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# Speciation of uranium(VI) extracted from acidic nitrate media by TODGA into molecular and ionic solvents

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## Abstract

The speciation of uranium(VI) extracted by a molecular extractant *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA) and a hydrophobic ionic liquid (IL), namely 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide [C<sub>4</sub>mim][Tf<sub>2</sub>N], mixture from acidic nitrate media in 1,2-dichloroethane (DCE), and, for comparison, with only TODGA dissolved in DCE or IL has been studied by UV-vis and EXAFS spectroscopy. Our results confirm that the extraction in the conventional system occurs *via* a common solvation mechanism, at high acidity the extracted complex was identified as [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TODGA)]. The addition of hydrophobic bistriflimide anions (Tf<sub>2</sub>N<sup>-</sup>) in the aqueous phase or IL in the organic phase results in a formation of another uranyl complex, in which two tridentate TODGA ligands directly coordinate metal cation and two NO<sub>3</sub><sup>-</sup> and/or Tf<sub>2</sub>N<sup>-</sup> anions are expelled in the outer sphere and act as charge balancing ions. When pure IL is used as diluent for TODGA ligand, the extracted uranyl complex has the same composition and stoichiometry as in the previous case, [UO<sub>2</sub>(TODGA)<sub>2</sub>]<sup>2+</sup>.

## 1. Introduction

In solvent extraction, also known as liquid-liquid distribution, the low solubility of most metal ions in water-immiscible molecular solvents, due to their hydrated solvation environment, is commonly overcome by the use of organic ligands.[1,2] These oleophilic ligands, also named solvent extractants, are able to induce the rearrangement in the metal solvation shell and to form stable, more hydrophobic and, in consequence, more extractable complexes with metal ions. Thus, the principal development in the solvent extraction field has taken place in the design, synthesis and evaluation of the novel organic extractant molecules, which possess a high affinity for target metal ions, in order to provide effective and selective extraction and separation. For instance, a large number of *O*- and *N*-donor ligands such as malonamides,[3] diglycolamides,[4] *bis*(1,2,4-triazine) ligands,[5,6] *etc.* was

proposed to solve a specific problem in the reprocessing of spent nuclear fuel, namely the separation of analogous 4f and 5f trivalent elements.

However, not only the organic ligands, but also the counterions present in the aqueous acidic solution play an important role in the formation of extracted metallic species. For example, the introduction of a small amount of bulky, hydrophobic and weakly bonding anions in the liquid-liquid ion extraction system opens the way to enhance the extraction and separation of metals. Naganawa et al.[7] reported a great enhancement of trivalent lanthanides (Ln) extraction with a carbamoylmethylene phosphine oxide (CMPO) and picrate anions (introduced as picric acid) from aqueous nitric acid solutions into benzene. Moreover, the extraction selectivity of the Ln(III) ions was also improved. The authors suggested that the strong cooperative effect originates from the difference in the hydrophobicity between picrate and nitrate anions involved in the metal complex formation. The effect of hydrophobic picrate anions was explained by the formation of ion pairs between europium(III)-CMPO cation and picrate ions, which are much less hydrated than those paired with nitrates. Suzuki et al.[8] studied the effect of tetrakis[3,5-*bis*(trifluoromethyl)phenyl] borate (TFPB<sup>-</sup>) anions on the extraction of Ln(III) with the neutral tetra(*n*-octyl)diglycolamide ligand (TODGA, Figure 1) from aqueous nitric acid solutions into toluene. The improved efficiency and selectivity of Ln(III) extraction was attributed to the dehydration of the metal ions under the influence of hydrophobic TFPB<sup>-</sup> anions. Turanov et al.[9-18] examined the effect of hydrophobic ionic liquids introduced in a small quantity in the organic phase as ionic liquid on the extraction of rare alkaline earth metals, scandium(III), strontium(II), rare earths elements, uranium(VI) and thorium(IV) with various solvent extractants from aqueous acidic solutions into molecular solvents. A great enhancement of the metal ions extraction was observed. The synergic effect of hydrophobic ionic liquids was explained by the formation of metal solvates in which the anionic counterpart of the acid, for example nitrate ions in the case of the extraction from aqueous nitric acid solutions, was partially or completely replaced by the hydrophobic ionic liquid anions that resulted in the formation of more hydrophobic extractable metal species.

In our recent work,[19] we studied the effect of hydrophobic *bis*(trifluoromethylsulphonyl)imide anions ((CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>, TFSA<sup>-</sup>, hereinafter indicated as Tf<sub>2</sub>N<sup>-</sup>) introduced as lithium salt to the aqueous phase or as an hydrophobic ionic liquid, 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulphonyl)imide, (abbreviated hereafter as [C<sub>4</sub>mim][Tf<sub>2</sub>N]) added to the extracting phase) on the extraction of uranium(VI) by TODGA into a molecular solvent. Our results showed that the distribution of Tf<sub>2</sub>N<sup>-</sup> anions between the two immiscible liquid phases is the dominant factor governing the extractability of uranium(VI) with the mixture of TODGA and ionic liquid as extractant. On the analysis of our experimental data, we proposed the extraction of UO<sub>2</sub>(TODGA)<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> species when the extraction is performed in presence of LiTf<sub>2</sub>N in neutral or HNO<sub>3</sub> aqueous solution. We postulated the extraction of the same species when [C<sub>4</sub>mim][Tf<sub>2</sub>N] is added to the organic phase in addition to TODGA, for 0.1 M HNO<sub>3</sub> aqueous phases. However, for higher HNO<sub>3</sub>

concentrations (typically 3 M), the extraction of mixed  $\text{UO}_2(\text{TODGA})_2(\text{Tf}_2\text{N})_x(\text{NO}_3)_y$  ( $x, y = 1, 2$ ) species could not be excluded, as well as the formation of monosolvate species.

Recently, the extraction of uranium(VI) with TODGA ligand was also studied in non-conventional extraction systems, in which the volatile organic solvent was entirely replaced by hydrophobic ionic liquid. The use of ionic solvents is a promising alternative way for a more efficient and eco-friendly metal extraction due to their unique physicochemical and solvation properties.[20,21] Moreover, the use of ionic liquids as diluents often results in the enhancement of metal extraction.[22] On the other hand, it was shown that the extraction in this kind of systems may involve the formation of unusual metallic species and more complex extraction mechanisms than in conventional systems with molecular solvents.[23-25] So, Panja et al. [26] studied the extraction of U(VI) with TODGA into three imidazolium-based ionic liquids  $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$  ( $n = 4, 6$  and  $8$ ) through batch type distribution studies. They determined with conventional slope analysis method, *i.e.* by plotting the logarithmic metal distribution ratio vs. logarithmic TODGA concentration, that the complex extracted into the ionic liquid phase from a 3 M  $\text{HNO}_3$  was the monosolvate  $\text{UO}_2(\text{TODGA})^{2+}$  and deduced a cation-exchange mechanism of extraction. Zhang et al.[27] examined the solvent extraction of U(VI) by TODGA into two 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids ( $[\text{C}_n\text{mim}][\text{PF}_6]$ ,  $n = 6$  and  $8$ ). The predominant mechanism of extraction was found to be neutral solvation. The complex extracted into the organic phase from a solution of low nitric acid concentration was deduced by slope analysis as the disolvate  $\text{UO}_2(\text{TODGA})_2(\text{NO}_3)_2$ , while from a solution of high  $\text{HNO}_3$  concentration a monosolvate complex was found.

Besides, the stoichiometry of extracted uranium(VI) species with TODGA even changes with the diluent, namely with its polarity. It is suggested that 1:1 and 1:2 U(VI)/TODGA complexes could be formed and extracted into polar solvents such as 1,2-dichloroethane and octanol, while the extraction in non-polar solvents like toluene and *n*-dodecane requires 2 or 3 molecules of TODGA.[28-30]

However, in all above-mentioned publications no detailed study, for example with experimental spectroscopic and/or computer simulation method, was carried out in order to determine the exact chemical form and solution structure of extracted uranium species, namely the number and coordination modes of TODGA and inorganic ligands, metal-ligand bond distances and local coordination geometry around uranium(VI) atom. In our previous papers, we showed that spectroscopic techniques such as UV-vis absorption spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy could provide helpful information about the speciation of uranyl extracted complexes with neutral organic ligands into hydrophobic ionic liquids that allow to deduce the extraction mechanism.[23,24]

In this paper, we attempt to determine using UV-vis and EXAFS spectroscopy techniques the composition and structure of the uranium(VI) complexes extracted by TODGA ligand from aqueous nitric acid solutions into molecular solvent, 1,2-dichloroethane (conventional

extraction system) and into hydrophobic ionic liquid [C<sub>4</sub>mim][Tf<sub>2</sub>N] (ionic liquid as diluent). We also aim to examine the speciation of uranium(VI) extracted with TODGA from HNO<sub>3</sub> solutions containing LiTf<sub>2</sub>N (addition of hydrophobic anions in the aqueous phase) and with TODGA and [C<sub>4</sub>mim][Tf<sub>2</sub>N] mixtures into 1,2-dichloroethane (synergic extraction system). The purpose of this work is to elucidate the mechanism of uranium(VI) extraction with TODGA in these various kinds of extraction systems.

## 2. Experimental

### 2.1. Materials

*N,N,N',N'*-tetra(*n*-octyl)diglycolamide (abbreviated as TODGA, > 97% purity, Figure 1) was purchased from Betulinines (Czech Republic). 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (high purity grade 99.5%) (hereinafter indicated as [C<sub>4</sub>mim][Tf<sub>2</sub>N]) and lithium *bis*(trifluoromethanesulfonyl)imide (LiTf<sub>2</sub>N, > 99% purity) were obtained from Solvionic (Toulouse, France). The synthesis of uranyl *bis*(trifluoromethanesulfonyl)imide UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> and 1-butyl-3-methylimidazolium nitrate [C<sub>4</sub>mim][NO<sub>3</sub>] were carried out by methods described in previous publication.[31] Uranyl nitrate hexahydrate salt UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was of chemical grade. Concentrated nitric acid (HNO<sub>3</sub>, Merck, 65 wt%) was of analytical grade. Molecular diluent 1,2-dichloroethane (DCE) of chemical grade was used without further purification. Deionized water from an Elga purification system of resistivity 18.2 MΩ.cm was used for aqueous solution preparations and dilutions.

### 2.2. Methods

#### 2.2.1. Sample preparation

The highly hygroscopic uranium and lithium salts, UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> and LiTf<sub>2</sub>N, and the ionic liquids, [C<sub>4</sub>mim][Tf<sub>2</sub>N] and [C<sub>4</sub>mim][NO<sub>3</sub>], were dried prior to use under a reduced pressure at 60±1°C for two hours and then for one hour at room temperature.[31]

The composition of samples analyzed by EXAFS and UV-vis spectroscopy is given in Table 1.

The first set (Samples A-F) was obtained by dissolving in neat [C<sub>4</sub>mim][Tf<sub>2</sub>N] or DCE weighted quantities of UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub>, [C<sub>4</sub>mim][NO<sub>3</sub>] and TODGA. An analytical balance (Sartorius, BP 2215 model) with an accuracy of ±0.1 mg was used for weighing the components. The final water content in those solutions was determined after EXAFS measurements by the coulometric Karl-Fisher technique (Hydranal®-Coulomat E, Fluka) and found below 100 ppm. The performance of the Karl-Fisher titrator (Toledo 32 Coulometer) was tested using a standard solution (Hydranal®-Water Standard, Fluka), containing 100 ppm of water. Samples A-F contained 10 mM of uranium(VI).

The second set of IL or DCE samples (samples S1-S12) was obtained by extraction of uranium(VI) with TODGA or with TODGA and [C<sub>4</sub>mim][Tf<sub>2</sub>N] mixtures from aqueous nitric acid solutions of various concentrations into DCE or ionic liquid [C<sub>4</sub>mim][Tf<sub>2</sub>N] at room temperature. A stock aqueous uranium solution was made by dissolving UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 1

M HNO<sub>3</sub>. An aqueous phase was prepared by mixing an aliquot of 1 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution, weighted amount of LiTf<sub>2</sub>N (if it was desired) and an aliquot of aqueous nitric acid solution. An organic phase was prepared by dissolving weighted quantities of TODGA in DCE or [C<sub>4</sub>mim][Tf<sub>2</sub>N], or of TODGA and [C<sub>4</sub>mim][Tf<sub>2</sub>N] in DCE. The pre-conditioning of the organic phase, *i.e.* its pre-equilibration with aqueous acidic solution, was not carried out. The extraction method is described in detail in our previous article.[19] The concentration of U(VI) in the organic phases was in the range from 7 to 17 mM depending on the extraction efficiency in the system under investigation.

The concentration of HNO<sub>3</sub> in the initial and equilibrium aqueous phase was determined by acid–base titration (SCHOTT instrument Titroline easy) using NaOH standard solutions (Carlo Erba).

The U(VI) concentration in stock and work solutions was determined by inductively coupled plasma mass-spectroscopy (ICP-MS, Agilent 7500i) after dilution to the concentration suitable for measurements by 2 vol% nitric acid solution, which contains 10 µg L<sup>-1</sup> thallium (Tl) as an internal standard.

### 2.2.2. UV-vis absorption spectroscopy study

UV-vis absorption spectra have been recorded at room temperature by a Varian Cary 100 spectrophotometer using a quartz cell (optical path length 1 cm) with neat [C<sub>4</sub>mim][Tf<sub>2</sub>N] as reference or pure DCE, accordingly.

### 2.2.3. EXAFS spectroscopy study

EXAFS spectroscopy is a technique which allows to determine the absorbing atom (here uranium) coordination sphere, *i.e.* the nature, distance and number of the neighbors atoms. If several kinds of species are present in solution, this technique will give an average of U(VI) coordination sphere. EXAFS measurements were carried out at the ROBL beamline (BM 20), ESRF (Grenoble, France) at ambient temperature, using a double crystal Si(111) monochromator. Analysis were made at the U L<sub>III</sub> (17 166 eV) edge in fluorescence mode using a 13-element germanium detector. The monochromator energy was calibrated by an yttrium metal foil (17 038 eV). Data were extracted using ATHENA software[32] and their analysis was carried out with the FEFFIT code,[33] using phase and backscattering amplitude functions generated with the FEFF 8.1 code.[34] Fits of the Fourier transform (FT)  $k^3$ -weighted EXAFS data to the EXAFS equation were performed in the  $R$ -space between 1 and 4.3 Å. The  $k$ -range used was 3.0–15 Å<sup>-1</sup>. The amplitude reduction factor ( $S_0^2$ ) was held constant to 1 for all fits. The shift in the threshold energy ( $E_0$ ) was allowed to vary as a global parameter for all atoms. In all fits, the coordination number of the uranyl axial oxygen atoms ( $O_{ax}$ ) was held constant at two. The multiple scattering paths from the axial oxygens were included in the fit by constraining its effective path-length to twice the values of the corresponding U- $O_{ax}$ . The multiple scattering contributions from nitrate groups were taken

into account without adding any fitted parameters ( $N$ ,  $\sigma^2$ , and  $R$  were linked to values obtained for the single scattering contribution U-O).

### 3. Results and discussion

#### 3.1. Reference samples of uranium(VI) in DCE and [C<sub>4</sub>mim][Tf<sub>2</sub>N]

The UV-vis absorption spectra of synthetic solutions prepared by dissolving UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> salt, TODGA ligand and [C<sub>4</sub>mim][NO<sub>3</sub>] ionic liquid in DCE (samples A and B, Table 1) or in the ionic liquid [C<sub>4</sub>mim][Tf<sub>2</sub>N] (samples C-F) are shown in Figure 2. At the first glance, all spectra of uranyl-TODGA solutions, *i.e.* in the presence or absence of nitrate anions, in both DCE and the IL exhibit similar spectral features, but a significant difference in the absorption maximum positions can be observed between 430 and 480 nm.

As can be seen, in the absence of nitrate ions, the uranium-TODGA spectra (samples A and C) exhibit the main peaks at the same positions, namely at 435, 447, 462 and 479 nm, probably indicating a similar composition of the uranium-TODGA complexes in both molecular and ionic liquid solvent. Taking into account that the constituent ionic liquid Tf<sub>2</sub>N<sup>-</sup> anions are generally weakly coordinating anions, we suggested that only TODGA ligands could bind directly to the uranyl(VI) in the equatorial plane, *i.e.* [UO<sub>2</sub>(TODGA)<sub>y</sub>]<sup>2+</sup> ( $y = 1$  and/or  $2$ ) species are observed in the samples A and C. Figure 3 shows a comparison of the EXAFS spectra and their corresponding Fourier transforms (FT) obtained for these samples. The fit results are listed in Table S1 of the Supplementary File. The analysis of these reference uranyl samples A and C confirms that the equatorial coordination sphere of uranyl ion is filled with 2 TODGA molecules, bound in a tridentate fashion. This type of coordination was reported recently for uranium(VI) complex in solid state with shorter alkyl chain diglycolamide ligand *N,N,N',N'*-tetramethyl-3-oxaglutaramide ( $L = NR_2C(O)CH_2)_2O$ ,  $R = \text{methyl}$ ) as [UO<sub>2</sub>L<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, [35] while Kannan et al. reported the crystal structures for [UO<sub>2</sub>X<sub>2</sub>L] ( $X = Cl^-$  or  $NO_3^-$ ,  $R = i\text{-Pr}$ ). [36] These results show that the solvated species in IL (sample C) is [UO<sub>2</sub>(TODGA)<sub>2</sub>]<sup>2+</sup>. This cationic complex is probably solvated by IL Tf<sub>2</sub>N<sup>-</sup> ions, as previously evidenced for other cationic species. [37] In DCE, one may expect the formation of a neutral species, so we may conclude on the formation of the complex [UO<sub>2</sub>(TODGA)<sub>2</sub>](Tf<sub>2</sub>N)<sub>2</sub> where the 2 Tf<sub>2</sub>N<sup>-</sup> counter-anions lie in the uranium outer-sphere. However, these anions could not be revealed by EXAFS spectroscopy because they probably lie at too large distances from the uranium atom to be detected by this technique.

Surprisingly, the introduction of nitrate ions in the composition of samples E and F with 2:1 TODGA-to-uranyl molar ratio (Table 1) did not result in the appearance of additional absorption bands on the UV-vis spectra, as compared to the spectrum of sample A for example. This observation probably indicates that the uranium-TODGA complexes in the reference samples A, C, E and F are identical regardless of solvent nature and do not contain nitrate ions in the inner coordination sphere of the uranyl(VI) ion. This was confirmed by EXAFS analysis which indicates that the uranium first coordination sphere is still composed of 2 TODGA molecules, and so, that uranyl is dissolved as [UO<sub>2</sub>(TODGA)<sub>2</sub>]<sup>2+</sup> in the IL. The UV-

vis spectra of samples B and D, both composed of 1 nitrate ion and 1 TODGA per uranium respectively in DCE and IL, differ significantly one to the other but we observe a shift of the main peaks towards larger wavelengths as compared to the sample A spectrum for example. The speciation in the reference sample B could not be determined by EXAFS, probably because the speciation in this DCE solution is not ruled by the presence of one major species, but by several species in comparable proportion. In sample D, the mixed complex  $[\text{UO}_2(\text{NO}_3)(\text{TODGA})]^+$  is formed, the TODGA molecule binding as tridentate ligand while the nitrate ions are bound in an ordinary bidentate fashion. We evidence here that the competition between nitrate and TODGA ligands allows nitrate ions to enter in the uranyl first coordination sphere only when the amount of TODGA in solution is not sufficient to fill it totally.

**To sum up, in the presence of weakly coordinating anions like bistriflimide anions in solution, TODGA molecules act as a tridentate ligands providing a 6 O inner-sphere coordination environment of uranyl(VI) ion. It results in the solvation of  $[\text{UO}_2(\text{TODGA})_2](\text{Tf}_2\text{N})_2$  species in DCE and  $[\text{UO}_2(\text{TODGA})_2]^{2+}$  in IL. In the presence of nitrate ions, the competition between TODGA and nitrate ligands for the place in the inner coordination shell of uranium(VI) is observed. As a result in DCE, a mixture of species is observed for nitrate/TODGA/U ratio of 1/1/1. In the IL, as long as TODGA-to-uranyl molar ratio is equal to 2, the sole species evidenced are  $[\text{UO}_2(\text{TODGA})_2]^{2+}$ , while the mixed complex  $[\text{UO}_2(\text{NO}_3)(\text{TODGA})]^+$  is formed for a  $[\text{TODGA}]/[\text{U}] = 1$ .**

### 3.2. Speciation of uranium(VI) extracted with TODGA from $\text{HNO}_3$ solutions into DCE

Let us turn now to the extracted samples. First we consider the speciation of uranium in the organic phase after liquid-liquid extraction in the conventional system, *i.e.* in which uranyl ions were extracted from nitric acid media into molecular solvent, 1,2-dichloroethane used as diluent for TODGA extractant.

In our previous study,[19] we examined the experimental data on the extraction of uranium(VI) with TODGA from  $\text{HNO}_3$  solutions into DCE by the conventional graphical slope method in order to determine the stoichiometry of the extracted complexes, *i.e.* the average number of TODGA molecules per one uranium. Thus, we proposed that at low aqueous acidity uranyl ions are rather extracted as disolvate species  $\text{UO}_2(\text{NO}_3)_2(\text{TODGA})_2$ , while the extraction from strong acidic solutions results mainly in the formation of monosolvate species  $\text{UO}_2(\text{NO}_3)_2(\text{TODGA})$ . It should be noted that part of the uranium ligands (nitrates or TODGA molecules) in  $\text{UO}_2(\text{NO}_3)_2(\text{TODGA})_2$  must be present in the outer-sphere of uranyl species, as the uranium equatorial sphere is limited to a 6-fold coordination. Here, we aim to determine the exact composition of uranium-TODGA species in the extracting phase obtained at low and high aqueous acidities, by spectroscopic techniques.

The UV-vis absorption spectra of uranium(VI) extracted with TODGA from 1.2 M and 5.0 M  $\text{HNO}_3$  solutions into DCE are shown in Figure 4 (Samples S1 and S2, Table 1). Looking at these



spectra, it is obvious that different species are extracted as a function of the initial acidity of the aqueous phase, even if in both cases one may expect the extraction of a neutral solvate  $\text{UO}_2(\text{NO}_3)_2(\text{TODGA})_y$ . The comparison of UV-vis spectra with the one of sample A also evidence that the uranium first coordination shell is not composed of 2 TODGA molecules so that at least one nitrate should be present. This was confirmed by the EXAFS analysis which allows to identify the nature of the species extracted from 5 M  $\text{HNO}_3$ , *i.e.*  $[\text{UO}_2(\text{TODGA})(\text{NO}_3)_2]$  (cf. Figure 5). It is interesting to note that this complex exhibits a rare structure, with both one bidentate nitrate group (usual in uranium(VI) nitrate-complexes) and one monodentate nitrate group (rare in uranium(VI) nitrate-complexes) bound to uranium. This crystal structure of uranyl complexes with shorter alkyl chain diglycolamides, *viz.*  $(\text{NR}_2\text{C}(\text{O})\text{CH}_2)_2\text{O}$  (R= *i*-Pr, *i*-Bu) has been reporting with an identical stoichiometry,  $\text{UO}_2(\text{NO}_3)_2(\text{L})$  and an unusual quasi-bidentate binding mode of one nitrate ligand oriented parallel to the dioxo  $\text{O}=\text{U}=\text{O}$  unit.[36]

Figure 4 also shows that the UV-vis spectrum of Sample S1 obtained for 1.2 M  $\text{HNO}_3$  is significantly different from those of Sample A. Unfortunately, EXAFS measurements did not allow us to resolve the composition and stoichiometry of the uranyl complexes extracted at this low nitric acid concentration with TODGA dissolved in DCE. It is likely that this sample is composed of a mixture of different neutral uranyl(VI)-TODGA-nitrate species. This is in accordance with our previous results[19] which indicates that a mixture of mono- and disolvate complexes.

To conclude, we postulated in our previous study[19] that uranium(VI) is extracted in DCE as a mixture of mono and di-solvate species,  $\text{UO}_2(\text{TODGA})(\text{NO}_3)_2$  and  $\text{UO}_2(\text{TODGA})_2(\text{NO}_3)_2$  **via a common solvation mechanism. It is confirmed in the present work, which shows also that at high nitric acid concentration (5 M), the  $\text{UO}_2(\text{TODGA})(\text{NO}_3)_2$  extracted complex dominates the speciation while at low acid concentration (1 M), both complexes are extracted.**

### **3.3. Speciation of uranium(VI) extracted by TODGA from aqueous $\text{HNO}_3$ + $\text{LiTf}_2\text{N}$ solutions into DCE**

In our previous work, we postulated that the uranyl ions are extracted with TODGA from the aqueous  $\text{HNO}_3$  solutions containing  $\text{LiTf}_2\text{N}$  salt into DCE as neutral  $\text{UO}_2(\text{TODGA})_2(\text{Tf}_2\text{N})_2$  species.[19] In order to confirm our hypothesis, we examine here three uranyl solutions (Samples S9-11, Table 1) prepared by extraction of uranium(VI) with TODGA from 0.01, 0.12 and 5.0 M  $\text{HNO}_3$  solutions containing 0.1 M  $\text{LiTf}_2\text{N}$ . The UV-vis absorption spectra of these organic phases are shown in Figure 6.

As can be seen, the spectra of Samples 9-11 exhibit very similar features with the spectrum of reference sample A containing the uranyl species in which the primary coordination shell of uranium was determined by EXAFS as  $[\text{UO}_2(\text{TODGA})_2]^{2+}$ . The fits of EXAFS spectra (Figure 5) confirm the presence of  $[\text{UO}_2(\text{TODGA})_2]^{2+}$  species in these samples. The extraction of

neutral species is expected in DCE, so 2 counter-anions must be present in the uranium outer-sphere. Unfortunately, their nature ( $\text{Tf}_2\text{N}^-$  or/and nitrates) could not be determined by EXAFS.

**We confirm here that adding  $\text{Tf}_2\text{N}^-$  anions in the  $\text{HNO}_3$  aqueous phase entails a change in the nature of extracted species. Even if we did not resolve experimentally the nature of counter-anions, our results further support that the formation of  $[\text{UO}_2(\text{TODGA})_2](\text{Tf}_2\text{N})_2$  species is responsible for the extraction enhancement.[19] In fact, if nitrate ions are involved in the formation of extracted uranium(VI) species, they should displace one TODGA molecule from the primary coordination shell (cf. samples D and S2). So, the presence of coordinately saturated complexes,  $[\text{UO}_2(\text{TODGA})_2]^{2+}$  in solution suggests that two bistriflimide anions work as charge balancers.**

A similar coordination behavior of uranium(VI) was reported by Yuan et al.[38] They postulate from FTIR, XRD and EXAFS analysis that U(VI) is extracted with *N,N'*-diethyl-*N,N'*-ditolyldipicolinamide ligand into  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  ionic liquid as  $[\text{UO}_2(\text{L})_2](\text{Tf}_2\text{N})_2$  species.[39,40]

#### **3.4. Speciation of uranium(VI) extracted with TODGA from $\text{HNO}_3$ solution into the ionic liquid $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$**

To investigate what kind of  $\text{UO}_2^{2+}$ -TODGA coordination complexes is formed and extracted in the liquid-liquid extraction system with hydrophobic ionic liquid used as diluent, the UV-vis absorption spectra of the organic phases after extraction from 0.1 M (Sample 3) and 4.6 M (Sample 4, Table 1)  $\text{HNO}_3$  solutions into  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  were recorded (Figure 7). It is obvious that the spectra of extracted samples S3 and S4 have a similar appearance to that of reference C containing  $[\text{UO}_2(\text{TODGA})_2]^{2+}$  species. Also, the shape of these spectra differs noticeably to the one of sample D composed of  $[\text{UO}_2(\text{NO}_3)(\text{TODGA})]^+$  complexes. This result indicates that the uranyl species extracted with TODGA into the ionic liquid could be of the same nature and composition regardless the initial aqueous acidity and that no nitrate ions are coordinated to uranium.

Fit of the EXAFS spectra (Table 1 and S1) confirms the UV-vis spectroscopy result, by evidencing the formation of the dicationic  $[\text{UO}_2(\text{TODGA})_2]^{2+}$  complex in both solutions, no nitrate or bistriflimide anions being detected in the uranyl first coordination sphere. So, the species extracted in the IL are of different nature than in DCE, which is probably connected to a different extraction mechanism of uranium(VI) in these two solvents. **With an ionic liquid as solvent, the extraction of neutral species is not required and a cation-exchange mechanism involving  $[\text{UO}_2(\text{TODGA})_2]^{2+}$  can be envisioned.** Panja et al.[26] have suggested that the extraction of uranium(VI) with TODGA from nitric acid media into  $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$  ( $n = 4, 6$  and  $8$ ) ionic liquids occurs *via* cation-exchange mechanism between IL constituent cations and monosolvate  $[\text{UO}_2(\text{TODGA})]^{2+}$  species. This is in line with our results.

### 3.5. Speciation of uranium(VI) extracted from HNO<sub>3</sub> solutions with TODGA + [C<sub>4</sub>mim][Tf<sub>2</sub>N] mixtures into DCE

Our previous work showed a strong enhancement of U(VI) extraction with TODGA by addition of some IL in the organic DCE phase. To explain this synergetic effect and eventually connect it to a change in the U(VI) extraction mechanism, we have investigated the nature and stoichiometry of extracted uranium(VI) species in the system composed of 0.1 M TODGA and [C<sub>4</sub>mim][Tf<sub>2</sub>N] diluted in DCE. Two IL concentrations were investigated, either 0.02 M (Figure 9) or 0.1 M (Figure 8), for ~ 1 M, ~ 3 M and ~ 5 M HNO<sub>3</sub> (see Table 1 for the exact extraction conditions). The corresponding UV-vis spectra are compared with reference spectra, *i.e.* samples S1 and S2 obtained by the same extracting system without IL, and sample A composed of UO<sub>2</sub>(TODGA)<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub>. As can be seen, there is a good agreement between the peak position of S5 and S7 spectra the reference sample A. It is confirmed by EXAFS that in these three samples, the inner coordination shell of U(VI) is filled with 2 TODGA molecules to form [UO<sub>2</sub>(TODGA)<sub>2</sub>]<sup>2+</sup>.

As can be seen from

Figure 9 for lower IL concentration (0.02 M), the spectrum of the uranyl complex present at 1.0 M nitric acid concentration (Sample S8) is similar to that of Sample S1, obtained in similar conditions but without IL. As for sample S1, it was not possible to obtain a good fit of the EXAFS spectrum of S8. But from the UV-vis spectra comparison, we can deduce that both solutions have obviously the same speciation which consists of a mixture of UO<sub>2</sub>(TODGA)(NO<sub>3</sub>)<sub>2</sub> and UO<sub>2</sub>(TODGA)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.

The similarity of the UV-vis spectra of Sample S12 and S2 (Figure 9), prepared from 4.6 M nitric acid solution, indicates that the extracted uranium(VI) is present in both solutions as monosolvate species UO<sub>2</sub>(TODGA)(NO<sub>3</sub>)<sub>2</sub>. It was confirmed by EXAFS.

**In summary, we show that a very small addition of IL to TODGA extractant in the organic phase is not sufficient to change the speciation of the uranium(VI) and its extraction mechanism in DCE. When IL concentration is significantly lower than TODGA one, we identified the same extracted uranyl complexes than in the conventional extraction system, *i.e.* without IL addition, namely the monosolvate UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TODGA) at high nitric acid concentration and a mixture of UO<sub>2</sub>(TODGA)(NO<sub>3</sub>)<sub>2</sub> and UO<sub>2</sub>(TODGA)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> at low acid concentration. It means that extraction occurs *via* conventional solvation mechanism. Nevertheless, at comparable concentrations of TODGA and IL in the mixture, we evidenced a change in the speciation of uranyl complexes in the organic phase. It is this change which underlies the mechanism of synergic effect observed in our previous work.[19] Here we show by EXAFS that only dicationic and disolvate species of uranyl [UO<sub>2</sub>(TODGA)<sub>2</sub>]<sup>2+</sup> are extracted regardless of aqueous phase acidity. As with adding of LiTf<sub>2</sub>N salt to the aqueous phase, we could not determine the nature of counter anions in the outer coordination**

**sphere of these species but the hydrophobic  $\text{Tf}_2\text{N}^-$  anions certainly plays in the formation of uranyl-TODGA complexes.**

#### **4. Conclusion**

In the present study, the speciation of uranium(VI) extracted by molecular TODGA extractant from aqueous nitric acid solutions into molecular solvent, 1,2-dichloroethane (conventional extraction system) and into hydrophobic ionic liquid  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  (ionic liquid used as diluent) was studied using UV-vis and EXAFS spectroscopy techniques. The extracted species were also examined in the synergetic extraction system where hydrophobic and weakly coordinating  $\text{Tf}_2\text{N}^-$  anions were added in the aqueous phase as  $\text{LiTf}_2\text{N}$  salt or in the organic extracting phase as  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  ionic liquid.

Our findings confirm that the extraction of uranyl ions by TODGA into 1,2-dichloroethane occurs *via* a common solvation mechanism. We confirm the hypothesis given in our previous work where we postulated that U(VI) extraction would occur *via* the formation of 2 species,  $\text{UO}_2(\text{TODGA})_2(\text{NO}_3)_2$  and  $\text{UO}_2(\text{TODGA})(\text{NO}_3)_2$ , the latter being favored at high nitric acid concentration. As a matter of fact, this is the sole species detected at 5 M  $\text{HNO}_3$ , while a mixture of uranyl complexes is evidenced at 1 M  $\text{HNO}_3$ .

When the molecular DCE solvent is replaced by an ionic liquid, we show that the extracted species is  $[\text{UO}_2(\text{TODGA})_2]^{2+}$  on the whole acidic range. This is obviously linked to a change in the extraction mechanism, which goes apparently from a solvation mechanism in DCE to an ion-exchange mechanism in IL media.

With 1,2-dichloroethane, the addition of  $\text{Tf}_2\text{N}^-$  anions in the aqueous acidic phase or in the extracting phase ( $[\text{IL}] \approx [\text{TODGA}]$ ) entails a change in the speciation of uranyl complexes, in which two tridentate TODGA ligands directly coordinate uranyl(VI) ion and two nitrate or bistriflimide ions act as charge balancing anions. Our results further support for the hypothesis that the larger and more hydrophobic  $\text{Tf}_2\text{N}^-$  anions favor the formation of  $[\text{UO}_2(\text{TODGA})_2](\text{Tf}_2\text{N})_2$  species that is responsible for the extraction enhancement.

In conclusion, even if  $\text{Tf}_2\text{N}^-$  anions are generally considered as weakly coordinating and “inert” ligands, they play an important role in the metal ion extraction. Our results show that the uranyl speciation is susceptible to change with the addition of these hydrophobic anions both in the aqueous and organic phase. One of the major findings of this study is that bistriflimide anions could be directly involved in the uranyl complex formation and this underlies in the change of the extraction mechanism and the enhancement of metal extraction.

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## Tables

**Table 1.** Composition of samples analyzed by EXAFS and UV-vis absorption spectroscopy.

<b>Samples made by salt dissolution in DCE or [C<sub>4</sub>mim][Tf<sub>2</sub>N]</b>				
<b>Sample ID</b>	<b>Solvent</b>	<b>[UO<sub>2</sub><sup>2+</sup>]/[NO<sub>3</sub><sup>-</sup>]/[TODGA]</b>	<b>U(VI) 1<sup>st</sup> coordination sphere obtained by EXAFS</b>	
A	DCE	1/0/3	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>	
B	DCE	1/1/1	Not determined	
C	IL	1/0/3	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>	
D	IL	1/1/1	[UO <sub>2</sub> (TODGA)(NO <sub>3</sub> )] <sup>+</sup>	
E	IL	1/1/2	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>	
F	IL	1/2/2	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>	
<b>Extracted Samples</b>				
<b>Sample ID</b>	<b>Solvent</b>	<b>Extractant, [TODGA]=0.1 M</b>	<b>Aqueous phase initial composition</b>	<b>U(VI) 1<sup>st</sup> coordination sphere obtained by EXAFS</b>
S1	DCE	TODGA	1.2 M HNO <sub>3</sub>	Not determined
S2	DCE	TODGA	5.0 M HNO <sub>3</sub>	UO <sub>2</sub> (TODGA)(NO <sub>3</sub> ) <sub>2</sub>
S3	IL	TODGA	0.12 M HNO <sub>3</sub>	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S4	IL	TODGA	4.6 M HNO <sub>3</sub>	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S5	DCE	TODGA + 0.1 M IL	1.2 HNO <sub>3</sub> M	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S6	DCE	TODGA + 0.1 M IL	2.8 M HNO <sub>3</sub>	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S7	DCE	TODGA + 0.1 M IL	5.3 M HNO <sub>3</sub>	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S8	DCE	TODGA + 0.02 M IL	1.0 M HNO <sub>3</sub>	Not determined
S9	DCE	TODGA	0.01 M HNO <sub>3</sub> + 0.1 M LiTf <sub>2</sub> N	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S10	DCE	TODGA	0.12 M HNO <sub>3</sub> + 0.1 M LiTf <sub>2</sub> N	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S11	DCE	TODGA	5.0 M HNO <sub>3</sub> + 0.1 M LiTf <sub>2</sub> N	[UO <sub>2</sub> (TODGA) <sub>2</sub> ] <sup>2+</sup>
S12	DCE	TODGA + 0.02 M IL	4.6 M HNO <sub>3</sub>	UO <sub>2</sub> (TODGA)(NO <sub>3</sub> ) <sub>2</sub>



## Captions for Figures

**Figure 1.** Chemical structures of 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid ([C<sub>4</sub>mim][Tf<sub>2</sub>N]) and *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA) extractant used in this study.

**Figure 2.** UV-vis absorption spectra of U(VI)-TODGA reference solutions (see nomenclature in Table 1).

**Figure 3.** EXAFS spectra (left) and their corresponding Fourier spectra (right) of reference samples described in Table 1. For sake of clarity, spectra are shifted along the y-axis.

**Figure 4.** UV-vis absorption spectra of uranium(VI) extracted by TODGA into 1,2-dichloroethane from 1.2 (Sample 1) and 5.0 M (Sample 2) HNO<sub>3</sub> solutions, compared with the reference spectra of uranium(VI) in 1,2-dichloroethane (see nomenclature of samples in Table 1).

**Figure 5.** EXAFS spectra (left) and their corresponding Fourier Transform of extracted samples. For sake of clarity, spectra are shifted along the y-axis.

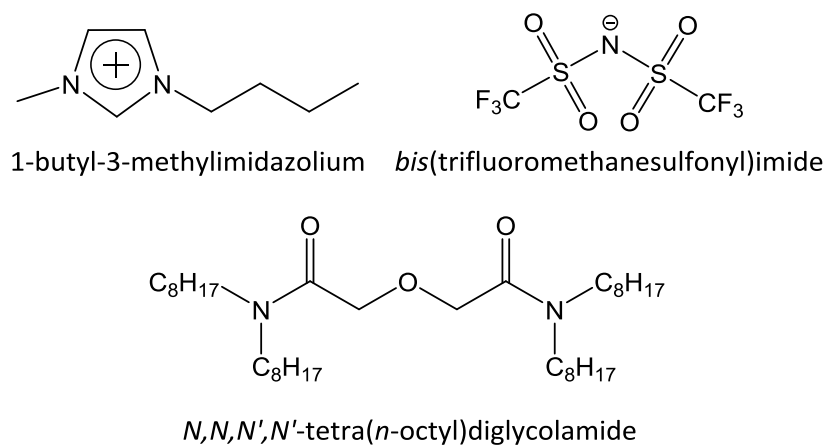
**Figure 6.** UV-vis absorption spectra of uranium(VI) extracted by TODGA into 1,2-dichloroethane from 0.01, 0.12 and 5.0 M HNO<sub>3</sub> solutions containing 0.1 M LiTf<sub>2</sub>N (Samples S9-11). The spectra compared with the reference spectra of uranium(VI) in 1,2-dichloroethane (see nomenclature of samples in Table 1).

**Figure 7.** UV-vis absorption spectra of organic-phase solutions of uranium(VI) produced by solvent extraction of UO<sub>2</sub><sup>2+</sup> from 0.1 (Sample S3) and 4.6 M (Sample S4) HNO<sub>3</sub> solutions into 0.1 M TODGA in the ionic liquid [C<sub>4</sub>mim][Tf<sub>2</sub>N], compared with the reference spectra of uranium(VI) in IL (Samples C and D) (see nomenclature of samples in Table 1).

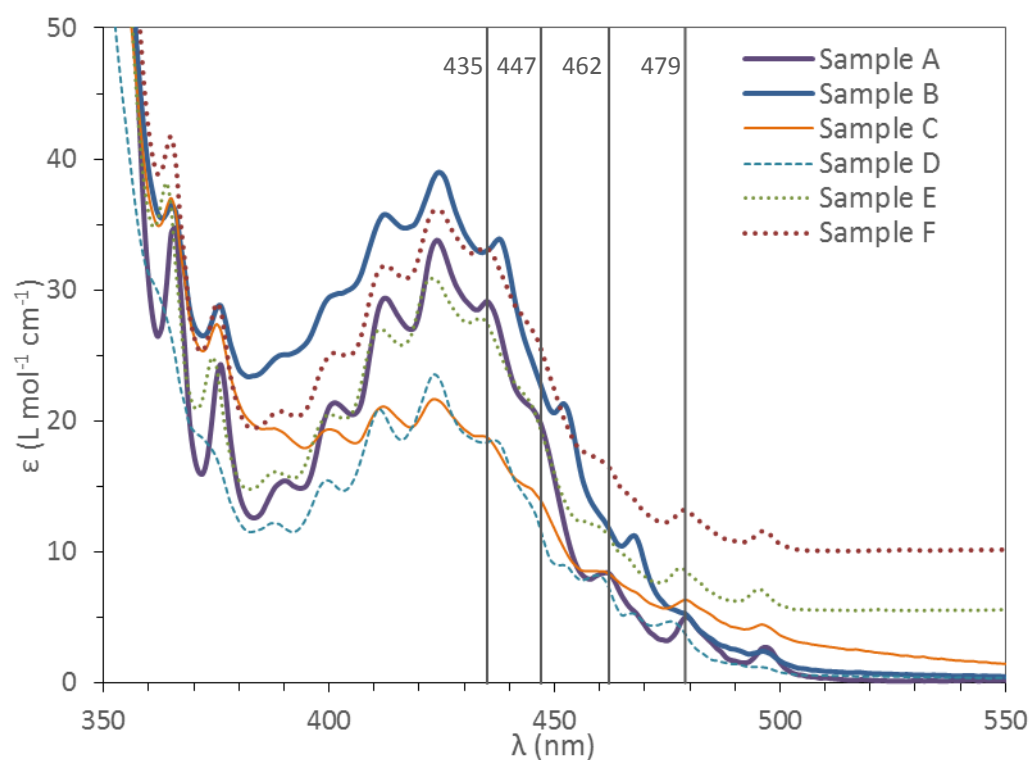
**Figure 8.** UV-vis absorption spectra of uranium(VI) extracted by TODGA and the ionic liquid [C<sub>4</sub>mim][Tf<sub>2</sub>N] mixture from 1.2 M (Sample S5) and 5.3 M (Sample S7) HNO<sub>3</sub> solutions, compared with the reference spectra of uranium(VI) in DCE (Samples A and B) (see nomenclature of Samples in Table 1).

**Figure 9.** UV-vis absorption spectra of uranium(VI) extracted by 0.1 M TODGA and the ionic liquid [C<sub>4</sub>mim][Tf<sub>2</sub>N] from 1.0 M (Sample S8) and 4.6 M (Sample S12) nitric acid solution, compared with the spectra of samples S1 and S2 ( see nomenclature of samples in Table 1).

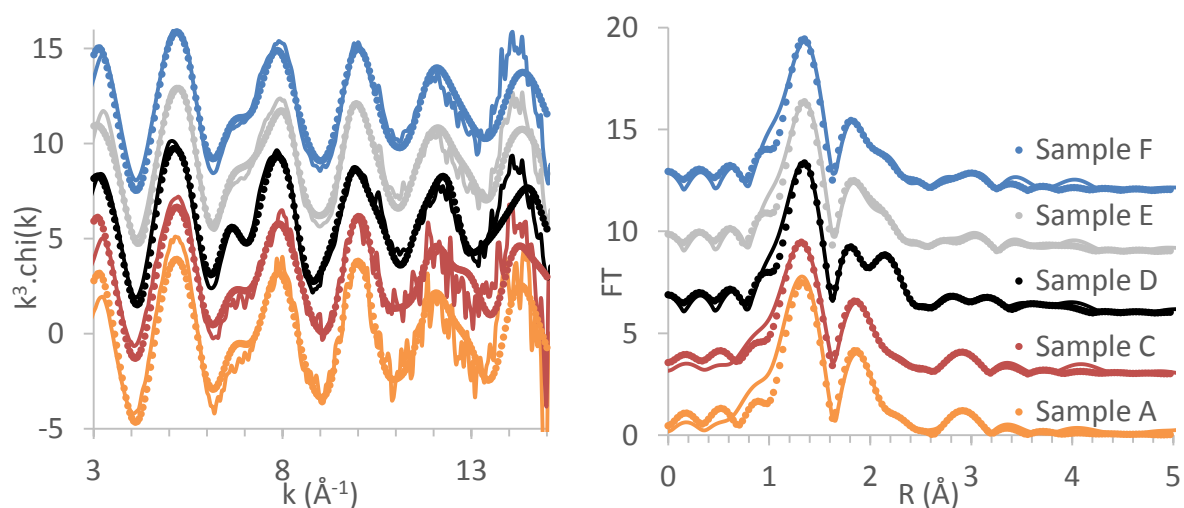
## Figures



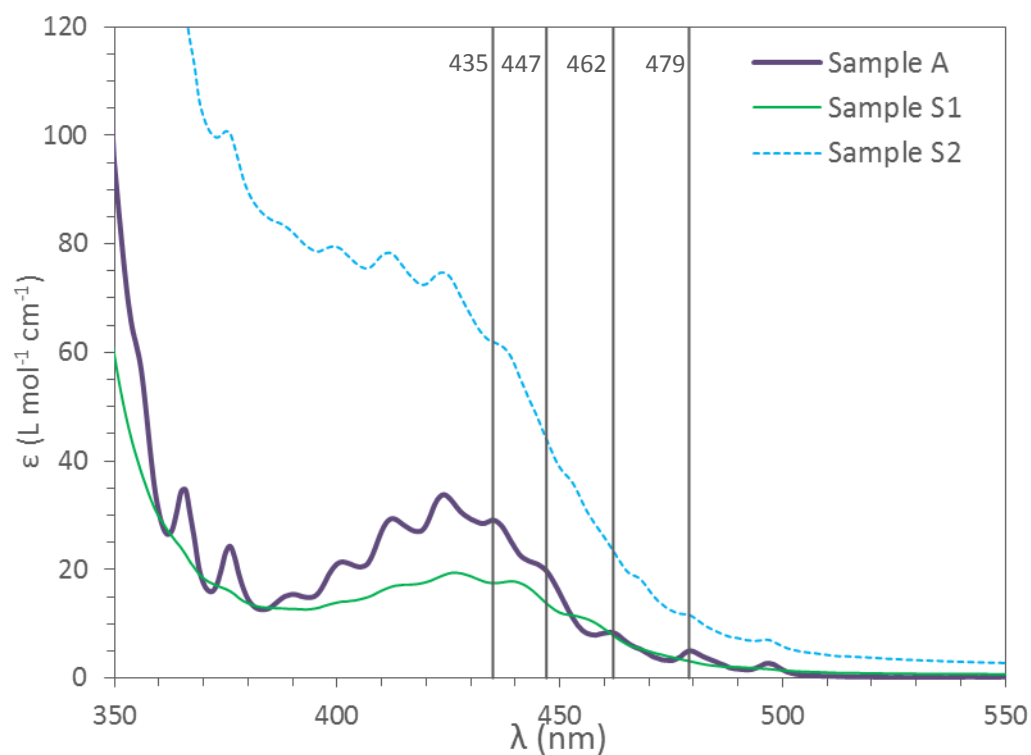
**Figure 1.** Chemical structures of 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid ( $[C_4mim][Tf_2N]$ ) and *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA) extractant used in this study.



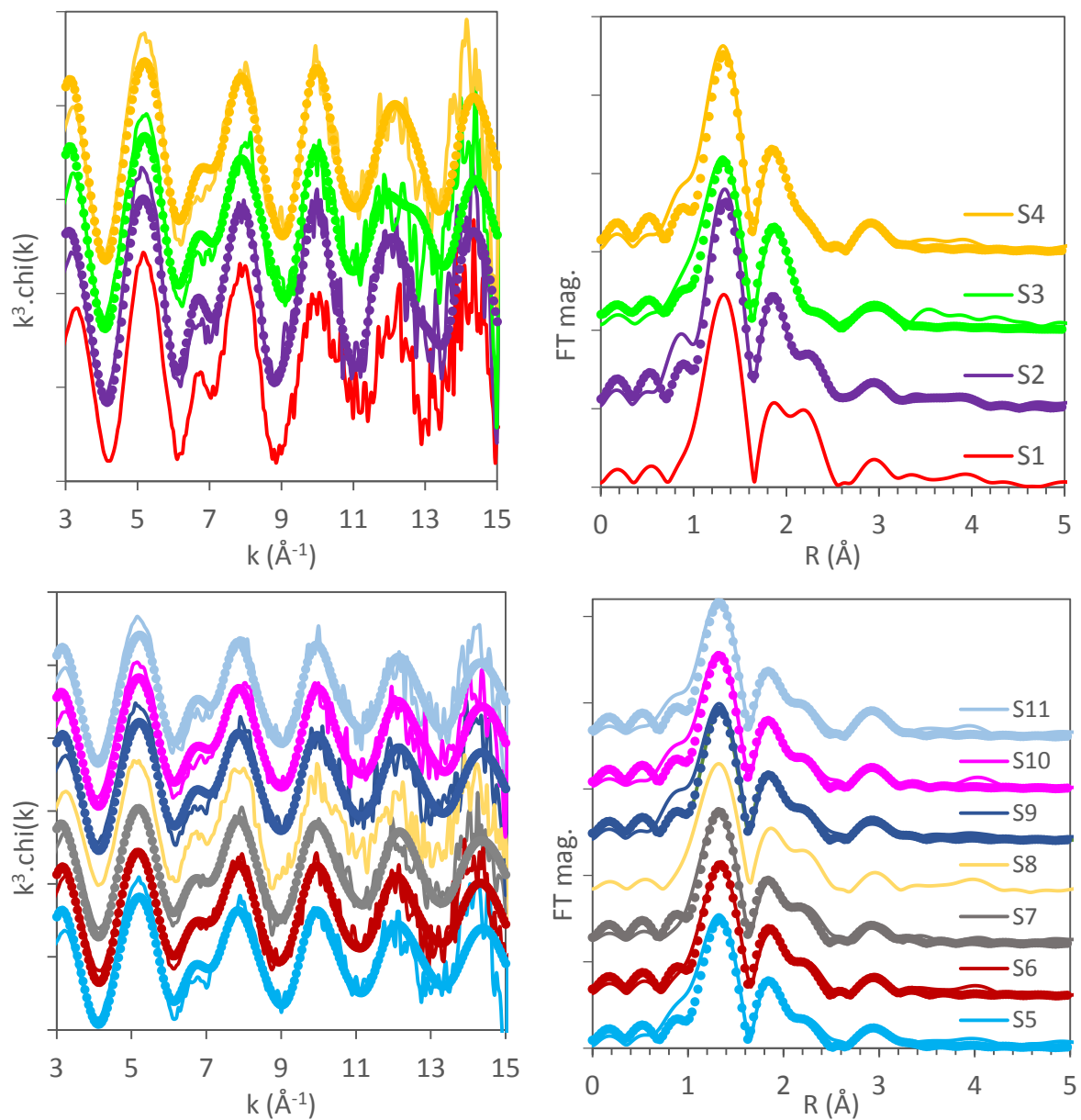
**Figure 2.** UV-vis absorption spectra of U(VI)-TODGA reference solutions (see nomenclature in Table 1).



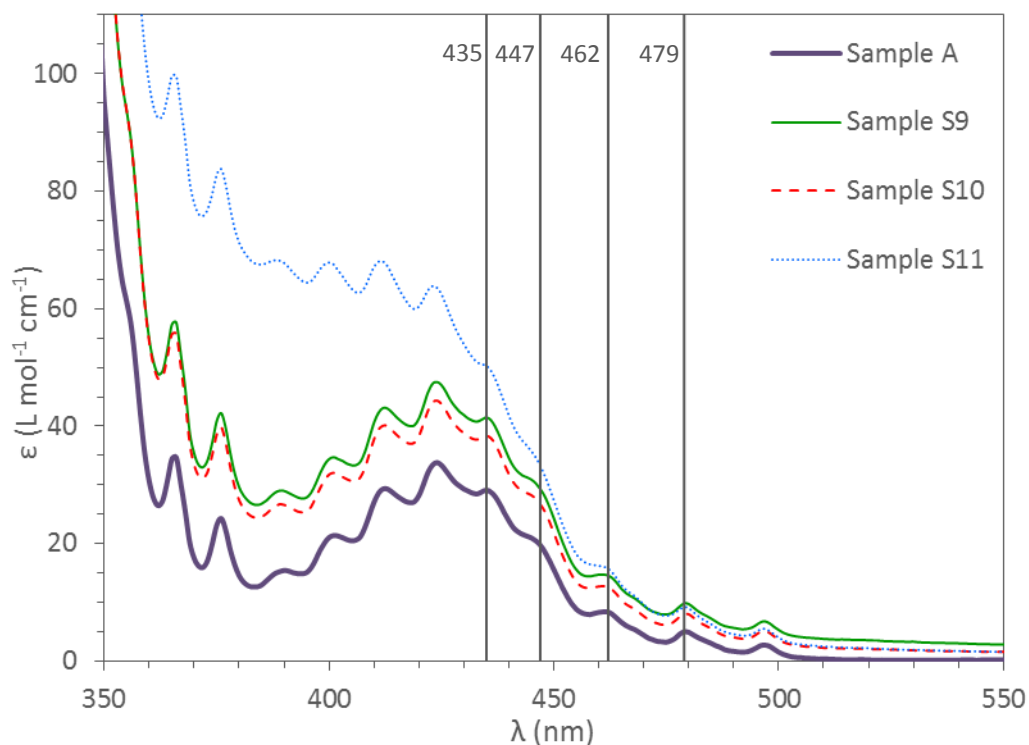
**Figure 3.** EXAFS spectra (left) and their corresponding Fourier spectra (right) of reference samples described in Table 1. For sake of clarity, spectra are shifted along the y-axis.



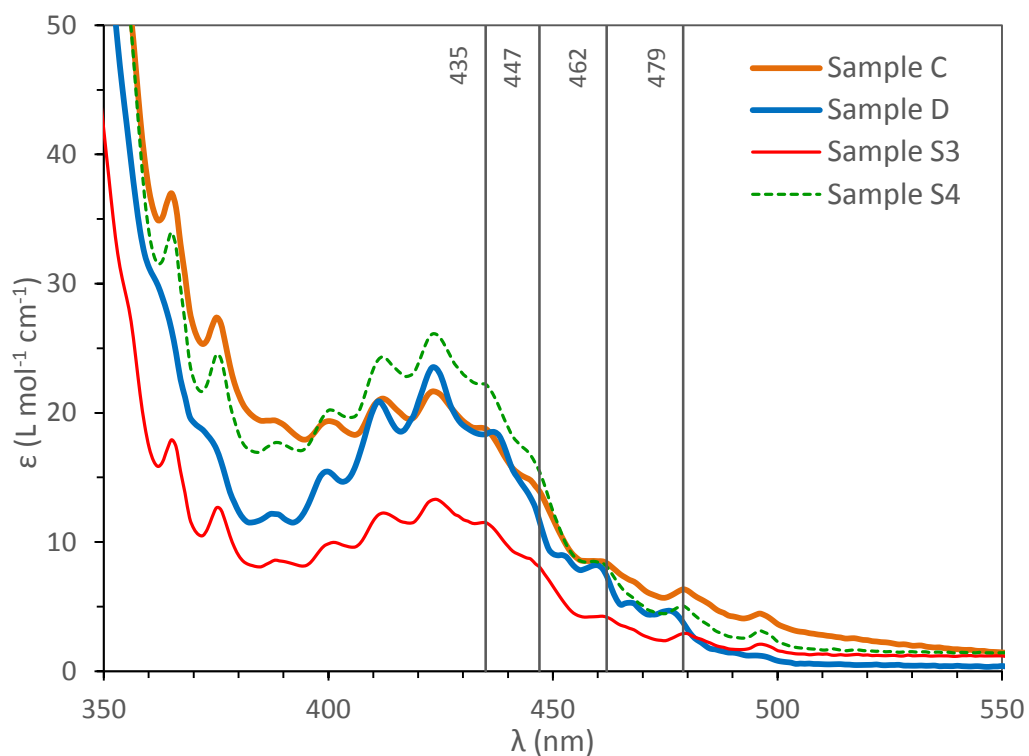
**Figure 4.** UV-vis absorption spectra of uranium(VI) extracted by TODGA into 1,2-dichloroethane from 1.2 (Sample 1) and 5.0 M (Sample 2)  $\text{HNO}_3$  solutions, compared with the reference spectra of uranium(VI) in 1,2-dichloroethane (see nomenclature of samples in Table 1).



**Figure 5.** EXAFS spectra (left) and their corresponding Fourier Transform of extracted samples. For sake of clarity, spectra are shifted along the y-axis.

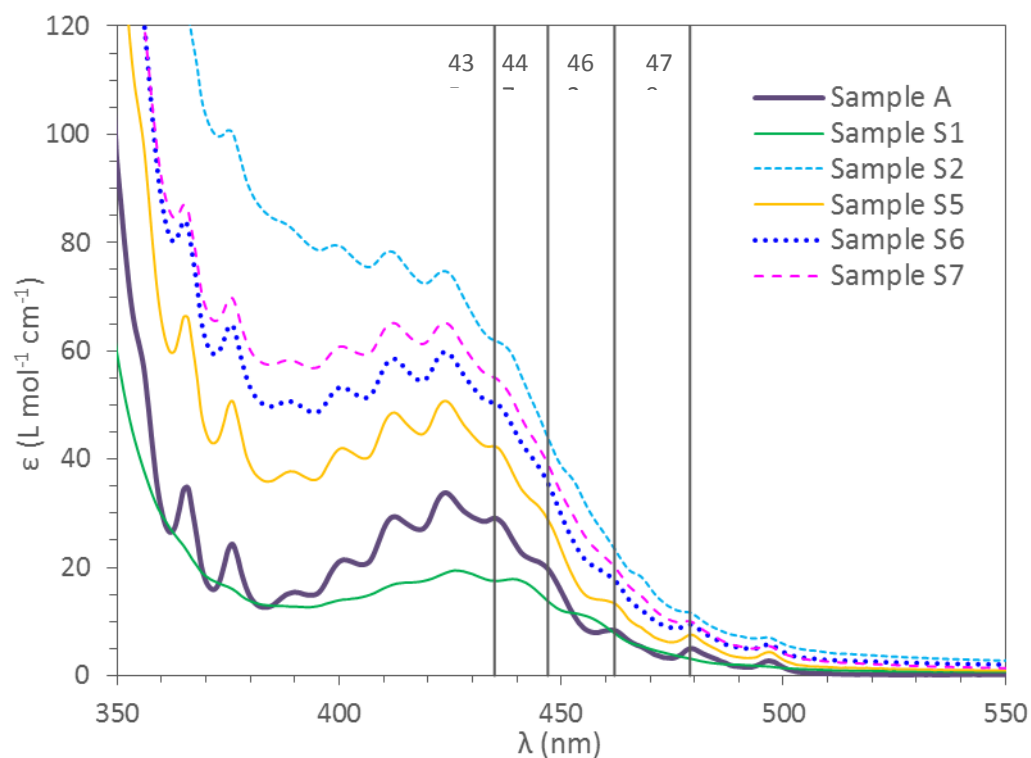


**Figure 6.** UV-vis absorption spectra of uranium(VI) extracted by TODGA into 1,2-dichloroethane from 0.01, 0.12 and 5.0 M  $\text{HNO}_3$  solutions containing 0.1 M  $\text{LiTf}_2\text{N}$  (Samples S9-11). The spectra compared with the reference spectra of uranium(VI) in 1,2-dichloroethane (see nomenclature of samples in Table 1).

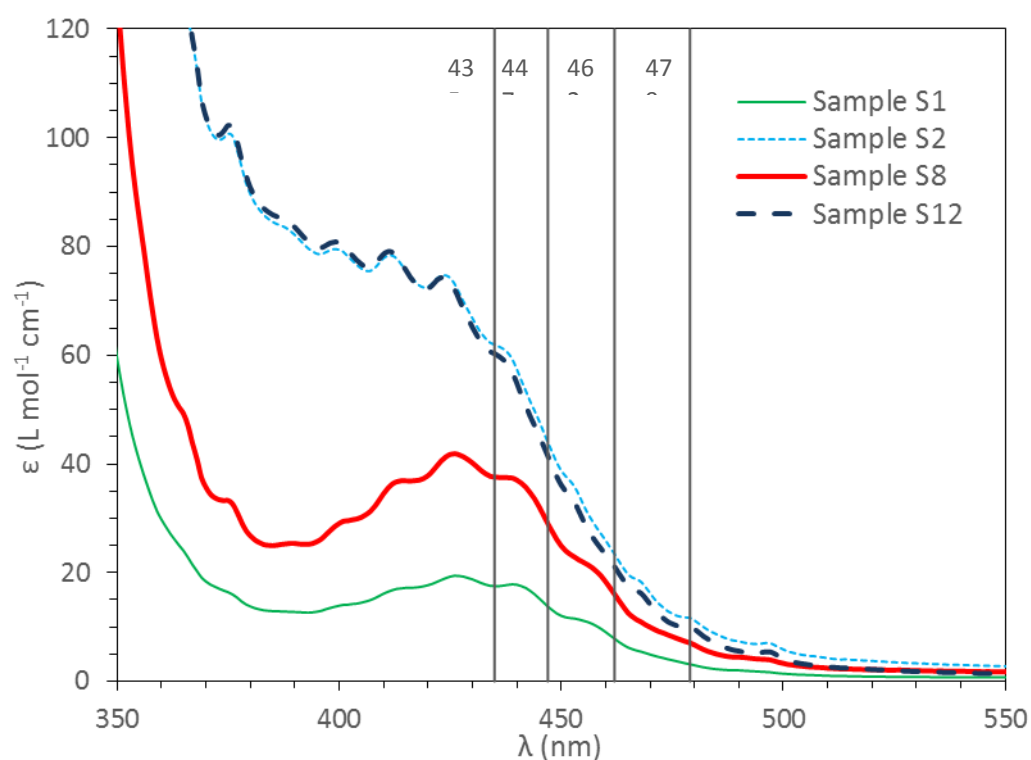


**Figure 7.** UV-vis absorption spectra of organic-phase solutions of uranium(VI) produced by solvent extraction of  $\text{UO}_2^{2+}$  from 0.1 (Sample S3) and 4.6 M (Sample S4)  $\text{HNO}_3$  solutions into 0.1 M TODGA in 1,2-dichloroethane.

the ionic liquid  $[C_4mim][Tf_2N]$ , compared with the reference spectra of uranium(VI) in IL (Samples C and D) (see nomenclature of samples in Table 1).

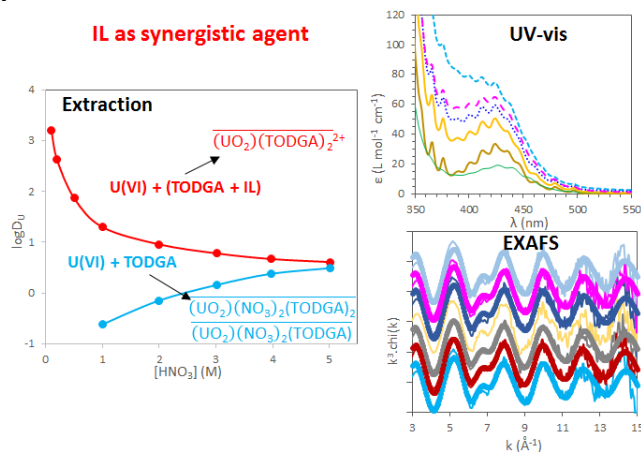


**Figure 8.** UV-vis absorption spectra of uranium(VI) extracted by TODGA and the ionic liquid  $[C_4mim][Tf_2N]$  mixture from 1.2 M (Sample S5) and 5.3 M (Sample S7)  $HNO_3$  solutions, compared with the reference spectra of uranium(VI) in DCE (Samples A and B) (see nomenclature of Samples in Table 1).



**Figure 9.** UV-vis absorption spectra of uranium(VI) extracted by 0.1 M TODGA and the ionic liquid  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  from 1.0 M (Sample S8) and 4.6 M (Sample S12) nitric acid solution, compared with the spectra of samples S1 and S2 ( see nomenclature of samples in Table 1).

### Table of contents graphic



### Table of contents synopsis

In the synergistic extraction system, the hydrophobic bistriflimide anions generally considered as weakly coordinating and "inert" ligands could be directly involved in the uranyl complex formation with TODGA and this underlies in the change of the extraction mechanism and the enhancement of metal extraction.