

Ionic Liquids

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Surface Enrichment and Depletion Effects of Ions Dissolved in an Ionic Liquid: An X-ray Photoelectron Spectroscopy Study*Florian Maier,* J. Michael Gottfried, Jürgen Rossa, Dirk Gerhard, Peter Steffen Schulz, Wilhelm Schwieger, Peter Wasserscheid, and Hans-Peter Steinrück*

Ionic liquids (ILs)—salts with melting points below 100°C—have found increasing scientific interest over the past decade.^[1,2] Attracted by their structural diversity and their unique physicochemical properties (for example, negligible

volatility,^[3] unusual solvation and miscibility properties,^[4] and electroconductivity^[5]), many research groups have studied applications of these materials in catalysis,^[6] electrochemistry,^[5] analytics,^[7] and as “engineering fluids” (for example, separation technologies^[8]). Several industrial applications have been reported recently.^[9]

While the “bulk” properties of common ILs have been studied to some extent, very little is known about their surface and interfacial properties.^[10–12] However, the latter are pivotal for multiphasic reactions with ILs, such as catalytic reactions involving gaseous reactants in contact with bulk ILs or IL films supported on surfaces (a concept known as supported ionic liquid phase (SILP) catalysis.^[13–15])

As a result of the very low vapor pressure of ILs, X-ray photoelectron spectroscopy (XPS)—well-established but usually limited to ultrahigh vacuum (UHV) conditions—can be used to access IL surfaces on a molecular level. XPS is an ideal tool in surface science because of the small mean free path of photoelectrons.^[16] Recently, the IL 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtOSO₃]) was studied for the first time by Licence et al. using XPS.^[17] They assigned the core-level signals of the atoms of the IL to different chemical environments and also observed signals of a dissolved Pd complex.

In our case, the salt [Pt(NH₃)₄]Cl₂ dissolved in [EMIM]-[EtOSO₃] was chosen because of our interest in ligand-exchange phenomena in ILs. Moreover, Pt salts are interesting as precursors for catalytic applications, for example, in Pt-catalyzed olefin hydroformylation.^[18] In particular, we were able to distinguish the concentration and chemical nature of ions and dissolved species in the top surface layer of the ionic solution from those in the layers beneath by selective detection of photoelectrons emitted under different angles ϑ to the surface normal. The probe depth, from which 90% of the XPS intensities originate, varies with $\cos \vartheta$ and decreases from about 3 nm for $\vartheta = 0^\circ$ (normal emission) to about 1 nm for $\vartheta = 70^\circ$ (grazing emission).^[19] In the latter case, XPS probes less than the first two molecular layers. Consequently, an increase in core-level intensity with increasing detection angle, and thus with increasing surface sensitivity, indicates enrichment of this element in the first layer.

An X-ray photoelectron (XP) spectrum of the pure IL is shown in Figure 1 (dashed curve). Besides IL-related signals (O 1s, C 1s, N 1s, S 2s, and S 2p; see inset of Figure 1), no other elements could be detected, thus proving that the surface was free from contaminants. (Note that the Si impurities observed by Licence et al.^[17] were avoided by using pure ILs from our own laboratories. See Supporting Information for synthesis details.) Taking the sensitivity factors for the individual core levels^[20] into account, these intensities agree with the expected ratios S/O/C/N = 1:4:8:2, thus confirming surface cleanliness. The XP spectra taken at 0° and 70° were virtually identical, which indicates homogeneous distribution of IL cations and anions, and randomly oriented molecules in the near-surface region of the pure IL (while orientation effects were observed for 1-butyl-3-methylimidazolium IL surfaces^[21]).

In contrast, we observed strong angle-dependent intensity variations on the solution of the Pt salt in the IL, as revealed

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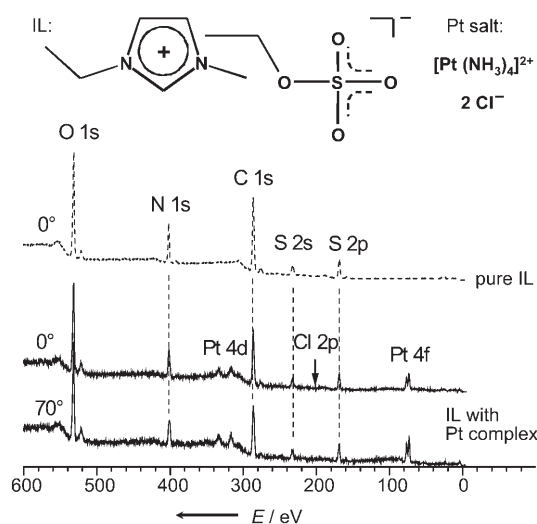


Figure 1. Survey XPS spectra of pure [EMIM][EtOSO₃] and a solution of [Pt(NH₃)₄]Cl₂ in the IL, taken at different emission angles; *E* = binding energy. Top: pure [EMIM][EtOSO₃] at 0°; middle and bottom: solution of [Pt(NH₃)₄]Cl₂ in [EMIM][EtOSO₃] at 0° (more bulk-sensitive) and 70° (more surface-sensitive).

by the O 1s, N 1s, and Pt 4f regions. Most striking is the increase of the Pt 4f signals (Figure 2a) at higher surface sensitivity, which indicates an increased density of Pt in the surface layer.

This finding is supported by the N 1s signals (Figure 2b). For the pure IL, the two nearly equivalent imidazolium nitrogen atoms (N(a)) lead to a single peak at 401.8 eV. In the case of the solution, the NH₃ ligands (N(b)) of the Pt complex contribute a second signal at 400.3 eV. The intensity related to N(a) decreases whereas that for N(b) increases with increasing surface sensitivity. Hence, our data provide unambiguous proof of a surface enrichment of species b and, thus, of the Pt complex at the expense of species a and, thus, of the IL cation. As the atomic ratio N(b)/Pt is close to 4:1, the expected ratio for [Pt(NH₃)₄]²⁺, we conclude that the Pt complex is stable in the IL under the conditions of our experiment. This conclusion is confirmed by the Pt 4f_{7/2} binding energy of 73.2 eV, which is close to that of solid Pt[NH₃]₄Cl₂ (73.4 eV^[22]).

To estimate the enrichment factor for the Pt complex, we make use of the fact that the N 1s spectrum taken at 70° predominantly probes the topmost molecular layer. With this argument, the atomic ratio N(a)/N(b) = 1:1.1 shows that the ratio of IL cations to complex Pt cations is about 2:1 in the surface, which is at least three times more than expected from the bulk concentration.

Surprisingly, no chloride-related signals were observed (for example, Cl 2p, expected at around 200 eV; see arrow in Figure 1), which proves that the near-surface region is depleted of chloride within our XPS detection limit for Cl of about 0.03 at %. In contrast to the described exchange of the imidazolium ions for the [Pt(NH₃)₄]²⁺ ions in the surface layer, distribution of the IL anion is apparently homogeneous and not influenced by the Pt complex. The O 1s signals in Figure 2 (with a shoulder that reflects the two different O atoms in the IL anion) as well as the sulfur signals are not

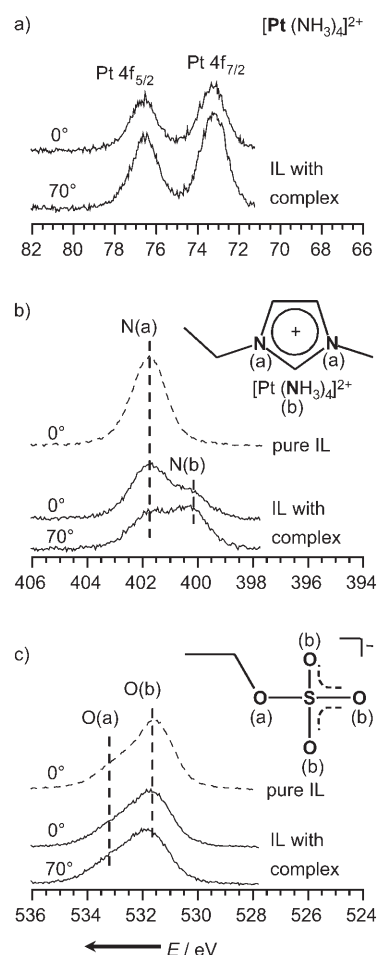


Figure 2. XP spectra of the Pt 4f (a), N 1s (b), and O 1s (c) regions of a solution of [Pt(NH₃)₄]Cl₂ in [EMIM][EtOSO₃]. All spectra were normalized to the same photon flux of the X-ray source and shifted. The spectra were taken at emission angles of 0° and 70°; spectra of the pure IL are added for comparison (-----).

affected by the detection geometry, neither for the pure IL nor for the solution.

The key to understanding the contrary behavior of the two ions, [Pt(NH₃)₄]²⁺ and Cl[−], is provided by previous theoretical and experimental studies of surfaces in aqueous and other solutions (see Refs. [23–25], and references therein). These studies show that the surface concentration of solvated ions at aqueous surfaces depends on their polarizabilities and is higher for large and more polarizable ions.^[24,25] This finding could explain qualitatively why the large [Pt(NH₃)₄]²⁺ ion is enriched at the surface, while the less polarizable Cl[−] ion is depleted. A similar effect was previously proposed by Law et al.^[11] for pure ILs where small anions like Cl[−] and Br[−] were not observed at the surface. Whether specific interactions between the ions of the IL and that of the Pt salt in our case are also involved (such as the surfactant effects known for detergents) will be a subject for future studies.

In conclusion, we have shown for the first time that soft Pt complex ions can be enriched in the top layer of an IL surface. Chloride, as the counterion of the Pt complex, is virtually absent from the surface, whereas the IL anion density is not

affected. Fundamentally, the presented methodology of surface-sensitive XPS in combination with a nonvolatile liquid may have substantial impact on the understanding of liquid surfaces in general. Practically, our finding that soft transition-metal ions can enrich in the top layer of an IL may give an important starting point to interpreting the kinetic data of transition-metal-catalyzed gas-phase reactions with ILs or supported ILs in a better and more realistic way. In addition, our findings give important hints for appropriate concepts to modify and design the surface properties (for example, surface tension) of ILs. From our results we would expect that the addition of small amounts of salts comprising soft ions should have a very strong effect on the surface properties of an IL.

Experimental Section

[Pt(NH₃)₄]Cl₂ (15 mg, 0.045 mmol) and [EMIM][EtOSO₃] (0.3 mL, 1.6 mmol) were shaken for 12 h under an argon atmosphere, which resulted in a turbid solution with some residual precipitate. A portion of this solution (0.02 mL) was deposited on a planar Au support (10 × 10 × 0.1 mm³) and introduced into a UHV system. After pumping for 10 h, the background pressure of 5 × 10⁻¹⁰ mbar hardly exceeded the base pressure in the system, which confirmed the very low vapor pressure of the IL and the absence of volatile impurities. XPS was performed with an ESCALAB 200 system with an Al_{Kα} source ($h\nu = 1486.6$ eV) and overall energy resolution of 0.9 eV. The Au 4f_{7/2} signal (binding energy $E_B = 83.55$ eV) was used as a reference for the reported binding energies. No charging was observed, which corroborated the sufficient conductivity of the IL film. Note that the absolute intensities of the signals related to the Pt complex slowly increased during the experiment by a factor of 2.4 to a maximum level, which was stable for several hours. We attribute this increase to dissolution of residual undissolved salt still present in the turbid solution, possibly induced by warming of the solution by the X-ray source, which also emits infrared radiation. However, all spectra showed the described enrichment and depletion effects, irrespective of absolute signal intensities and duration of the experiment. The displayed XP spectra were repeatedly and reproducibly recorded over a period of more than 6 h when no intensity variations with time were observed. To check for beam damage effects, ¹H NMR spectra of the IL and the solution were taken before and after the XPS experiments (detection limit for proton-containing impurities ≈ 1 mol%). These spectra did not reveal any changes induced by the experiment. All signals could be exclusively assigned to the expected components.

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