

Adsorption of Sulfonyl-group based Anions from Ionic Liquids: an *in situ* STM and Impedance Study

Georg Gorbatovski^{*}, Ove Oll, Jinfeng Zhao and Enn Lust

Institute of Chemistry, University of Tartu

** georg.gorbatovski@ut.ee*

Adsorption of particles, such as molecules or ions, is an important basis for many everyday phenomena, such as corrosion inhibition or chromatographic separation. With regard to electrochemical technology, it provides a basis for energy storage in supercapacitors as well as helps to mitigate many important faradic processes via the formation of the electrical double layer (EDL). However, in many cases, the particles themselves adsorb at the surface by chemical bonding, thereby contributing to an effect called specific adsorption, which means that the adsorbed species can no longer be considered as components of the diffuse phase at a solid|liquid interface. Therefore, as part of the solid interface, they contribute strongly to the interfacial properties, such as energy storage, reactivity and interaction with other interfaces. It is of interest to look at such systems whereby there are no neutral particles within the liquid phase, such as ionic liquids (IL). Composed of ions, ILs constitute a large variety of liquidous electrolyte media that can be specifically tuned for an application in mind. This allows ILs to have a varied range of applications, such as electrolytes for energy storage, separation of ionic or organic species and catalytic media for organic synthesis.

Although the formation of the EDL in ILs has been in the scientific focus for over a decade, there is still a lack of understanding with regard to the specific interaction of ions at IL|metal interfaces [1]. This is partially due to the difficulties in describing such interactions from a modelling perspective, as well as the complexity of the systems in electrochemical experiments.

To overcome these problems, both classical electrochemical methods (cyclic voltammetry and electrochemical impedance spectroscopy) as well as *in situ* scanning tunneling microscopy (STM) method have been applied to observe the interfacial structuring at electrode|IL interfaces. Single crystal bismuth electrodes have been chosen as the working electrodes due to their variable metallic properties and stable surface structure. Three sulfonyl-group based anions - triflate (OTf), mesylate (Mes) and bistriflimide (TFSI) have been chosen for their potential ability to chemically bond to the surface through the sulfonyl groups, which has been demonstrated in aqueous solutions, but not ILs. These anions have been combined with aliphatic imidazolium cations that are generally thought to not specifically adsorb at the metallic electrodes. It is observed that sulfonyl-group anions show a largely different adsorption behavior at Bi electrodes compared to that of halide anions studied in our previous paper: adsorption of OTf, Mes and TFSI anions is a very slow process and the adsorbed layer acts as a dielectric at the surface, therefore considerably lowering the amount of charge that can be stored.

It should be noted that adsorbed sulfonyl-anions form two stable polarization regions (electrostatic and dielectric chemisorbed regions) that can be switched between by varying the applied potential value, possibly contributing to a new electronic memory type system.

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