 ROBL-CRG	<b>Experiment title:</b> EXAFS characterization of uranium (VI) complexes in an ionic liquid by TBP and malonamide extractants	<b>Experiment number:</b> 20-01-730
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 13/07/2013 to: 16/07/2013	<b>Date of report:</b> 27/02/2014
<b>Shifts: 9</b>	<b>Local contact(s):</b> Christoph Hennig	<i>Received at ROBL:</i>
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## Report:

The aim of this project was to determine by EXAFS the stoichiometry of extracted uranium(VI) from an aqueous nitric acid phase to an ionic liquid phase, using two extractant molecules: tributyl phosphate (TBP) and the malonamide N,N' dimethyl-N,N' dibutylmalonamide (DMDDBMA). Those experiments follow extensive studies that allow us to build an extraction model, from which we propose a double extracting mechanism involving uranium anionic species at high acidic concentration ( $\text{UO}_2(\text{NO}_3)_3 \cdot x\text{TBP}$ ) and uranium cationic species at low acidic concentration ( $\text{UO}_2^{2+} \cdot x\text{TBP}$ ). Thus, U extraction may not be achieved through the formation of a neutral complex (formed in the usual organic solvents), but by *an ion exchange process* between a charged complex and the IL ions.

At this stage, EXAFS measurements of extracted solutions were the last step needed to get an experimental confirmation of our extraction data modelling. During the 9 shifts of measurements at the uranium  $L_3$  edge on the HZDR-ROBL beamline, we had time to analyse only TBP-based samples.

Fit of the data allows us to confirm the stoichiometry of the extracted complex at low acidic concentration, i.e. the formation of a cationic species  $\text{UO}_2^{2+} \cdot x\text{TBP}$  ( $x = 2$  or  $3$ ). At high acidic concentration, EXAFS results indicate also the formation of a cationic species, that includes 1 bidentate nitrate groups ( $\text{UO}_2(\text{NO}_3)^+ \cdot x\text{TBP}$  ( $x = 2$  or  $3$ )). This latter result is thus contradictory with the stoichiometry of extracted species that was postulated from the fit of extraction data, and we are now collecting new experimental data in order to explain this discrepancy. But the existence of an ion-exchange process for the recovery of uranyl in an IL phase is clearly evidenced. This is the first time that such mechanism is experimentally assessed in the liquid-liquid extraction field.

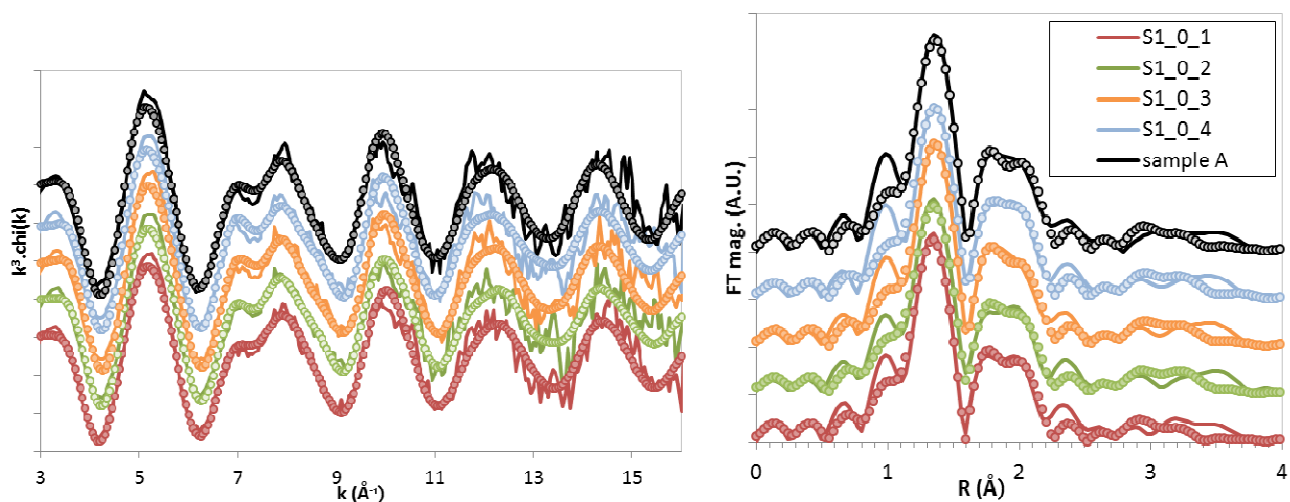


Figure 1: EXAFS and corresponding Fourier Transform of extracted uranyl with TBP in an ionic liquid phase, from acidic aqueous phases ( $[\text{HNO}_3] = 0.15 \text{ M}$  (black)), compared to reference samples. Fit of the data are displayed as dots.

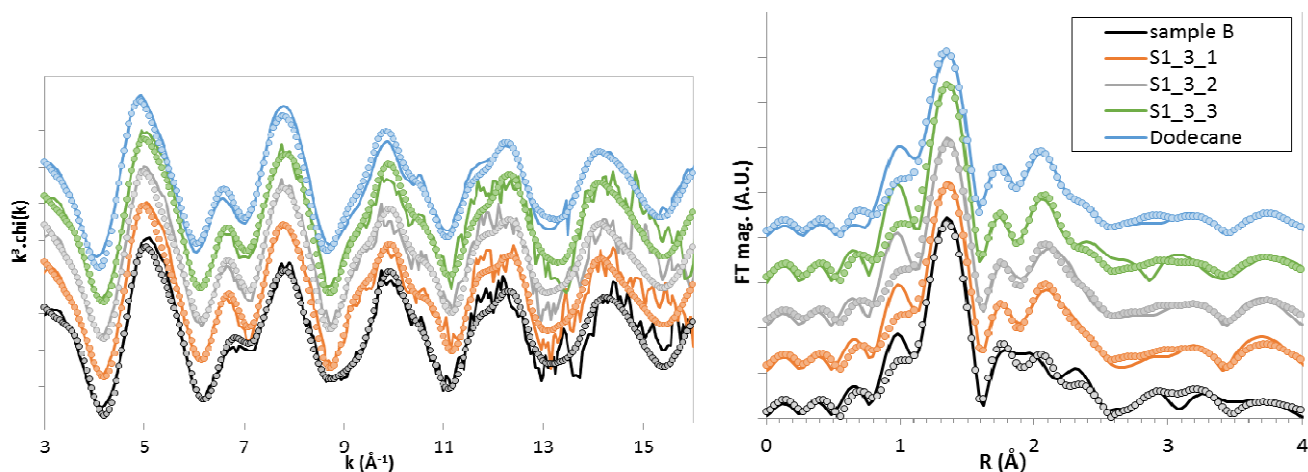


Figure 2: EXAFS and corresponding Fourier Transform of extracted uranyl with TBP in an ionic liquid phase, from acidic aqueous phases ( $[\text{HNO}_3] = 4 \text{ M}$  (black)), compared to reference samples. Fit of the data are displayed as dots.

