

Neptunium coordination in room-temperature ionic liquids (BmimCl, BmimMsu and BmimSCN)

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Introduction: This investigation aims at a better understanding of the interaction between neptunium(IV) and room-temperature ionic liquids (RTILs). They might be useful for the recycling of nuclear fuel and the separation of actinides and fission products from waste solutions. To evaluate the potential of RTILs for waste treatment, the behaviour of radionuclides in RTILs has to be studied [1, 2].

Experimental: Three $\sim 0.2 - 0.4$ mM $^{237}\text{Np(IV)}$ /RTIL test solutions were prepared in a glove box (Ar): BmimCl (1-butyl-3-methylimidazolium chloride), BmimMsu (1-butyl-3-methylimidazolium methylsulfate) and BmimSCN (1-butyl-3-methylimidazolium thiocyanate). To remove traces of water, the $^{237}\text{Np(IV)}$ /RTIL solutions were dried by heating under reduced pressure. The EXAFS measurements were performed at the Np L_{III} edge (17.6 keV) at room temperature in fluorescence mode using a multi-element germanium detector. The EXAFS analysis was performed with the software packages Athena, EXAFSPAK and FEFF 8.20. To obtain the theoretical phase and amplitude functions, clusters from literature [3, 4, 5] were used.

Results: Analysis of the EXAFS measurements of Np(IV) in BmimCl (Fig. 1, Tab. 1) shows that Np(IV) has more Cl⁻ ions in the first coordination sphere than in aquatic systems.

Table 1: EXAFS parameters of Np(IV)/BmimCl solution ($\Delta E_0 = 2.1$ eV) and comparison with aqueous solution: Np(IV) in 10 M HCl [6]

	N	R [Å]	σ^2 [Å ²]
Cl	4.3±0.8 2.0±0.4 ^a	2.62±0.01 2.69±0.01 ^a	0.0070±0.0018 0.0040 ^{b,a}
N	1.8±0.6	2.23±0.02	0.0031±0.0010
O	7.7±1.1 ^a	2.44±0.012 ^a	0.0075 ^{b,a}

^a: Ref. [6], ^b: Parameters fixed during the fit

As can be seen from Tab. 1, Np is coordinated by four Cl⁻ ions and two additional ligands, probably the Bmim cation. In aqueous media, the highest Cl⁻ coordination number is $N_{\text{Cl}} = 2$ with 7-8 additional water molecules in the equatorial shell [6].

Table 2: EXAFS parameters of Np(IV)/BmimMsu solution ($\Delta E_0 = 13.0$ eV) and comparison with aqueous solution: Np(IV) in 3 M (NH₄)₂SO₄²⁻ [7]

	N	R [Å]	σ^2 [Å ²]
O _{bid}	6.7±1.0	2.38±0.02	0.0128±0.0028
	8.9±1.3 ^c	2.39±0.02 ^c	0.011 ^c
S _{bid}	3.3 ^b	3.04±0.01	0.0062 ^b
	3.3 ^c	3.07 ^c	0.0049 ^c
N	2.3±0.3	2.28±0.01	0.0021±0.0013

^b: Ref. [7], ^c: Parameters linked during the fit

The EXAFS measurement of Np(IV) dissolved in BmimMsu suggests coordination by three methylsulfate ions and two additional ligands, probably the cation of

the RTIL. The short U-S distance of 3.04 Å (Fig. 1, Tab. 2) indicates a bidentate coordination mode. In aquatic sulfate systems, tetravalent actinides are usually coordinated by both bi- and monodentate sulfate ligands [7].

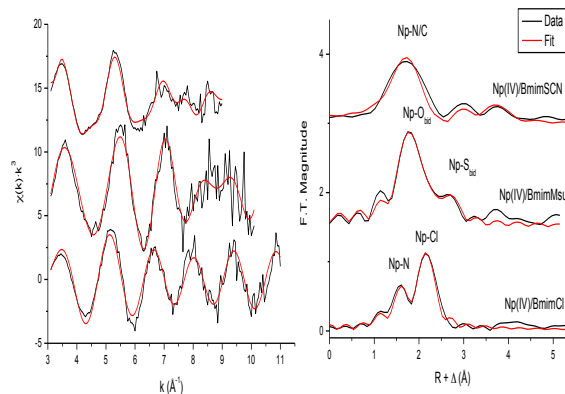


Fig. 1: Np L_{III}-edge k^3 -weighted EXAFS spectra (left) and corresponding Fourier transform magnitudes (right) of Np(IV)/RTIL solutions

In BmimSCN Np(IV) is coordinated by 8-9 thiocyanate ligands (Fig. 1, Tab. 3), the nearest neighbor of Np is nitrogen with a distance of 2.28 Å followed by carbon with a distance of 3.40 Å.

Table 3: EXAFS parameter of Np(IV)/BmimSCN ($\Delta E_0 = 10.1$ eV)

	N	R [Å]	σ^2 [Å ²]
N	8.6±0.9	2.28±0.02	0.0185±0.0085
C	8.6 ^c	3.40±0.03	0.0185 ^c
C _{ms}	17.2 ^c	3.42±0.04	0.0370 ^c

^c: Parameters linked during the fit

Conclusions: The EXAFS measurements of the Np(IV)/RTIL test solutions provide new information about the Np complexation with Cl⁻, Msu and SCN⁻. Compared to U(VI) [8], which is solely surrounded by the anions of the RTIL, Np(IV) has additional ligands. Probably because of the different geometry compared to the uranyl entity, a complexation by the voluminous Bmim cation of the RTIL is possible.

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