	Determination of the synergistic mechanism of extraction of uranium (VI) with TODGA in presence of ionic liquids	**Experiment number**: CH-4656
Beamline: BM20	**Date of experiment**: from: 15/04/2016 to: 19/04/2016	**Date of report**: 01/08/2016
Shifts: 12	**Local contact(s)**: Christoph Hennig	*Received at ESRF:*

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Report:

The aim of the EXAFS measurements carried out for 4 consecutive days on the ROBL beamline was to determine the nature of the uranium (VI) species extracted by TODGA ligand (L) in dichloroethane, and under the synergetic effect of the ionic liquid (IL) $[C_4mim][Tf_2N]$. This study is related to our work published recently [1] in which the stoichiometry of the extracted complexes were postulated. In pure DCE, the extraction of $UO_2(NO_3)_2L_2$ at low acid concentration and $UO_2(NO_3)_2L$ at high HNO_3 concentration is expected, while in presence of ionic liquid, the complex formed is supposed to be of the form $UO_2(NO_3)_x(Tf_2N)_yL_z$, the stoichiometric coefficients needed to be determined.

A total of 15 samples obtained by liquid-liquid extraction under different experimental conditions were analysed at the U L_3 edge. Typically, different nitric acid concentrations or IL concentrations were investigated. Reference samples with known ligands, nitrates, and Tf_2N^- stoichiometries were also investigated.

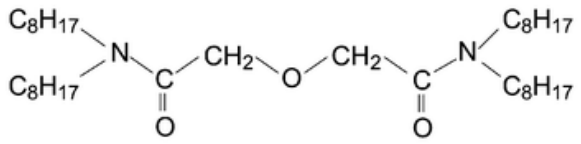

Figure 1: The TODGA ligand structure

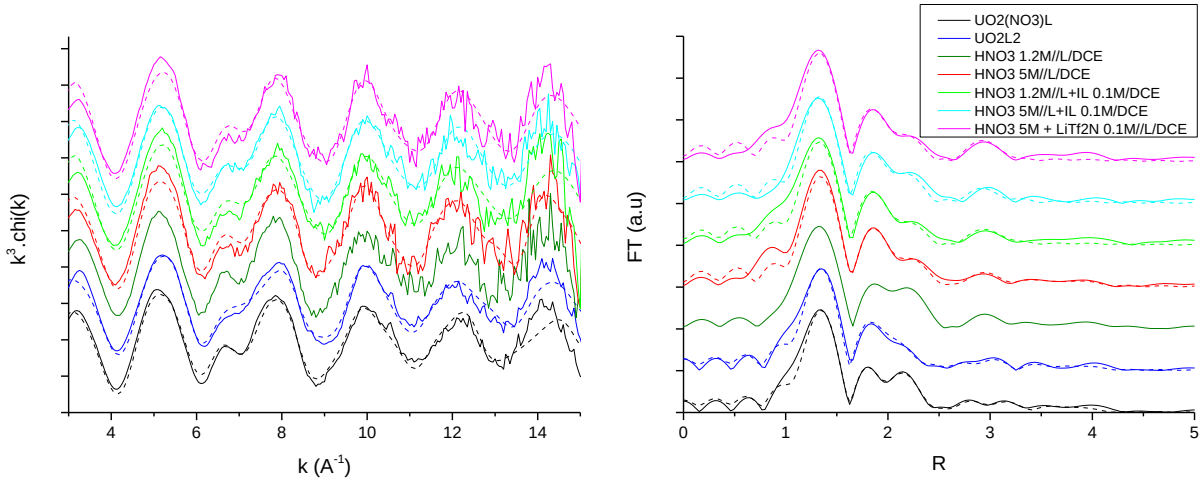

Figure 2: EXAFS and corresponding FT spectra of analysed samples.

With its etheric oxygen (see figure 1), the TODGA ligand (L) is a tridentate ligand to uranium (VI). So a maximum of 2 organic ligands may complex in the uranyl equatorial plane. Actually, EXAFS results show that the uranyl coordination sphere is filled only with 2 ligands TODGA (L) for most of the investigated systems. Thus, the $[UO_2L_2]^{2+}$ entity is characterized when the extraction is performed in dichloroethane, with or without addition of ionic liquid. The exception is for extraction at high HNO_3 concentration (5 M) in pure DCE, where the $UO_2(NO_3)L$ complex is detected. This is in agreement with the postulated species.
As the extracted species need to be overall neutral, these EXAFS results show that the counter-anions, whether they are nitrate and/or Tf_2N^-, are in the uranyl *second* coordination sphere. This is quite unusual, as one would have expected at least one nitrate (which is a strong complexant to U(VI)) to be present in the first sphere.
These results will be published before the end of the year in an international peer reviewed journal.

[1] A. N. Turanov, V. K. Karandashev, M. Boltoeva, C. Gaillard, V. Mazan, “Synergistic extraction of uranium(VI) with TODGA and hydrophobic ionic liquid mixtures into molecular diluent”, Separation and Purification Technology, 164 (2016) 97.