Charge distribution at the free surface of imidazolium-based ionic liquids: Effect of chain length and added water

C. Ridings¹*, Vera Lockett², Gunther Andersson¹

¹ Flinders Centre for NanoScale Science and Technology, Flinders University, PO Box 2100, Adelaide SA 5001, Australia
² Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia

* e-mail: chris.ridings@flinders.edu.au

Ionic liquids (ILs) provide a liquid-system comprised totally of ions, where the organic nature of the cation and/or anion provide a range of competing forces that contribute towards the organisation of species at the IL/vapour interface. Therefore understanding of the surface structure of ionic liquids is important for both applications involving ILs as well as for fundamental understanding of these surface forces. The work presented here are the first investigations into the surface structure, and in particular the charge distribution, of imidazolium-based ILs as a function of cation aliphatic chain length and added water content. This is of particular relevance as it represents the first study into the charge distribution along the surface normal for the IL/vacuum interface. Studying the effect of chain length provides qualitative information on the importance of competitive forces on the charge distribution along the surface normal, while studying the effect of water provides valuable information on the effect of water as a surface impurity in ILs. The latter is important as the vast majority of ILs are highly hygroscopic. The studies are conducted using the concentration depth profiling technique, neutral impact collision ion scattering spectroscopy (NICISS). NICISS is an ion-scattering technique that is able to determine the concentration depth profiles of the elements in soft-matter samples, with a depth range of 20 nm and resolution of a few Angstrom. The concentration depth profiles of the elements in the IL samples directly give the charge distribution along the surface normal.

It was found that by increasing the cation aliphatic chain length in the 1-alkyl-3-methylimidazolium tetrafluoroborate homologous series from n=6 to n=10 leads to a decreasing positive surface charge due to the cation ring being shifted toward the bulk to a greater extent than the anion [1]. The charge distribution along the surface normal is given in figure 1.

![Charge distribution graph](image-url)
Fig. 1. Charge distribution along the surface normal as a function of cation aliphatic chain length in the [C\textsubscript{n}mim][BF\textsubscript{4}] homologous series.

Additionally, the effect of water as a surface impurity in 1-hexyl-3-methylimidazolium chloride was investigated by measuring the concentration depth profiles of the elements as a function of added water (as determined by Karl-Fischer titration) \[2\]. The results show that at lower water content the carbon (cation) is enriched at the surface with the anion sitting below the cation chains. With increased water content the carbon excess at the surface is decreased, followed by an increased surface excess of chloride as seen in figure 2. This results in a more negative surface charge due to the presence of small amounts of water.

Fig. 2. Concentration depth profile of carbon (cation) and chloride (anion) in [C\textsubscript{6}mim][Cl] as a function of water content.