

Surface Properties of Ionic Liquids: A Mass Spectrometric View Based on Soft Cluster-Induced Desorption

K. Bomhardt, P. Schneider, T. Glaser, and M. Dürr

Institute of Applied Physics, Justus Liebig University Giessen, 35392 Giessen, Germany
karolin.bomhardt@ap.physik.uni-giessen.de

Ionic liquids (IL) feature a large technological potential, e.g., in catalysis or as designer solvents; with respect to their bulk properties, they have been intensively investigated. However, since in most applications the interaction proceeds via the surface of the IL, e.g., in the case of catalytic reactions, the surface properties are of equal or even higher interest.

Here we show the application of Desorption/Ionization Induced by Neutral SO_2 Clusters (DINeC) [1] in combination with mass spectrometry (MS) for the investigation of the molecular composition of the surface of IL. Clear and fragmentation-free spectra of the cations and anions present in the sample are obtained after DINeC from bulk and thin film samples of IL (Fig. 1, left). Based on both softness [2] and surface sensitivity [3] of DINeC-MS, accumulation of either cations or anions was discriminated on the surface of bulk IL, depending on the molecular structure of the IL components (Fig. 1, right). In particular, cations with long alkyl chains were found to aggregate on the surface, but this tendency is the more reduced the larger the respective anion is; in the case of larger anions and smaller cations, the effect is found to be even reversed.

For thin layers of IL, the ratio between cations and anions as detected in the mass spectra is further influenced by the surface of the substrate; structural inhomogeneities such as the formation of islands of bulk material as well as the dynamical behavior of the thin film layer are deduced from the temporal evolution of the mass spectra and the relative intensities of cations and anions.

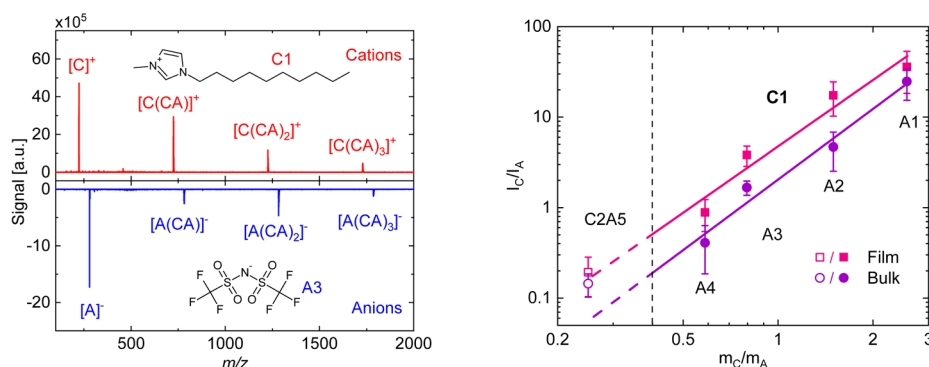


Figure 1 – Left: DINeC mass spectra in positive and negative ion mode as obtained from the surface of a bulk sample of an ionic liquid with the indicated cations and anions. Right: Intensity of the cationic mass peaks with respect to the intensity of the anionic mass peaks, I_C/I_A , as a function of the mass ratio of cations and anions, m_C/m_A . Data are shown for bulk IL (dots) and thin film samples (squares). The different anions A1 to A4 were measured in combination with C1 as cation (1-decyl-3-methylimidazolium, compare left); A5 (tris(pentafluoroethyl)trifluorophosphate) was measured with C2 (1-ethyl-3-methylimidazolium) as cation.

References:

- [1] C. R. Gebhardt, et al., *Angew. Chem., Int. Ed.* 48, 4162 (2009).
- [2] A. Portz, et al., *Biointerphases* 15, 021001 (2020).
- [3] A. Portz, et al., *Biointerphases* 13, 03B405-1 (2018).