

**Experiment title:**

Influence of Electric Fields on the Structure of Ionic-Liquids at Solid Interfaces

Experiment number:

SI-1610

Beamline:

ID15A

Date of experiment:

from: 14/02/2008 to: 21/02/2008

Date of report:**Shifts:**

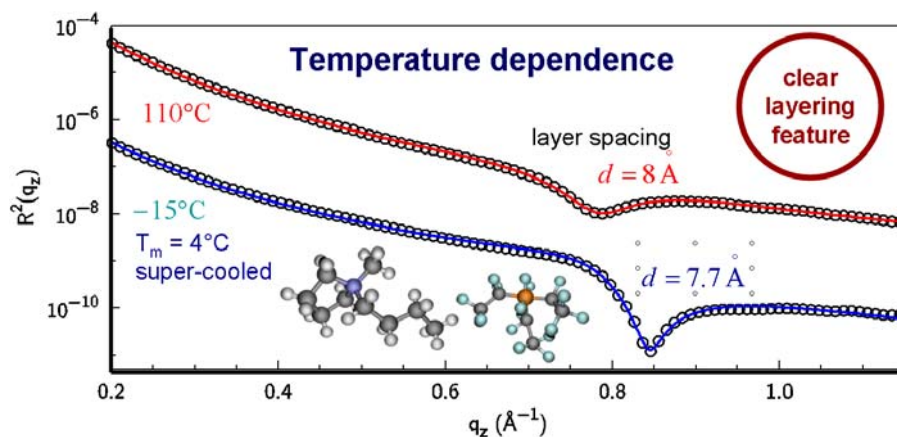
18

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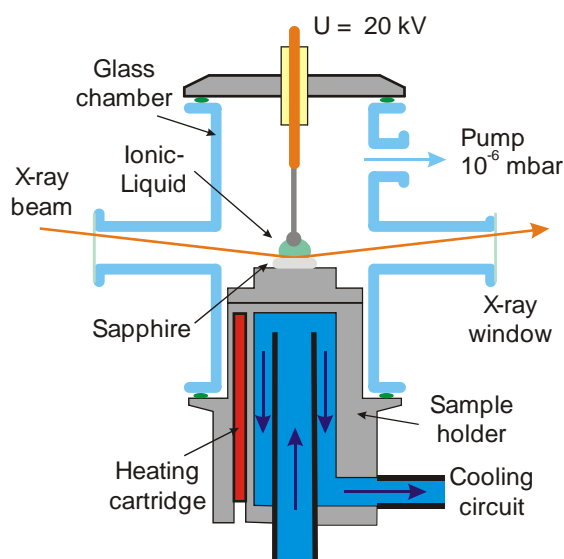
Room temperature ionic liquids (RTILs) are promising candidates for a variety of new technological processes ranging from applications as special solvents in green chemistry to catalytic reactions in biotechnology and electrodeposition of corrosion protection layers. Although crucial for the understanding of solvent properties, only little is known about the structural rearrangement of the anions and cations at solid interfaces. First indications of layering at a free surface were found by direct recoil spectrometry, later by sum frequency generation (SFG) spectroscopy and in a single x-ray reflectivity study. Due to the limited



number of experimental methods suitable to study deeply buried interfaces, up to now only two studies on the solid-liquid SiO₂ interface using SFG have been performed, where a strong interaction of the imidazolium cation with the SiO₂ was found, leading to a structural rearrangement of the

alkyl chains. Further experiments suggested a strong influence of electric fields on the structure (ordering) of ionic liquids at solid walls.

In this project we have used high energy x-ray reflectivity to get precise and direct information on the structure of ILs at solid walls under the influence of electric fields. For this purpose we have built a sample cell which is suitable for temperature control and the application of electric fields. In a first experiment we used 1-Butyl-1-methylimidazolium (bmpy) tris(pentafluoroethyl)trifluorophosphate (FAP) in contact with sapphire. In a first step the structure of the RTIL at the sapphire interface was determined. The high energy x-ray reflectivity measurements showed a strong dip indicating the presence of interfacial layering (see Figure 1, the two ion species are depicted at the bottom). Detailed fitting of the reflectivity curves confirmed the presence of a new type of interfacial ordering, where the two ionic species are arranged in double layers at the interface with well separated charges. The layering extends several nanometers deep into the liquid with a (temperature-dependent) decay length of approximately 2 double layers. This result strongly indicates that the RTIL is not governed by the electrostatic Coulomb interactions alone. Size effects, van-der Waals interaction and/or hydrogen bonding must be taken into account for a full understanding of this unusual interfacial ordering effect.



In a second step we applied a high voltage to the sample in order to determine the effect of electric fields on the layered structure at the interface (see Figure 2). The upper limit for the high voltage was 5kV, at which the RTIL started to creep and create a short cut. Figure 3 shows the Fresnel normalized reflectivity at two different high voltage settings with opposite polarity. Switching the polarity clearly affects the measured reflectivity. For a positive voltage of 3kV the dip in the reflectivity characterizing the layering structure is identical to the field-free measurement, while the application of a negative voltage of -5kV changes the features in the reflectivity curve significantly.

A detailed analysis of the interfacial structure is currently underway.

