

Surfaces studies of ionic liquids^[P1-P3]

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Ionic liquids (ILs) are salts with melting points below 100°C; they typically consist of large organic ions as shown in Figure 1. Many ILs are liquid at room temperature and have extremely low vapour pressures of below 10⁻⁹ mbar. Unlike conventional liquids, they can thus be studied with surface science techniques in UHV. We have taken advantage of this exceptional property in several closely related projects, which were performed in collaboration with Peter Wasserscheid, Florian Maier and Ivana Ivanovic (all at the Universität Erlangen).

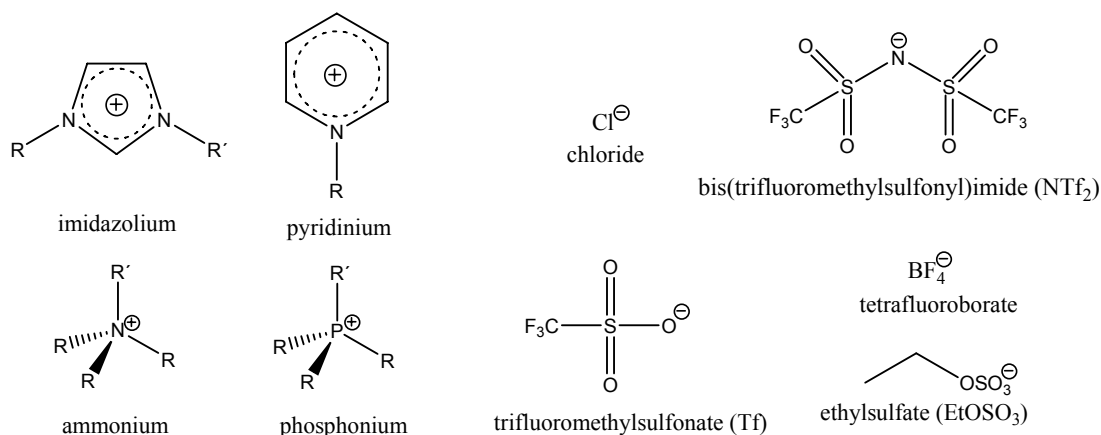


Figure 1. Typical cations (left) and anions (right) forming ionic liquids.

Surface science of ionic liquids and their solutions^[P1-P3]

This collaborative project is part of the DFG Priority Program SPP 1191 and focuses on the general surface properties of ILs, on solutions of metal complexes in ILs, and on their reaction with gases. Initially, our studies focused on the following questions: (a) Is it possible to apply X-ray photoelectron spectroscopy to surfaces of ionic liquids? (b) What are the requirements for obtaining a "clean" IL surface? (c) Is it possible to study dissolved species such as metal complexes and are there differences between bulk and surface concentrations of these species?

As model systems, we used various samples of 1-ethyl-3-methylimidazolium ethylsulfate [EMIM] [EtOSO₃] and solutions of the complex tetramminplatinum(II) chloride [Pt(NH₃)₄]Cl₂ in this IL. The initial studies of a commercial [EMIM] [EtOSO₃] sample with angle-resolved XPS showed that the surface was contaminated with a silicon-containing impurity (possibly a polysiloxane), even though the bulk concentration of silicon was below the detection limit of atomic emission spectrometry (ICP-AES, ~5 ppm). Depth profiling by variation of the photoelectron detection angle revealed that the silicon impurity is strongly enriched in the topmost layers of the IL. This result has important implications for all surface studies on ionic liquids, because it shows that even

samples of high bulk purity can be unsuitable for these studies if a minor contaminant, despite its very low bulk concentration, is enriched at the surface.^[P1]

Other [EMIM] [EtOSO₃] samples were synthesized in the laboratory of P. Wasserscheid specifically for surface studies and great care was taken to avoid contact with surface-active contaminants such as silicone grease. These samples indeed showed a clean surface; the relative peak intensities agreed with the nominal stoichiometry of the IL and did not vary with the emission angle, indicating a random distribution of the ions.^[P1]

As the next step, a solution of the complex [Pt(NH₃)₄]Cl₂ in surface-clean [EMIM] [EtOSO₃] was studied with angle-resolved XPS. The solubility of the complex is so low (8 mmole per liter) that Pt related signals should be almost invisible if the complex is uniformly distributed in the bulk and at the surface. However, the Pt signals appeared with a similar intensity as the IL-related signals, along with an additional N 1s component from the NH₃ ligands of the complex. Angle-dependent measurements showed that this NH₃ related N 1s signal increases relative to the N 1s signal of the [EMIM]⁺ ion when going from normal emission to the more surface-sensitive grazing emission geometry (Figure 2). This and the concurrent increase of the Pt related signals indicates that the Pt complex is enriched at the surface at the expense of the [EMIM]⁺ ions. Similar angle-dependent measurements for the O 1s level show that the [EtOSO₃]⁻ anion is only marginally affected by the enrichment of the complex. Likewise, the chloride anion of the complex is not enriched at the surface.^[P2]

Comparison of the relative XPS signals with the bulk concentration of the Pt complex (as determined by ICP-AES) shows that the complex is enriched at the surface by a factor of ~200. This is a very important result with respect to multiphasic catalysis with ionic liquids, in which catalytically active metal complexes are dissolved in an IL, while the reactants and products are in another (liquid or gaseous) phase. Because of this spatial separation of reactants and catalyst, diffusion can limit the overall reaction rate. In such cases, surface or interface enrichment of the catalyst would be favourable, since it ensures that the catalyst concentration is highest directly at the interface, keeping the diffusion ways short.^[P2]

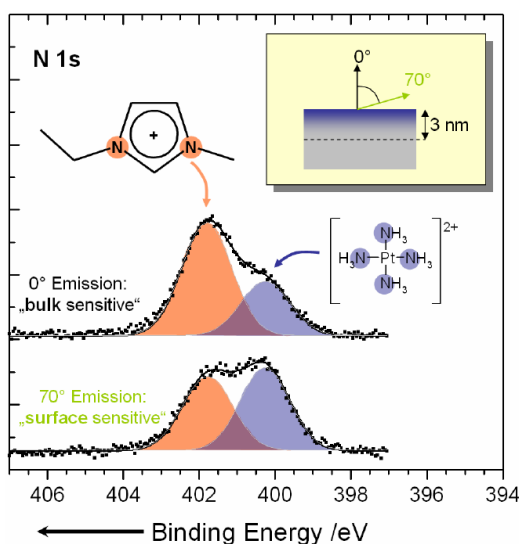


Figure 2. N 1s XP spectra of the surface-near region of a solution of [Pt(NH₃)₄]Cl₂ in [EMIM][EtOSO₃]. The spectra were taken at detection angles of 0° and 70°. At higher surface sensitivity (70°), the peak related to the [Pt(NH₃)₄]²⁺ ion is more intense, while the EMIM related signal decreases. This is a clear indication that the Pt complex is enriched at the surface on the expense of the EMIM ions.

Electrochemical surface studies with ionic liquids

Many ionic liquids have a wide electrochemical window (often >5 V), which means that they can resist large anodic or cathodic potentials without engaging in electrochemical reactions. (Water, for comparison, has a thermodynamic electrochemical window of only 1.229 V.) This makes ionic liquids suitable for the electrodeposition of reactive metals such as Ca, Al and Li, which cannot be deposited from aqueous solutions, or semiconductors such as Si, Ge, GaAs, InSb and CdTe.^[En08] Furthermore, ILs are interesting as solvents in electrosynthesis; there are examples for electrosynthetic Diels-Alder reactions and various electrocatalytic organometallic reactions in ILs.^[Bu04]

To study such reactions with surface analytical techniques, especially XPS, we have designed several UHV compatible electrochemical cells, two of which are shown in Figure 3, and a sample holder that is equipped with the corresponding contacts. The three-electrode trough cell in Figure 3a has an Au mesh (mesh width 25 μm) as the working electrode. The Au mesh ideally only touches the surface of the electrolyte and thus allows for the direct observation of the chemical composition of the electrode-electrolyte interface. In the thin film cell (Figure 3b), the electrolyte is a thin, vapor deposited IL film (see ref. [P3] for details about the vapor deposition of ILs). The cell can be used to study electrochemical transport processes in films of varying thickness by means of XPS imaging (lateral resolution with the Scienta SES-200 electron energy analyzer ~ 10 μm). The cells have been extensively tested with cyclic voltammetry under ex-situ conditions using a solution of [PMIM] I in [EMIM] [EtOSO₃]. The investigated model reaction was the oxidation of iodide (I^-) to I_3^- .

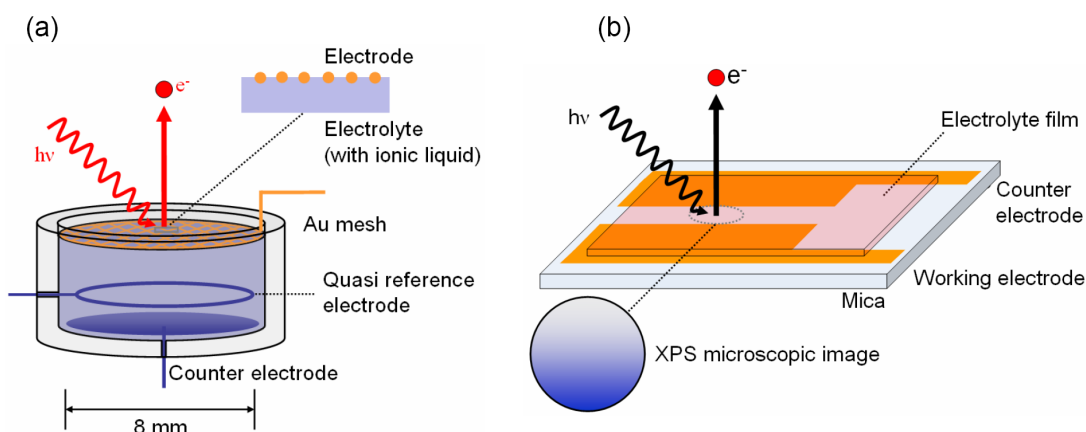


Figure 3. Electrochemical cells for in-situ XPS investigations of electrochemical reactions in ionic liquids. (a) Three-electrode trough cell with a Au mesh as working electrode on top of the trough. (b) Thin film electrochemical cell with a vapor deposited IL electrolyte film. The electrodes in (b) are produced by partially removing a vapor-deposited Au film from a thin mica sheet.

Ionic liquids and metalloporphyrins

In another project, we study the coordination of axial ligands such as NO and NH₃ to adsorbed metalloporphyrins by direct dosing of the respective gases into the UHV apparatus. This procedure, however, cannot be applied for the important class of ionic ligands, such as CN⁻ (cyanide) or O₂⁻ (superoxide), which cannot be dosed efficiently without their counterions. A convenient solution of this problem is to study these metalloporphyrins in ionic liquids, in which the respective ligands can be dissolved. The first measurements of this type were performed with a substituted Fe(III) porphyrin and the –biologically very important– superoxo ligand (O₂⁻), which was supplied by dissolving potassium superoxide (KO₂) along with the iron porphyrin in [EMIM] [NTf₂]. Our preliminary measurements show that the surface concentration of the Fe porphyrin is sufficient (probably again due to surface enrichment) for studying changes of the oxidation state of the metal center induced by the additional ligand.

References

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