EXAFS study of U(VI) coordination in room-temperature ionic liquids (BmimCl, BmimMsu, BmimSCN)

A. Ölcer, S. Amayri, T. Reich
Institut für Kernchemie, Johannes Gutenberg-Universität, D-55128 Mainz, Germany

Introduction: There is the assumption that room-temperature ionic liquids (RTILs) might be useful for the recycling of nuclear fuel and the recovery of uranium from waste solutions [1]. To evaluate the potential of RTILs for waste treatment, the chemical behaviour especially of U(VI), in RTILs has to be studied. By reason that the anions of the RTILs have a strong influence on their chemical and physical properties, this work is focused on the complexation of hexavalent uranium by the counterions Cl^-, $MeOSO_3^-$ and SCN^- of RTILs based on 1-butyl-3-methylimidazolium (Bmim).

Experimental: The test solutions were prepared under Ar atmosphere by dissolution of $UO_2(C_2O_4)$ ([U]~0.5 mM) in BmimCl, BmimMsu, and BmimSCN, respectively. Traces of water were removed from the RTILs by heating under reduced pressure. The U L_{III}-edge EXAFS measurements were performed at the INE beamline at ANKA. The EXAFS spectra were measured at room-temperature in fluorescence mode using a multi-element germanium detector. EXAFS analysis was performed with the software packages Athena, EXAFSPAK and FEFF 8.20. To obtain the theoretical phase and amplitude functions, three different uranium clusters were used [2-4]. The parameter S_0^2 equaled 0.9.

Results: The analysis of the EXAFS spectra shows that in all solutions the uranyl entity is coordinated solely by the counterions of the RTILs. This is in contrast to aqueous solutions where water molecules are always coordinated to the uranyl entity.

Table 1: EXAFS parameters of U(VI)/BmimCl solution (ΔE_0 = 12.8 eV) and comparison with aqueous solution: U(VI) in 9 M Cl^- [5]

	N	R [Å]	σ^2 [Å^2]
O_{ax}	2.3 ± 0.19 2.0^a	1.77 ± 0.01 1.76^a	0.0042 ± 0.0008 0.0014^a
O_{eq}	- 1.4^a	- 2.51^a	- 0.0050^a
Cl	3.1 ± 0.33 2.7^a	2.69 ± 0.01 2.74^a	0.0053 ± 0.0009 0.0050^a

[a]: Ref. [5]

In BmimCl (Fig. 1) the uranyl entity is solely coordinated by chloride ions (Tab. 1). In aqueous media the highest coordination is N_{Cl} = 3 with an additional water molecule in the equatorial shell [5].

Table 2: EXAFS parameters of U(VI)/BmimMsu solution (ΔE_0 = 14.8 eV) and comparison with aqueous solution: U(VI) in 3 M SO_4^{2-} [6].

	N	R [Å]	σ^2 [Å^2]
O_{ax}	2.4 ± 0.18 2.0^c	1.76 ± 0.01 $1.77^{c]}$	0.0026 ± 0.0009 0.0014^c
O_{eq}	4.8^b 2.5^c 2.4^c	2.39 ± 0.01 2.35^c 2.49^c	0.0093 ± 0.0004 0.0055^c 0.0055^c
S_{bid}	2.4^b ± 0.36 2.0^c	3.07 ± 0.01 3.12^c	0.0063 ± 0.0009 0.0060^c

[b]: Parameters linked during the fit, [c]: Ref. [6]

The EXAFS measurement of U(VI) dissolved in BmimMsu suggests coordination by 2 methylsulfate ions (Fig. 1).The short U-S distance of 3.07 Å indicates a bidentate coordination mode (Tab. 2).

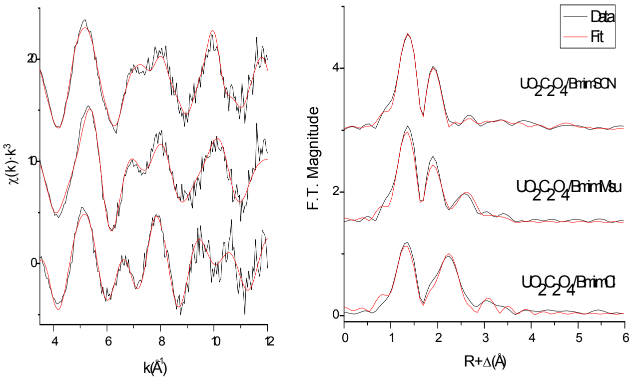

Fig. 1: U L_{III}-edge k^3-weighted EXAFS spectra (left) and corresponding Fourier transform magnitudes (right) of U(VI)/RTIL solutions

In BmimSCN U(VI) is coordinated by 4 thiocyanate ligands (Fig. 1). The nearest neighbour of uranium is nitrogen; therefore it can be identified as an uranium isothiocyanate charge transfer complex (Tab. 3)

Table 3: EXAFS parameter of U(VI)/BmimSCN (ΔE_0=14.3 eV)

	N	R [Å]	σ^2 [Å^2]
O_{ax}	2.7 ± 0.23	1.77 ± 0.01	0.0028 ± 0.0009
N	3.7^b ± 0.17	2.43 ± 0.02	0.0031 ± 0.0007
C	3.7^b	3.72	0.0021
S	3.7^b	5.15	0.0068

[b]: Parameters linked during the fit

Conclusions: The EXAFS measurements of the U(VI)/RTIL systems provide new information about the uranium complexation. Traces of water possibly remaining in the RTILs (< 50 ppm) and the counterion of the uranium compound ($C_2O_4^{2-}$) have no influence on the coordination mode of the uranyl entity. Uranium(VI) is solely surrounded by the anions of the RTIL. By reason of this remarkable behaviour, further investigations of the coordination chemistry of actinides in RTILs would be interesting.

Acknowledgement

We acknowledge the Synchrotron Light Source ANKA for provision of beamtime at the INE beamline and we would like to thank Dr. Kathy Dardenne and Dr. Jörg Rothe for their assistance.

References

[1] A.E. Visser, R.D. Rogers, J. Sol. State Chem., **171**, 109 (2003)
[2] A.C. Bean et al., Inorg. Chem., **41**, 6775 (2002)
[3] L.A. Hayden, P.C. Burns, J. Sol. State Chem., **163**, 313 (2002)
[4] I.V. Medrish, Russ J. Inorg. Chem., **53**, 1040 (2008)
[5] C. Hennig et al., Inorg. Chem., **44**, 6655 (2005)
[6] C. Hennig et al., Radiochim. Acta, **96**, 607 (2008)