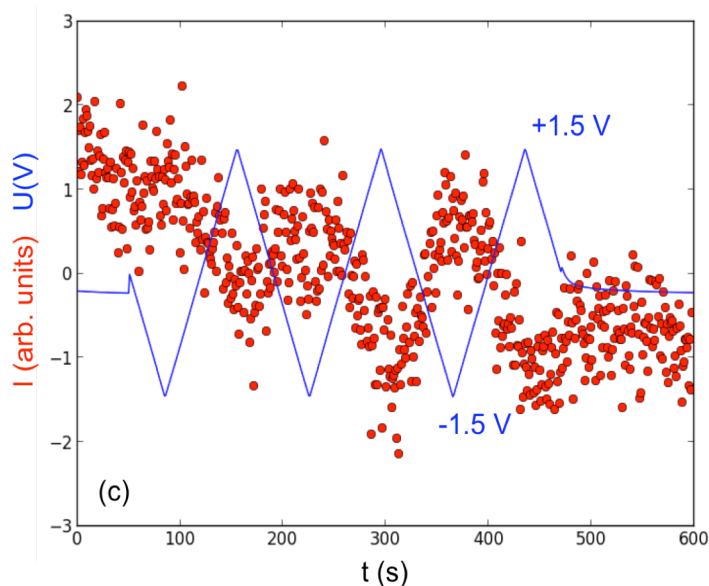


Figure 3: Time resolved XRR signal (red symbols) at $q = 1.2\text{ nm}^{-1}$ during cyclic voltammetry between -1.5 V and $+1.5\text{ V}$ (blue curve) from the $[bmpy]^+[FAP]^-$ - CoCl_2 aqueous solution interface.