Surface enrichment of uranyl oxalate dissolved in room temperature ionic liquids

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Room temperature ionic liquids (RTILs) are salts with a melting point below 100 °C. The cations are usually organic compounds with large side chains to inhibit crystallization. Because of their structural diversity, RTILs exhibit interesting chemical and physical properties, e. g., they are chemical and thermally stable, have a wide electrochemical window, are considered to be inflammable, and have a very low vapour pressure [1]. The latter property allows to investigate RTILs with X-ray photoelectron spectroscopy (XPS). XPS is a surface sensitive analytical method, which provides chemical information of the first few nm of the sample surface. The measurement takes place under ultra-high vacuum, so it is not possible to investigate conventional liquids but RTILs. The XPS spectrometer used in this work (Specs GmbH, Berlin, Germany) employs non-monochromatic Kα radiation from a twin anode (Mg/Al) X-ray source XR-50. The XPS spectra were recorded with a constant analyzer pass energy of 50 eV using the hemispherical energy analyzer PHOIBOS 100 MCD.

Two different stock solutions have been prepared. Uranyl oxalate was diluted in 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-butyl-3-methylimidazolium thiocyanate (BmimSCN) (Fig. 1), respectively the uranium concentration of both stock solutions was about 8 mmol/L.

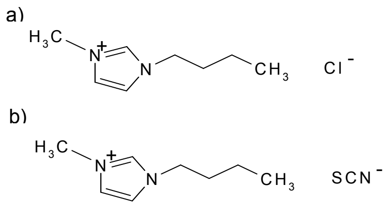

Figure 1: Chemical formula of 1-butyl-3-methylimidazolium chloride (BmimCl) (a) and 1-butyl-3-methylimidazolium thiocyanate (BmimSCN) (b)

The uranium to RTIL ratio in solution was expected to be lower than the detection limit of XPS. But in both cases there is a surface enrichment of uranium. Figure 2 shows XPS spectra of the different stock solutions. In this energy range the N 1s and U 4f lines are visible. Due to the different oxidation states of nitrogen in BmimSCN, its XPS spectrum exhibits two well-resolved N 1s peaks. Using the relative intensities of the XPS lines, it was possible to calculate the atomic ratio between uranium and the RTIL at the surface of the sample.

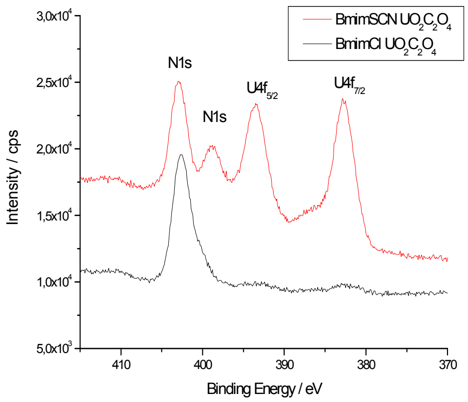

Figure 2: XPS spectra (E_p = 50 eV) of uranium oxalate dissolved in 1-butyl-3-methylimidazolium thiocyanate (red) and 1-butyl-3-methylimidazolium chloride (black)

The result is that uranium shows a strong enrichment at the surface, especially in the case of the BmimSCN stock solution. In Table 1 the calculated and the measured U/RTIL ratios are given. The calculated ratio is the amount of uranium, which was expected for a homogenous distribution in the volume. A similar behaviour has been found by Maier [2] concerning platinum coordination compounds in RTILs.

Molecular ratio (U/RTIL) BmimCl		Molecular ratio (U/RTIL) BmimSCN	
calculated	**measured**	**calculated**	**measured**
$1.4 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	0.2

Table 1: Ratio between uranium and the two RTILs at the surface of the samples

A reason for the lower enrichment of uranium in the BmimCl stock solution might be the higher viscosity that is caused by the different anions of the RTILs.

Reference:

[1] Binnemans K., Chem., Rev. **107**, 2592-2614 (2007)
[2] Maier F. et al.; Angew. Chem. Int. Ed. **45**, 7778-7780 (2006)