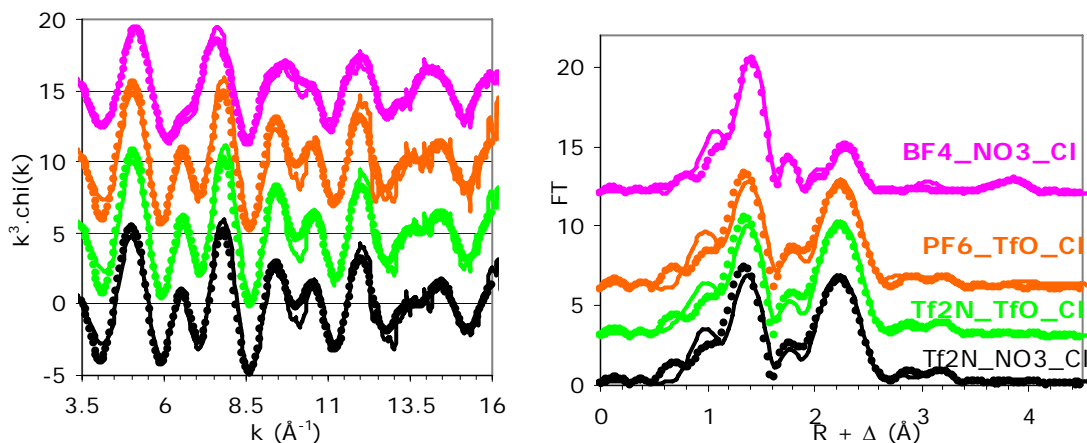
 ROBL-CRG	<b>Experiment title:</b> <b>Solvation and complexation of uranium(VI) in room temperature ionic liquids</b>	<b>Experiment number:</b>  <b>20-01-654</b>
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 22.02.2006      to: 25.02.2006	<b>Date of report:</b> 24.11.2006
<b>Shifts:</b> 9	<b>Local contact(s):</b> C. Hennig	<i>Received at ROBL:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  C. Gaillard*, I. Billard, A. Ouadi*, J. Champion* Institut Pluridisciplinaire Hubert Curien, Chimie Nucléaire, Strasbourg, France.		

## Report:

The aim of this work is to gain insights on the coordination properties of uranyl in room temperature ionic liquids (ILs), as a function of the nature of the uranyl counterions, and of the ionic liquid. Using UV-visible spectroscopy and EXAFS, we investigate the coordination sphere of uranyl after dissolution of various uranyl salts ( $\text{UO}_2\text{X}_2$  with  $\text{X}^- = \text{NO}_3^-$ , triflate  $\text{TfO}^-$ ,  $\text{ClO}_4^-$ ) in four different ionic liquids. Three of them ( $\text{C}_4\text{mimPF}_6$ ,  $\text{C}_4\text{mimTf}_2\text{N}$  and  $\text{C}_4\text{mimBF}_4$ ) are based on the imidazolium cation ( $\text{C}_4\text{mim} = 1\text{-methyl-3-butyl-imidazolium}$ ) and differ by their anionic components ( $\text{PF}_6^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  hereafter noted  $\text{Tf}_2\text{N}^-$  and  $\text{BF}_4^-$ , respectively) while the  $\text{Me}_3\text{NBuTf}_2\text{N}$  liquid is based on a quaternary ammonium  $\text{Me}_3\text{NBu}^+$  cation, allowing us to assess the role of anionic and cationic components of the liquid. We also investigate the reactivity of the uranyl towards chloride ions introduced in solutions. EXAFS experiments were carried out at ROBL-ESRF beamline, at the U  $L_{\text{III}}$  edge, in transmission mode using argon-filled ionisation chambers at ambient temperature. Fits of the Fourier transform (FT)  $k^3$ -weighted EXAFS data to the EXAFS equation were performed in R-space between 1 and 4 Å. The k-range used was 3.5-16 Å<sup>-1</sup>.

The dissolution of uranyl salts, in absence of chlorides, could be achieved only in  $\text{C}_4\text{mimTf}_2\text{N}$  and  $\text{Me}_3\text{NBuTf}_2\text{N}$ . EXAFS experiments, coupled with UV-visible measurements, show that the counter-anions triflate, perchlorate and nitrate remain, at least partially, in the uranium first coordination

sphere. Thus, dissolution of the salts does not imply the uranyl solvation by  $\text{Tf}_2\text{N}^-$  anions of the solvent. No influence of the IL cationic part was observed. Introduction of chlorides in solution was shown to improve the solubility of uranyl salts, in particular in  $\text{C}_4\text{mimPF}_6$  and  $\text{C}_4\text{mimBF}_4$ . The ratio  $[\text{Cl}]/[\text{U}]$  in solutions was equal to 4. EXAFS clearly show that the tetra-chloro complex of uranyl  $\text{UO}_2\text{Cl}_4^{2-}$  is formed in all samples, excepting in  $\text{C}_4\text{mimBF}_4$  (see figure 1). In the latter, the complexation is not total ( $N_{\text{Cl}} \sim 1$ ), probably because of the presence of fluoride ions likely formed by the decomposition of  $\text{BF}_4^-$  anions.



**Fig. 1:** Influence of the uranyl salt and of IL on the complexation of uranium(VI) with chlorides: EXAFS spectra and their corresponding Fourier Transform. For sake of clarity, EXAFS and FT were shifted along the y-axis.