



	Experiment title: Complexation between uranium(VI) and rhenium(VII) in an hydrophobic ionic liquid	Experiment number: CH3206
Beamline: BM20	Date of experiment: from: 25/09/2010 to: 28/09/2010	Date of report: 26/01/2011
Shifts: 9	Local contact(s): Andre Rossberg	<i>Received at ESRF:</i>
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Report:

We aim at determining by EXAFS the stoichiometry and structure of the complexes formed between UO_2^{2+} and ReO_4^- in hydrophobic ionic liquids. ReO_4^- is used here as the stable chemical surrogate of TcO_4^- , which is an abundant fission product. Those two ions are known to have weak interactions in water, but our first studies have shown that they form complexes in ionic liquids. The characterisation of those species, which have never been evidenced in a liquid medium, will constitute a basis for our further investigation of the mechanism of extraction of UO_2^{2+} and TcO_4^- by tributylphosphate in an ionic liquid.

Solutions containing different $[\text{Re(VII)}]/[\text{U(VI)}]$ ratio were made (R, from zero to 10), in two hygroscopic ionic liquids, $\text{C}_4\text{mimTf}_2\text{N}$ and $\text{Bu}_3\text{MeNTf}_2\text{N}$, and in acetonitrile, the latter for comparison purpose between a conventional molecular solvent and an ionic liquid. All solutions were dried before their measurements, to be sure that water molecules will not interfere in the U-Re complexation phenomenon that we want to observe.

Measurements were led at the ROBL beamline using a Si(111) monochromator. During the experiment a total of nine samples were measured at the U- L_3 edge (17166 eV) in transmission mode (calibration with a Y foil at 17038 eV) and when it was possible, at the Re L_3 -edge (10535 eV) in fluorescence mode (calibration with a Zn foil at 9659 eV). In this report, we will focus on results obtained at the U edge.

Figure 1 displays the Fourier-transforms of EXAFS spectra obtained at the U L₃-edge for solutions made in two solvents (an ionic liquid Me₃BuNTf₂N and acetonitrile), containing different [Re(VII)]/[U(VI)] ratio.

Surprisingly, no U-Re contribution could be observed on the FT spectra. According to data available in the literature, we could expect the presence of this contribution at a distance (on the FT, i.e. non corrected distance) between 3.8 and 4 Å. Nevertheless, data available are for solid compounds and not liquid state compounds, for which distances may be longer. In this case, we would be at the limit of the EXAFS technique.

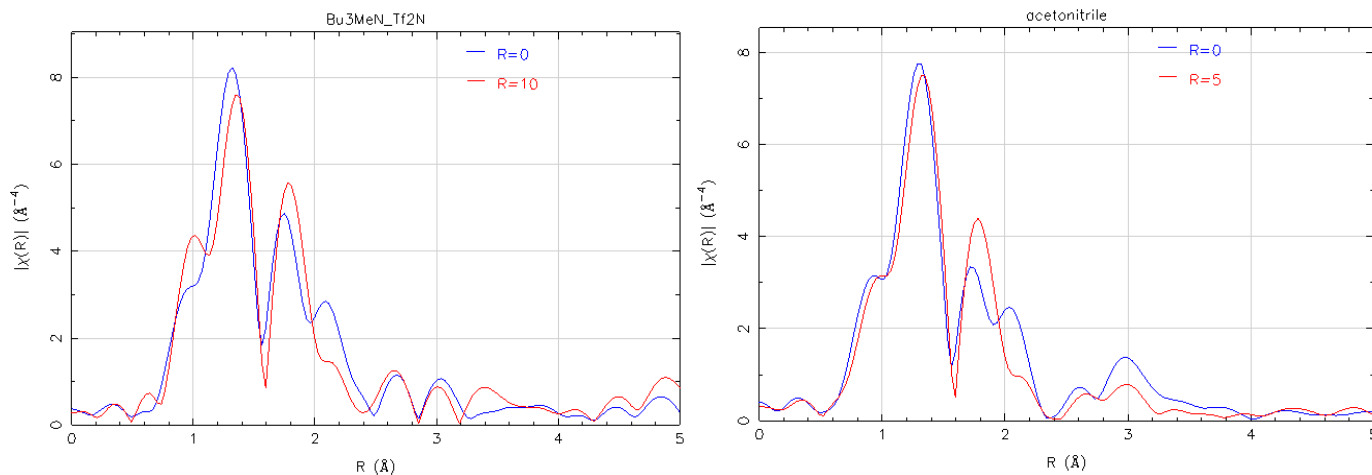


Figure 1: Fourier transforms of spectra obtained at the U-L₃ edge: evolution of the U environment as a function of the rhenium (VII) concentration ($R = [\text{Re(VII)}]/[\text{U(VI)}]$) in two solvents, an ionic liquid Me₃BuNTf₂N (left) and acetonitrile (right).

In both solvents, it is clear that adding rhenium to the uranyl solutions entails a change in the equatorial coordination sphere (contribution between 1.6 and 2.2 Å on the FT). Fit of the spectra reveals a significant shortening of the U-O_{eq} distance upon addition of rhenium (VII): in the ionic liquid Bu₃MeNTf₂N, it goes from 2.43 Å ($R = 0$) to 2.37 Å ($R = 10$). The former value, obtained for an uranyl salt dissolved in the dry ionic liquid, is consistent with previous measurements obtained in other ionic liquids [1, 2]. In dried acetonitrile, uranium is surrounded by MeCN molecules, and thus, its equatorial shell is composed of nitrogen atoms, found by the fit at a distance of 2.47 Å. After addition of rhenium (VII) at a high ratio, uranium is found coordinated by O atoms at a distance of 2.38 Å. It must be noticed here that EXAFS does not allowed a direct discrimination between N and O atoms, but this can be done according to the equatorial distances found by the fit.

As a conclusion, those measurements allowed us to confirm results obtained by other techniques, and in particular UV-vis. spectroscopy, showing that there is a complexation between U(VI) and Re(VII) in ionic liquids. Even though we could not determine the complexes stoichiometry of the species formed, we could get useful information on the environment of uranyl. In particular, it seems that the complexation between the two ions occurs at the same extend in an ionic liquid and in a conventional molecular solvent. Those results will be part of an article which is currently being written.

References:

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- [2] C. Gaillard, A. Chaumont, I. Billard, C. Hennig, A. Ouadi, S. Georg, G. Wipff *Inorg. Chem.* **2010**, 49, 6484.