 ROBL-CRG	<b>Experiment title:</b>  EXAFS characterization of extracted uranium(VI) complexes in an ionic liquid by malonamides extractants	<b>Experiment number:</b>  20-01-743
<b>Beamline:</b>  BM 20	<b>Date of experiment:</b> from: 24/10/14                      to: 27/10/2014	<b>Date of report:</b>  27/02/2015
<b>Shifts: 11</b>	<b>Local contact(s):</b> Christoph Hennig	<i>Received at ROBL:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Clotilde GAILLARD*, Institut de Physique Nucléaire de Lyon, France. Maria BOLTOEVA*, Institut Pluridisciplinaire Hubert Curien, Strasbourg, France. Isabelle BILLARD, Institut Pluridisciplinaire Hubert Curien, Strasbourg, France and Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces, Grenoble, France. Ali OUADI, Institut Pluridisciplinaire Hubert Curien, Strasbourg, France.		

## Report:

The aim of these EXAFS measurements is to determine the nature of uranium (VI) species extracted in an ionic liquid (IL) by two kinds of extractant molecules (a neutral malonamide-base extracting molecule (DMDBMA) and an ionic liquid functionalized with a CMPO group (FIL-CMPO)), as a function of the acidic aqueous solutions (HNO<sub>3</sub> or HClO<sub>4</sub>, at different concentrations). The extraction of charged complexes, instead of neutral complexes formed in the usual organic solvents, was postulated from our data. We now want to determine experimentally the structure of extracted uranyl species, i.e. the stoichiometry, ligands nature and number.

During the allocated beam time, we have analysed 15 samples at the uranium L<sub>3</sub> edge in transmission and fluorescence detection. 8 solutions are reference samples containing a known [extractant molecule]/[NO<sub>3</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup>]/[UO<sub>2</sub><sup>2+</sup>] ratio, the others were obtained by liquid liquid extraction of uranium in different experimental conditions (nature and concentration of the acid, nature of the extractant molecule).

The analysis of the spectra show that uranyl is extracted as a divalent cationic complex at low acidic concentration, whatever the extraction molecule and acid nature. This is in line with our previous results with TBP extractant molecule, where we showed that the divalent uranyl solvate is extracted by a cationic exchange with 1 proton and 1 IL cation. In the HNO<sub>3</sub>//DMDBMA/IL system, the nature of the extracted species in the IL phase changes when the aqueous acidic concentration increases, with the formation of a neutral complex. On the contrary for the HNO<sub>3</sub>//FIL-CMPO/IL and

HClO<sub>4</sub>/FIL-CMPO/IL, the increase of the acidic concentration does not change the nature of the extracted uranyl species which remain as [UO<sub>2</sub>.3X]<sup>2+</sup> (X = DMDBMA or FIL-CMPO). Those 2 results, at high acid concentrations, are unexpected considering our previous results with TBP. We now carry out complementary experiments in order to model the extraction mechanisms.

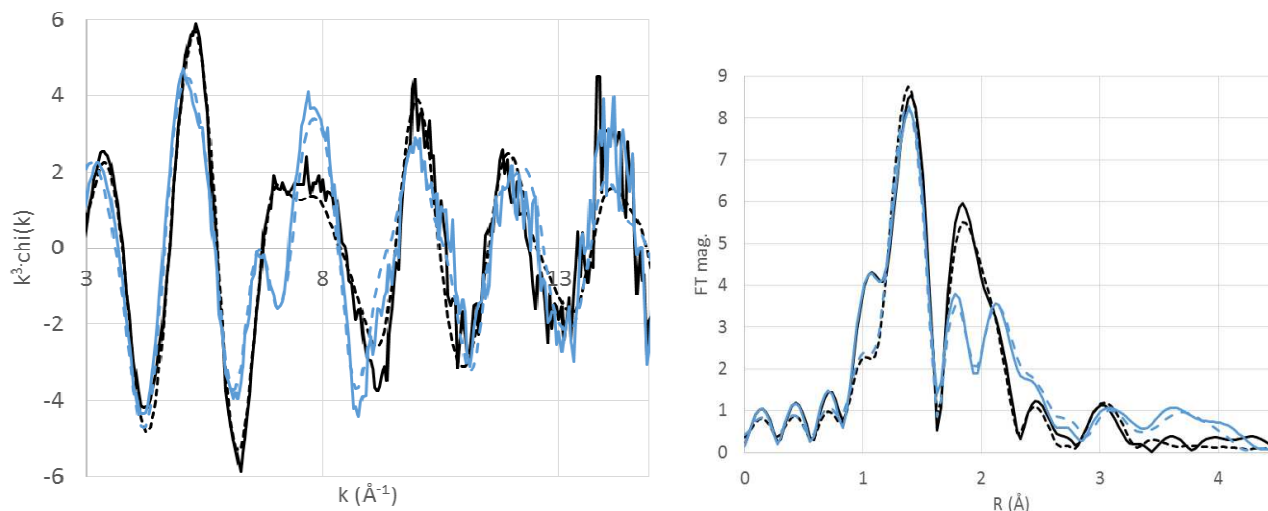


Figure 1: EXAFS and corresponding Fourier Transform of extracted uranyl with DMDBMA in an ionic liquid phase, from acidic aqueous phases ( $[\text{HNO}_3] = 0.5 \text{ M}$  (black) and  $[\text{HNO}_3] = 6 \text{ M}$  (blue)). Fit of the data are displayed as dashed lines.

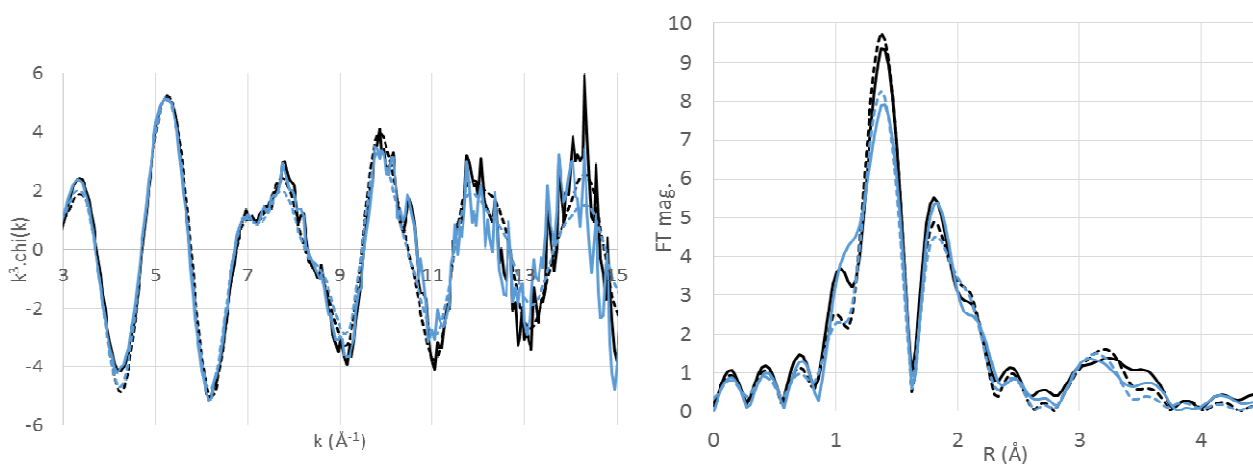


Figure 2: EXAFS and corresponding Fourier Transform of extracted uranyl with CMPO-FIL in an ionic liquid phase, from acidic aqueous phases ( $[\text{HNO}_3] = 6 \text{ M}$  (black) and  $[\text{HClO}_4] = 6 \text{ M}$  (blue)). Fit of the data are displayed as dashed lines.