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# Synergistic extraction of uranium(VI) with TODGA and hydrophobic ionic liquid mixtures into molecular diluent



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## ABSTRACT

The extraction of uranium(VI) from aqueous nitric acid solutions with a neutral extractant, *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA), and with the mixtures of TODGA and a hydrophobic ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mim][Tf<sub>2</sub>N]), into a molecular diluent, 1,2-dichloroethane, has been systematically investigated. The extraction efficiency of U(VI) ions was greatly enhanced by addition of a small amount of ionic liquid to an organic phase containing TODGA. The synergistic effect comes from the higher hydrophobicity of U(VI) extracted species formed by TODGA and weakly coordinating Tf<sub>2</sub>N<sup>−</sup> anions as compared to those formed by TODGA and NO<sub>3</sub><sup>−</sup> anions as counterions in the conventional extraction system. Based on our experimental results, we concluded that the partition of Tf<sub>2</sub>N<sup>−</sup> anions between the two liquid phases is the dominant factor governing the extractability of uranium(VI) with the mixture of TODGA and ionic liquid as extractant. We showed that the extraction of U(VI) from aqueous nitric acid solutions both by TODGA alone and its mixtures with [C<sub>4</sub>mim][Tf<sub>2</sub>N] into 1,2-dichloroethane can be quantitatively described on the basis of the solvation extraction mechanism. However, in the extraction system with added hydrophobic ionic liquid, the partition of Tf<sub>2</sub>N<sup>−</sup> anions between the two immiscible phases and the interaction between bis(trifluoromethylsulfonyl)imide acid, HTf<sub>2</sub>N, and TODGA molecules in the organic phase should be taken into account.

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## 1. Introduction

Ionic liquids (ILs) are a class of compounds composed solely of ions and having a melting point below 373 K [1]. Recently, their use as new separation media in liquid–liquid extraction processes has been actively investigated [2–25]. Due to a unique combination of physicochemical properties of ILs, such as negligible vapor pressures, nonflammability and excellent solvation properties, they are regarded as possible alternatives to conventional molecular organic solvents [26,27]. Moreover, it has been recognized that the simple replacement of organic diluent by hydrophobic ionic liquid often greatly enhances the extraction efficiencies of many well-known extracting agents. For instance, the pioneering work of Dai et al. [3] reported remarkably high metal distribution ratios in the extraction of strontium(II) from water by dicyclohexano-18-

crown-6 ligand into several *N,N'*-dialkylimidazolium-based ILs as compared to those obtained with any conventional organic diluents. Visser and Rogers [4] showed that the extraction of plutonium(IV), thorium(IV) and uranium(VI) into 1-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>mim][PF<sub>6</sub>]) with a mixture of two complexing organic ligands, octyl(phenyl)-*N,N'*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) and tri-*n*-butyl phosphate (TBP), is at least an order of magnitude higher than the one obtained for the same extractant concentration in dodecane. Nakashima et al. [5] found that CMPO dissolved in [C<sub>4</sub>mim][PF<sub>6</sub>] ionic liquid greatly enhances the extractability and selectivity of lanthanide cations compared to their solutions in conventional organic diluents. The higher extraction efficiency was attributed to some synergistic factors: (i) ion-recognition capabilities of complexing ligands; (ii) unique ionic solvation environments provided by ILs for ionic species; (iii) ion-exchange capabilities of ILs [8].

It should be noted that the great enhancement of the extraction efficiency of neutral donor extractants towards metal ions is

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observed only with ionic diluents with relatively short alkyl chain radicals attached to the cationic part of ILs [28–31]. The noticeable aqueous solubility of this kind of ILs leads to the contamination of the aqueous phase with IL component ions [13,32]. This drawback as well as the high cost and viscosity of ILs limit their industrial application as diluents.

In our previous works [33–38], we found that ILs used as additives to the traditional extraction systems is a way to improve liquid–liquid extraction systems of metal ions. A considerable synergistic effect was observed in the presence of even small amounts of ILs in the organic phase containing diglycolamide ligand [33,36], carbamoylmethylphosphine oxides [34,37,38] and tetraphenylmethylenediphosphine dioxides [35], when lanthanide and alkaline earth cations were extracted from nitric acid solutions. Pribylova et al. [39,40] reported the increase of americium (III) extraction from nitric acid solutions by more than two orders of magnitude when a small amount of IL was added to a diphenyl (dibutyl)carbamoylmethylphosphine oxide in dichloroethane.

It seems that this kind of synergistic extraction system is very promising for the preconcentration and separation of metal ions at least on a laboratory scale. The addition of a small amount of IL to molecular solvents does not lead to modification of the organic phase viscosity [41]. Moreover, the large number of possible “extracting agent–hydrophobic IL–molecular diluent” mixtures offers the possibility to design an extraction system for each particular application. This approach allows maintaining the high efficiency and selectivity of the extraction processes with the IL without any significant rise in price.

Several recent studies have shown that alkyl-substituted diglycolamide ligands demonstrate a high extraction ability towards actinides and lanthanides ions in nitric acid media [42–46]. Diglycolamides (DGA) contain three oxygen atoms, so they act as tridentate ligands. As compared to bidentate neutral organophosphorus compounds, DGA have advantages such as an easy synthesis, milder stripping requirements and a chemical composition of fully incinerable elements. The hydrophobicity of DGA extractants is controlled by the length of the alkyl radicals linked to the amidic N atoms. In the case of *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA), the octyl chains give sufficient lipophilicity of the TODGA molecule to dissolve in various organic diluents [47].

To date, several studies have investigated the extraction behavior of actinides and lanthanides in DGA–IL systems [16]. Solutions of DGA extractants in 1-alkyl-3-methylimidazolium hexafluorophosphate ( $[C_n\text{mim}][\text{PF}_6]$ ,  $n = 4, 6$ , and  $8$ ) [48,49] and 1-alkyl-3-methylimidazolium *bis*(trifluoromethylsulfonyle)imide ( $[C_n\text{mim}][\text{Tf}_2\text{N}]$ ,  $n = 4, 6$ , and  $8$ ) [50] provide an efficient extraction of U(VI) ions from aqueous solutions under low acidity conditions, whereas they show a negligible extraction in traditional organic solvents such as chloroform. Higher distribution ratios were obtained for short alkyl chain ILs which was attributed to their higher ion-exchange capabilities as compared to the hydrophobic long alkyl chain imidazolium ILs [50].

In this work, we report our experimental results on the investigation of the hydrophobic ionic liquid  $[C_4\text{mim}][\text{Tf}_2\text{N}]$  as synergist in the extraction of U(VI) with TODGA dissolved in organic diluent 1,2-dichloroethane. In order to elucidate the extraction mechanism in this extraction system, we aim: (i) to investigate the distribution of nitric acid and water between aqueous acidic phase and 1,2-dichloroethane solutions of TODGA; (ii) to measure the distribution of hydrophobic ionic liquid anions  $\text{Tf}_2\text{N}^-$  in the liquid–liquid system containing TODGA and  $[C_4\text{mim}][\text{Tf}_2\text{N}]$  in the organic phase and  $\text{HNO}_3$  in the aqueous phase; (iii) to determine the effect of various parameters on the extraction of uranium(VI) with TODGA alone and its mixtures with  $[C_4\text{mim}][\text{Tf}_2\text{N}]$ ; (iv) to compare the extraction mechanism in the synergistic extraction system containing TODGA and  $[C_4\text{mim}][\text{Tf}_2\text{N}]$  in the organic phase to that in

the conventional extraction system. The results obtained are discussed on the basis of the solvation extraction mechanism. The findings of this study are of interest for the understanding of the complicated chemistry and mechanisms involved in metal ions extraction in the presence of ILs and for the development of organic extractant mixtures for preconcentration and separation of metal ions from aqueous solutions.

## 2. Experimental

### 2.1. Chemical reagents

*N,N,N',N'*-tetra(*n*-octyl)diglycolamide (abbreviated as TODGA) was prepared, purified and characterized according to the published method [51]. 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyle)imide ionic liquid (designated as  $[C_4\text{mim}][\text{Tf}_2\text{N}]$ ) was synthesized and purified as reported previously [52]. The salts, namely uranyl nitrate hexahydrate  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , lithium *bis*(trifluoromethylsulfonyle)imide  $\text{LiTf}_2\text{N}$ , ammonium nitrate  $\text{NH}_4\text{NO}_3$ , nitrates of Fe(III), Cr(III), Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) Pb(II), Sr(II), and nitric and hydrochloric acids were of chemical and analytical grade and used as supplied. Molecular diluent 1,2-dichloroethane (DCE) of chemical grade was used without any further purification. All aqueous acidic solutions were prepared from distilled water and concentrated acid.

### 2.2. Extraction procedure

In this study, the batch experiments were carried out at room temperature.

A stock uranium solution was made by dissolving  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  salt in water and diluting down to  $1 \cdot 10^{-5}$  M U(VI) with aqueous  $\text{HNO}_3$  solution. An organic phase was prepared by dissolving weighed quantities of TODGA and  $[C_4\text{mim}][\text{Tf}_2\text{N}]$  in 1,2-dichloroethane.

The preconditioning of the organic phase, i.e., its pre-equilibration with aqueous acidic solution, before measurements of the distribution ratio was not carried out. All extraction samples were prepared using precisely weighed aliquots of each phase in centrifuge tubes equipped with sealing plugs. A 1:1 volume ratio of organic and aqueous phases was employed. The biphasic mixtures obtained by putting together aqueous and organic phases were shaken vigorously using a rotor mixer at the rate of 60 rpm for 1 h. It was checked in the preliminary trials that this time of phase contact is sufficient to achieve the equilibrium. To promote phase separation, the extraction tubes were centrifuged and then the aliquots of each phase were sampled for further analysis.

The values of the distribution ratio  $D_U$  were calculated as  $[\text{U}]_{\text{org}}/[\text{U}]$ . The subscript “org” denotes the uranium species in the organic phases, while it is omitted for the species in the aqueous phase.

Duplicate experiments showed that the reproducibility of the  $D_U$  measurements was within 10%.

### 2.3. Analysis

The concentration of U(VI) in the aqueous phase was determined using inductively coupled plasma mass spectrometry (ICP-MS) on a mass spectrometer X-7 (Thermo Electron, USA) according to the previously described procedure [53].

Aqueous  $\text{Tf}_2\text{N}^-$  concentrations were determined by sulfur content measurement using inductively coupled plasma atomic emission spectrometry (ICP-AES) on an ICAP-61 spectrometer (Thermo Jarrel Ash).

The concentration of  $\text{HNO}_3$  in the aqueous phase was determined by potentiometric titration of the protons  $\text{H}^+$  with NaOH

solution. The extraction of nitric acid into the organic phase was also checked by measuring  $H^+$  back-extracted into water. The completeness of  $HNO_3$  stripping was monitored by repeated back-extractions.

The total water content in the organic phase was determined by the coulometric Karl-Fisher technique (Hydranal®-Coulomat E, Fluka). The performance of the Karl-Fisher titrator (Toledo 32 Coulometer) was tested using a standard solution (Hydranal®-Water Standard, Fluka).

### 3. Results and discussion

In the present article, we denote the extraction systems as  $M/HX/(L + IL)/MS$ , where  $M$  is the metal ion,  $HX$  is the mineral acid,  $L$  is the organic ligand,  $IL$  is the ionic liquid and  $MS$  is the molecular solvent.

In order to fully understand and describe the uranium(VI) extraction behavior in the synergistic extraction system, the effect of each solute in both aqueous and organic phases on the equilibrium in the liquid–liquid system should be examined. Thus, we consider the extraction systems from simple to more complex, i.e., in order: (i) liquid–liquid system without metal ions in the aqueous phase,  $HNO_3/TODGA/DCE$  and  $HNO_3/(TODGA + IL)/DCE$ ; (ii) traditional extraction system without  $IL$  in organic phase,  $U(VI)/HNO_3/TODGA/DCE$ ; (iii) synergistic extraction system with the presence of  $IL$  in the organic phase,  $U(VI)/HNO_3/(TODGA + IL)/DCE$ .

#### 3.1. Extraction of nitric acid with TODGA into DCE

Let us consider first the simplest case, i.e., the liquid–liquid system  $HNO_3/TODGA/DCE$ . Each phase is a two components solution: (i) aqueous phase is a nitric acid solution (no uranium); (ii) organic phase is composed of TODGA and DCE (no  $IL$ ).

TODGA is a neutral solvating extractant which facilitates the extraction by coordination with the metal ion through three oxygen atoms, leading to the formation of a neutral complex [54]. Being a sort of Lewis base, TODGA is also known to interact with nitric acid [55]. It has been demonstrated that the  $HNO_3$  amount extracted by TODGA molecules depends on the nature of the organic diluent [47,56]. Since the metal extraction proceeds from a relatively high nitric acid concentration, the nitric acid and the metal ion are competing for the same binding sites in TODGA. Thus, we have first examined the nitric acid uptake with TODGA into DCE.

The  $HNO_3$  uptake with pure DCE is found to be negligible for an aqueous acidity lower than 2 M. Fig. 1 shows the experimental data on the organic phase concentration of nitric acid in DCE containing 0.1 M TODGA as a function of the initial aqueous  $HNO_3$  concentration. The nitric acid content in the organic phase is calculated by subtraction of the  $HNO_3$  uptake with DCE solution of TODGA and with pure DCE when the aqueous acidity was higher than 2 M. It can be seen that above an aqueous acidity of 2.5 M, the amount of extracted  $HNO_3$  exceeds the TODGA quantity, i.e., one molecule of TODGA solvates more than one  $HNO_3$  molecule. Thus, the formation of  $HNO_3 \cdot TODGA$  and  $(HNO_3)_2 \cdot TODGA$  complexes should be taken into account for the description of the uranium (VI) extraction with TODGA into DCE.

The hydration of TODGA (hereinafter abbreviated as  $L$ ) and its nitric acid species,  $HNO_3 \cdot L$  and  $(HNO_3)_2 \cdot L$ , was also checked by measuring the co-extracted water amount into the organic phase. Fig. S1 in Supplementary file shows the concentration of  $H_2O$  in the organic phase consisting of pure DCE and 0.1 M TODGA in DCE as a function of the initial aqueous  $HNO_3$  concentration. It can be seen that a small amount of water is extracted by pure

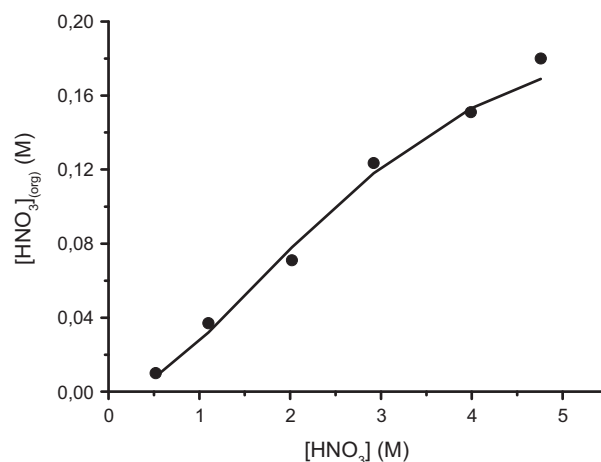
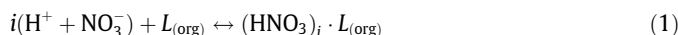


Fig. 1.  $HNO_3$  extraction with 0.1 M TODGA in 1,2-dichloroethane as a function of initial aqueous  $HNO_3$  concentration. The solid line indicates the calculated values from Eq. (6).

DCE. The water co-extracted by TODGA in DCE is independent on the aqueous acidity and its amount is nearly equal to the TODGA concentration. This implies that only mono-hydrated species,  $L \cdot H_2O$ ,  $HNO_3 \cdot L \cdot H_2O$  and  $(HNO_3)_2 \cdot L \cdot H_2O$  are formed in the organic phase under the chemical conditions used in the present study. Data on the water uptake in the organic phase as a function of the initial TODGA concentration for 3 M  $HNO_3$  solutions further support the idea of mono-hydrate complexes of TODGA (Fig. S2).

Hence, the equilibrium equation of  $HNO_3$  extraction with TODGA into DCE can be presented as follow:



where  $L$  is TODGA and  $i$  is the number of  $HNO_3$  molecules involved in the formation of  $(HNO_3)_i \cdot TODGA$  complex ( $i = 1, 2$ ). In this equilibrium,  $H_2O$  molecules have been omitted for TODGA and TODGA- $HNO_3$  species in the organic phase because of their equality [42].

The corresponding conditional extraction constants  $K_{HNO_3(i)}$  are:

$$K_{HNO_3(i)} = [(HNO_3)_i \cdot L]_{(org)} a^{-i} [L]_{(org)}^{-1} \quad (2)$$

$$a = [H^+][NO_3^-] \gamma_{\pm}^2 \quad (3)$$

where  $[L]_{(org)}$  is the concentration of free, i.e. unbound with nitric acid, TODGA,  $a$  is the  $HNO_3$  activity in the equilibrium aqueous phase defined by Eq. (3), and  $\gamma_{\pm}$  is the activity coefficient for  $HNO_3$  in the aqueous phase. The values of  $\gamma_{\pm}$  are taken from article [57]. Because of the lack of information on the organic phase activity coefficients, we assume that the ratio of organic activity coefficients for mono-hydrates of TODGA and its complexes with  $HNO_3$  is constant. This approximation implies that the  $K_{HNO_3(i)}$  constants are only conditional ones. By introducing the mass balance, the expression of  $HNO_3$  concentration in the organic phase is:

$$\begin{aligned} [HNO_3]_{(org)} &= [HNO_3 \cdot L]_{(org)} + 2[(HNO_3)_2 \cdot L]_{(org)} \\ &= K_{HNO_3(1)} [L]_{(org)} a + 2K_{HNO_3(2)} [L]_{(org)} a^2 \end{aligned} \quad (4)$$

and the mass balance equation for the initial TODGA concentration in the organic phase is:

$$\begin{aligned} [L]_o &= [L]_{(org)} + [HNO_3 \cdot L]_{(org)} + [(HNO_3)_2 \cdot L]_{(org)} \\ &= [L]_{(org)} + K_{HNO_3(1)} [L]_{(org)} a + K_{HNO_3(2)} [L]_{(org)} a^2 \end{aligned} \quad (5)$$

where  $[L]_o$  is the initial extractant concentration in the organic phase.

The total concentration of  $\text{HNO}_3$  complexes with TODGA in the organic phase can be written as:

$$[\text{HNO}_3]_{(\text{org})} = [L]_o (K_{\text{HNO}_3(1)}a + 2K_{\text{HNO}_3(2)}a^2) \times (1 + K_{\text{HNO}_3(1)}a + K_{\text{HNO}_3(2)}a^2)^{-1} \quad (6)$$

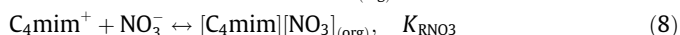
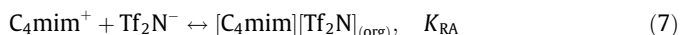
The values of the  $\text{HNO}_3$  conditional extraction constants calculated from the experimental data in Fig. 1 by the nonlinear least squares method are  $K_{\text{HNO}_3(1)} = 0.625 \pm 0.030$  and  $K_{\text{HNO}_3(2)} = 0.0566 \pm 0.0030$  (Table 1). As can be seen, the solid line calculated from Eq. (6) shows a very good agreement with the experimental data.

These findings suggest that the significant  $\text{HNO}_3$  uptake with TODGA at high aqueous acidity results in the decrease of the free extractant concentration in the organic phase. Hence, this feature can affect the metal extraction and it should be taken into account for the description of the extraction system behavior.

### 3.2. Distribution of hydrophobic $\text{Tf}_2\text{N}^-$ anions in $\text{HNO}_3/(\text{TODGA}+\text{IL})/\text{DCE}$

The addition of hydrophobic and weakly coordinating anions to the extraction system is known to enhance significantly the extraction efficiency and selectivity of metals, particularly for aqueous solutions of low ionic strength [55]. These anions work as counterions to neutralize the charge of metal cations in the extracted complexes. In the present study, we focused on the effect of the hydrophobic ionic liquid,  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ , on the extraction of uranium(VI) with TODGA from  $\text{HNO}_3$  solutions. It is known that this ionic liquid is slightly soluble in water and considerably in aqueous acidic solutions [32,58]. Therefore, we have considered the distribution of the ionic liquid anions,  $\text{Tf}_2\text{N}^-$ , between an aqueous  $\text{HNO}_3$  phase and an organic phase composed of TODGA, a small quantity of ionic liquid and 1,2-dichloroethane.

As illustrated in Fig. 2, the distribution of IL anions ( $D_{\text{Tf}_2\text{N}} = [\text{Tf}_2\text{N}^-]_{\text{org}}/[\text{Tf}_2\text{N}^-]_{\text{aq}}$ ) depends on the aqueous nitric acid concentration. Without TODGA in the organic phase,  $D_{\text{Tf}_2\text{N}}$  decreases gradually (i.e. the aqueous  $\text{Tf}_2\text{N}^-$  solubility increases) with the aqueous  $\text{HNO}_3$  concentration (Fig. 2a). This issue can be explained by the formation of the  $[\text{C}_4\text{mim}][\text{NO}_3]$  ionic liquid in the organic phase. This ionic liquid is probably less lipophilic than  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ . The partitioning reactions for ionic liquids can be written as:



where  $K_{\text{RA}}$  and  $K_{\text{RNO}_3}$  are the conditional equilibrium constants.  $K_{\text{RA}}$  is 7940 for  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  and  $K_{\text{RNO}_3}$  is 2.6 for  $[\text{C}_4\text{mim}][\text{NO}_3]$  [33].

The distribution ratio of  $\text{Tf}_2\text{N}^-$  anions between the two immiscible phases can be written as:

$$D_{\text{Tf}_2\text{N}} = K_{\text{RA}}[\text{Tf}_2\text{N}^-](1 + K_{\text{RNO}_3}[\text{NO}_3^-] \cdot \gamma_{\pm})^{-1} = K_{\text{RA}}[\text{IL}]_o(1 + D_{\text{Tf}_2\text{N}})^{-1}(1 + K_{\text{RNO}_3}[\text{NO}_3^-] \cdot \gamma_{\pm})^{-1} \quad (9)$$

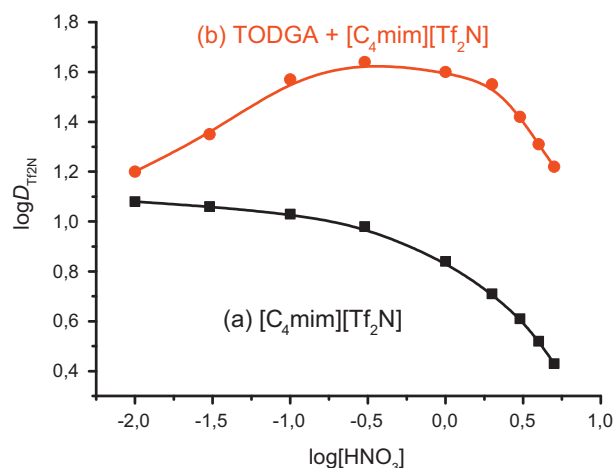


Fig. 2. Effect of the initial  $\text{HNO}_3$  concentration in the aqueous phase on the distribution ratio of  $\text{Tf}_2\text{N}^-$  anion. Organic phase: (a) 0.02 M  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  in 1,2-dichloroethane; (b) 0.02 M  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  and 0.02 M TODGA in 1,2-dichloroethane. The solid lines are guide for the eye.

or

$$D_{\text{Tf}_2\text{N}}(1 + D_{\text{Tf}_2\text{N}}) = K_{\text{RA}}[\text{IL}]_o(1 + K_{\text{RNO}_3}[\text{NO}_3^-] \cdot \gamma_{\pm})^{-1} \quad (10)$$

where  $[\text{IL}]_o$  is the initial concentration of  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  in the organic phase and  $\gamma_{\pm}$  is the activity coefficient for  $\text{NO}_3^-$  anion.

It can be seen that the  $\text{Tf}_2\text{N}^-$  distribution ratio dependence on nitric acid is significantly influenced by the presence of TODGA molecules in the organic phase (Fig. 2b). At 0.02 M TODGA in the organic phase, the distribution ratio of  $\text{Tf}_2\text{N}^-$  anions increases (i.e. the aqueous  $\text{Tf}_2\text{N}^-$  solubility decreases) with  $\text{HNO}_3$  concentration. The highest  $D$ -value of 43.7 is reached for 0.3 M  $\text{HNO}_3$ . A further increase of the aqueous nitric acid concentration leads to a decrease of  $D_{\text{Tf}_2\text{N}}$ .

The higher  $D_{\text{Tf}_2\text{N}}$  in the presence of TODGA in the organic phase can be explained by the extraction of  $\text{Tf}_2\text{N}^-$  anions with TODGA molecules (Fig. 2). However, the competitive uptake of nitric acid by TODGA molecules becomes predominant at high aqueous  $\text{HNO}_3$  concentration, leading to a decrease of  $\text{Tf}_2\text{N}^-$  extraction.

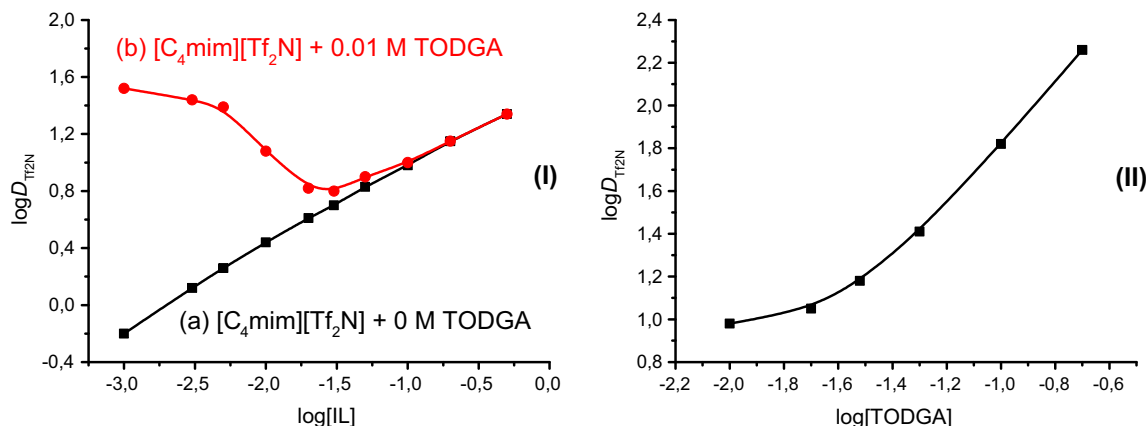
The distribution ratio of  $\text{Tf}_2\text{N}^-$  anions as a function of the initial  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  concentration in the organic phase was also determined for various TODGA concentrations, at fixed aqueous  $\text{HNO}_3$  concentration. When  $[\text{TODGA}] = 0$  M,  $D_{\text{Tf}_2\text{N}}$  increases (aqueous  $\text{Tf}_2\text{N}^-$  solubility decreases) with the increase of the  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  concentration in DCE (Fig. 3I, a). These data are consistent with Eq. (10). However, it can be seen that the dependence of the  $\text{Tf}_2\text{N}^-$  distribution ratio as a function of the IL concentration is more complex when TODGA is introduced in the organic phase (Fig. 3I, b). The addition of a large excess of TODGA over the IL (left region of Fig. 3I, b) leads to an increase of  $D_{\text{Tf}_2\text{N}}$ . This result can be

Table 1

Solvent extraction dependence and equilibrium constants for the liquid–liquid systems studied in the present work.

Moiety	Aqueous phase	Organic phase	Dependencies			Proposed extracted species	Equilibrium constant
			$\text{NO}_3^-$	L	$\text{Tf}_2\text{N}^-$		
TODGA	$\text{HNO}_3$	L	1, 2	–	–	$(\text{HNO}_3)_2\text{L}$ $(\text{HNO}_3)_2\text{L}$	$K_{\text{HNO}_3(1)} = 0.625$ $K_{\text{HNO}_3(2)} = 0.0566$
$\text{UO}_2^{2+}$	$\text{LiTf}_2\text{N}$	L	–	2	2	$\text{UO}_2(\text{L})_2(\text{Tf}_2\text{N})_2$	$\log K_{\text{ex}} = 12.5$
$\text{UO}_2^{2+}$	$[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$	L	–	1.8	2		$\log K_{\text{ex}} = 12.4$
$\text{UO}_2^{2+}$	$\text{HNO}_3$	L	2	1.6	–	$\text{UO}_2(\text{L})(\text{NO}_3)_2$ $\text{UO}_2(\text{L})_2(\text{NO}_3)_2$	$\log K_{\text{U}(1)} = 1.32$ $\log K_{\text{U}(2)} = 3.31$
$\text{UO}_2^{2+}$	$\text{HNO}_3$	L, IL	–	2	2	$\text{UO}_2(\text{L})_2(\text{Tf}_2\text{N})_2$	$\log K'_{\text{ex}} = 4.62$





**Fig. 3.** Effect of the  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  (I) and TODGA (II,  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  initial concentration in the organic phase is 0.1 M) concentration in 1,2-dichloroethane on the distribution ratio of  $\text{Tf}_2\text{N}^-$  anion. Aqueous phase: 3 M  $\text{HNO}_3$ . The solid lines are guide for the eye.

explained by the  $\text{Tf}_2\text{N}^-$  extraction from the aqueous acidic phase by TODGA molecules as  $\text{HTf}_2\text{N}:\text{TODGA}$  complexes. The effect of the TODGA presence on the  $D_{\text{Tf}_2\text{N}}$  values is smoothed with the further addition of  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  in the organic phase (Fig. 3I). A possible explanation might be the decrease of free, non-binding, extractant concentration in the organic phase due to  $\text{HTf}_2\text{N}$  extraction by TODGA.

In order to confirm this hypothesis, we investigated the IL anion partition as a function of the TODGA concentration, for fixed IL and  $\text{HNO}_3$  concentrations. As can be seen in Fig. 3II,  $D_{\text{Tf}_2\text{N}}$  rises proportionally with the increase of TODGA concentration. This confirms the  $\text{HTf}_2\text{N}$  extraction by TODGA.

To conclude, the TODGA presence in the organic phase considerably changes the distribution of the IL anion between the organic and aqueous acidic phases. This issue is caused by availability of TODGA to extract  $\text{HTf}_2\text{N}$  from the aqueous acidic phase, especially at low aqueous  $\text{HNO}_3$  concentrations. At high  $\text{HNO}_3$  concentration, the difference between the two liquid–liquid systems,  $\text{HNO}_3/\text{IL}/\text{DCE}$  and  $\text{HNO}_3/(\text{TODGA} + \text{IL})/\text{DCE}$ , is weak due to the competitive  $\text{HNO}_3$  uptake by TODGA molecules.

### 3.3. Extraction of Uranium(VI) with TODGA from neutral aqueous solutions

Let us focus first on a simplified extraction system without  $\text{HNO}_3$ :  $\text{U(VI)}/\text{TODGA}/\text{DCE}$ . In order to establish the role of the hydrophobic  $\text{Tf}_2\text{N}^-$  anions in the uranium(VI) extraction, the  $\text{LiTf}_2\text{N}$  salt and  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  ionic liquid were added to the aqueous phase. The absence of nitric acid makes easier the experimental data treatment because of there is no competition between the acids,  $\text{HNO}_3$  and  $\text{HTf}_2\text{N}$ , and the metal ion extraction with TODGA.

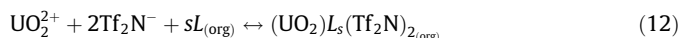
Fig. 4I presents the U(VI) extraction from water with TODGA/DCE solution as a function of the initial aqueous  $\text{LiTf}_2\text{N}$  concentration. In these experiments, no distribution of lithium was observed, within the experimental error. As can be seen, the distribution coefficient of uranium(VI) rises gradually with increasing  $\text{LiTf}_2\text{N}$  concentration. Table 2 shows that the extraction of U(VI) comes with a decrease of the equilibrium aqueous concentration of  $\text{Tf}_2\text{N}^-$  anions. These data suggest that the hydrophobic  $\text{Tf}_2\text{N}^-$  anions play a counterions role in the U(VI) extracted species.

From the mass balance, the following equation for  $\text{Tf}_2\text{N}^-$  anions concentration in the aqueous phase can be written as:

$$[\text{Tf}_2\text{N}]_{\text{init}} = [\text{Tf}_2\text{N}^-] + 2[\text{UO}_2^{2+}]_{(\text{org})} \quad (11)$$

where  $[\text{Tf}_2\text{N}^-]_{\text{init}}$  and  $[\text{Tf}_2\text{N}^-]$  are the initial and equilibrium  $\text{Tf}_2\text{N}^-$  concentrations in the aqueous phase and  $[\text{UO}_2^{2+}]_{(\text{org})}$  is the

concentration of extracted U(VI) species in the organic phase. The slope analysis allows us to determine the stoichiometry of the extracted uranyl species. The plot of  $\log D_{\text{U}}$  versus  $\log[\text{Tf}_2\text{N}^-]$  is a straight line with a slope of 2 (Fig. 4). This result suggests that the U(VI) extracted complexes are neutral  $(\text{UO}_2)(\text{L})_2(\text{Tf}_2\text{N})_2$  species (where L is TODGA molecule). Therefore, the extraction of U(VI) ions from neutral aqueous media into an organic diluent containing TODGA can be described by the following equilibrium:



It is assumed that, in our experimental conditions (initial aqueous concentration of U(VI) of  $1 \cdot 10^{-5} \text{ M}$ ), TODGA is present in 1,2-dichloroethane as a monomer and that a mononuclear complex of U(VI) is extracted. The corresponding extraction equilibrium constant,  $K_{\text{ex}}$ , can be written as:

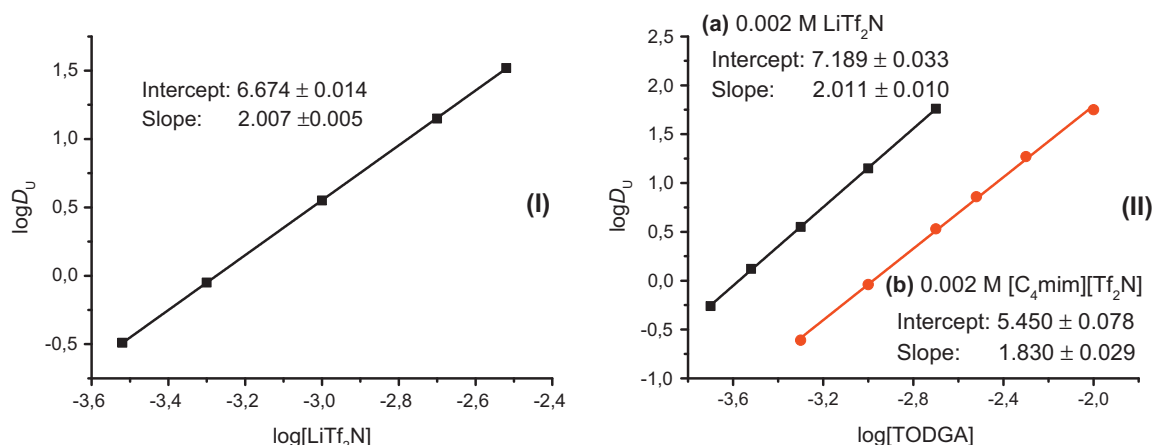
$$K_{\text{ex}} = \frac{[(\text{UO}_2)_s(\text{Tf}_2\text{N})_{2s}(\text{L})_s]_{(\text{org})}}{[\text{UO}_2^{2+}]^{-1} [\text{Tf}_2\text{N}^-]^2 [\text{L}]_{(\text{org})}^{-s}} \quad (13)$$

By introducing the expression for U(VI) distribution ratio,  $D_{\text{U}}$ , and assuming that  $[\text{L}]_0 = [\text{L}]_{(\text{org})}$  (where  $[\text{L}]_0$  and  $[\text{L}]_{(\text{org})}$  are the initial and equilibrium extractant concentrations in the organic phase) when  $[\text{L}]_0 \gg [\text{U}]_{\text{org}}$ , the logarithmic expression of Eq. (13) is:

$$\log D_{\text{U}} = \log K_{\text{ex}} + \log[\text{L}]_0 + 2\log[\text{Tf}_2\text{N}^-] \quad (14)$$

In order to determine the number of TODGA molecules in the  $(\text{UO}_2)_s(\text{Tf}_2\text{N})_{2s}$  extracted species, we also applied the slope method, i.e. we measured  $D_{\text{U}}$  values as a function of the initial concentration of TODGA in the organic phase, for a 0.002 M  $\text{LiTf}_2\text{N}$  concentration (see Fig. 4II, a). The plot  $\log D_{\text{U}}$  against  $\log[\text{L}]_0$  shows a slope of 2, which means that U(VI) is extracted with TODGA as disolvate species,  $(\text{UO}_2)(\text{L})_2(\text{Tf}_2\text{N})_2$ . Thus, the value of the conditional extraction constant, calculated from Eq. (14), is  $\log K_{\text{ex}} = 12.5 \pm 0.4$  (Table 1).

For comparison, the extraction of U(VI) with TODGA from aqueous neutral  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  solutions into 1,2-dichloroethane was also studied. The data in Fig. 4II, b reveal that at equal aqueous concentrations of  $\text{LiTf}_2\text{N}$  and  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  and for a given TODGA concentration, the  $D_{\text{U}}$  values are much higher in the system with added  $\text{LiTf}_2\text{N}$  salt. We suppose that this can be due to the decrease of the equilibrium concentration of  $\text{Tf}_2\text{N}^-$  anions in the aqueous phase. In fact, when  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  is dissolved in the aqueous phase, the extraction of U(VI) ions (Eq. (12)) is accompanied by the IL partition between the aqueous and organic phases described by Eq. (7). The relationship between the equilibrium and initial  $\text{Tf}_2\text{N}^-$  concentrations ( $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]_{\text{init}} = [\text{Tf}_2\text{N}^-]_{\text{init}}$ ) in the aqueous phase can be expressed as:



**Fig. 4.** Effect of the aqueous  $\text{LiTf}_2\text{N}$  concentration (I,  $[\text{TODGA}] = 0.001 \text{ M}$ ) and TODGA concentration in 1,2-dichloroethane (II) on the extraction of U(VI) with TODGA from aqueous solutions of  $\text{LiTf}_2\text{N}$  (I and II, a) and  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  (II, b). The solid line is a result of the least squares method approximation.

**Table 2**

Aqueous equilibrium concentration of  $\text{Tf}_2\text{N}^-$  anions as a function of initial concentration of uranyl ions in the aqueous phase.

$[\text{UO}_2^{2+}]_{\text{aq,init}}, \text{mM}$	$[\text{UO}_2^{2+}]_{\text{aq,eq}}, \text{mM}$	$[\text{Tf}_2\text{N}^-]_{\text{aq,eq}}, \text{mM}$
0.5	$9.6 \cdot 10^{-3}$	2.02
1.0	0.13	1.26
1.3	0.31	1.02
1.5	0.46	0.92
1.7	0.62	0.84

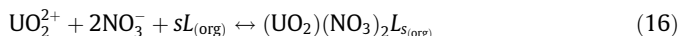
$$[\text{Tf}_2\text{N}^-] = [\text{Tf}_2\text{N}^-]_{\text{init}}(1 + K_{\text{RA}}[\text{Tf}_2\text{N}^-])^{-1} \quad (15)$$

The values of the conditional extraction constant for the U(VI) extraction with TODGA from neutral aqueous solutions containing  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  into DCE, calculated from experimental data in Fig. 4II using Eqs (14) and (15), is  $\log K_{\text{ex}} = 12.4 \pm 0.4$  (Table 1). Within experimental error,  $\log K_{\text{ex}}$  values for the U(VI) extraction from a neutral aqueous phase into a TODGA/DCE solution are equal whether  $\text{Tf}_2\text{N}^-$  are added as  $\text{LiTf}_2\text{N}$  or  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ . We can thus conclude that in both cases, U(VI) is extracted by TODGA into DCE from neutral aqueous solutions as the neutral  $(\text{UO}_2)(\text{TODGA})_2(\text{Tf}_2\text{N})_2$  species.

### 3.4. Extraction of Uranium(VI) with TODGA from $\text{HNO}_3$ solutions

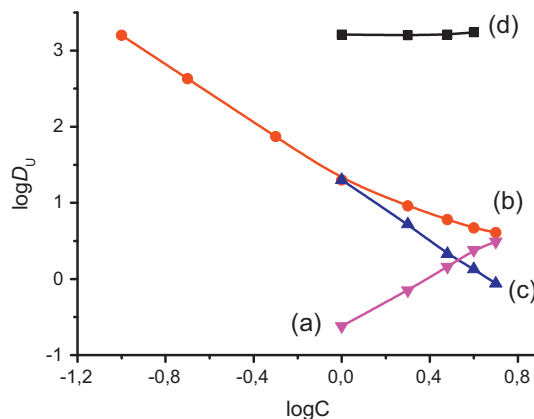
In the present part, we examine the U(VI) extraction from aqueous nitric acid solutions by TODGA into 1,2-dichloroethane, i.e. the traditional extraction system.

Fig. 5a presents the nitric acid dependence of the U(VI) extraction with 0.05 M TODGA. As can be seen,  $D_{\text{U}}$  values increase as the initial aqueous  $\text{HNO}_3$  concentration increases. This kind of acid dependence indicates that uranyl extraction proceeds via a solvation mechanism:

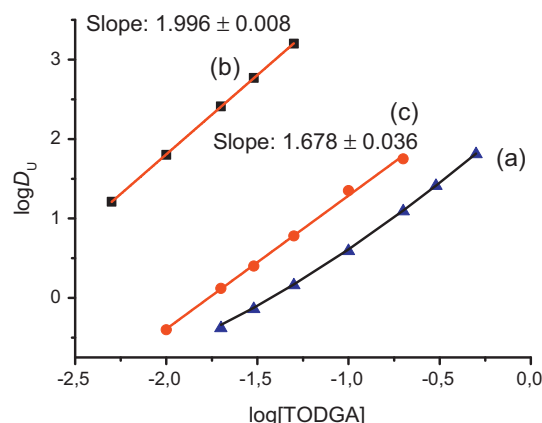


As it was discussed above, the significant nitric acid uptake by TODGA molecules for  $[\text{HNO}_3]_{\text{init}} > 5 \text{ M}$  results in a considerable decrease of the free extractant concentration in the organic phase. This leads to a weakening of U(VI) extractability for high aqueous  $\text{HNO}_3$  concentrations (Fig. 5a).

The effect of TODGA concentration on the U(VI) extraction was also studied at 3 M  $\text{HNO}_3$  (Fig. 6a). The plot of  $\log D_{\text{U}}$  versus  $\log[L]_{\text{o}}$  yields to a straight line with a slope of 1.6. This non-integer slope value can indicate the formation of a mixture of mono- and



**Fig. 5.** Effect of the  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_4\text{NO}_3$  concentrations in the aqueous phase on the extraction of uranium(VI) in: (a)  $\text{U(VI)}/\text{HNO}_3//0.05 \text{ M TODGA/DCE}$ ; (b)  $\text{U(VI)}/\text{HNO}_3//0.05 \text{ M TODGA} + 0.1 \text{ M } [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]/\text{DCE}$ ; (c)  $\text{U(VI)}/\text{HCl}/0.05 \text{ M TODGA/DCE}$ ; (d)  $\text{U(VI)}/\text{NH}_4\text{NO}_3//0.05 \text{ M TODGA/DCE}$ . The solid lines are guide for the eye only.



**Fig. 6.** Effect of the TODGA concentration in the organic phase on the extraction of U(VI) in: (a)  $\text{U(VI)}/3 \text{ M HNO}_3//\text{TODGA/DCE}$ ; (b)  $\text{U(VI)}/(0.1 \text{ M HNO}_3 + 3 \text{ M NH}_4\text{NO}_3)/(\text{TODGA} + 0.1 \text{ M } [\text{C}_4\text{mim}][\text{Tf}_2\text{N}])/ \text{DCE}$ ; (c)  $\text{U(VI)}/3 \text{ M HNO}_3/(\text{TODGA} + 0.1 \text{ M } [\text{C}_4\text{mim}][\text{Tf}_2\text{N}])/ \text{DCE}$ . The solid lines are the calculated values from Eq. (17) (a) and result of the least squares method approximation (b, c).

disolvate uranyl species,  $(\text{UO}_2)(\text{TODGA})(\text{NO}_3)_2$  and  $(\text{UO}_2)(\text{TODGA})_2(\text{NO}_3)_2$ . Thus, U(VI) extraction by TODGA into DCE from nitric acid media can be described as:

$$D_U = K_{U(1)}[\text{NO}_3^-]^2 \gamma_U^3 [L]_o f^{-1} + K_{U(2)}[\text{NO}_3^-]^2 \gamma_U^3 [L]_o^2 f^{-2} \quad (17)$$

where  $K_{U(1)}$  and  $K_{U(2)}$  are the extraction constants of the U(VI) mono- and disolvate,  $\gamma_U$  is the activity coefficient for  $\text{UO}_2(\text{NO}_3)_2$  in the aqueous phase taken from Ref. [59] and  $f$  is the coefficient which takes into account the interaction of TODGA with  $\text{HNO}_3$  from Eq. (6) ( $f = 1 + K_{\text{HNO}_3(1)}a + K_{\text{HNO}_3(2)}^2$ ). The values of U(VI) extraction constants, calculated from the experimental data in Fig. 6a using Eq. (17) by the nonlinear least squares method, are  $\log K_{U(1)} = 1.32 \pm 0.06$  and  $\log K_{U(2)} = 3.31 \pm 0.07$ . Thus, a good agreement between experimental and calculated data is obtained.

The mole fraction of extracted disolvate complexes,  $(\text{UO}_2)(\text{TODGA})_2(\text{NO}_3)_2$ , in the organic phase,  $\alpha_2$ , can be calculated from the equation:

$$\alpha_2 = K_{U(2)}[L]_o(K_{U(1)}f + K_{U(2)}[L]_o)^{-1} \quad (18)$$

From Fig. S3, it is obvious that both the increase of the initial TODGA concentration in the organic phase and the decrease of the aqueous  $\text{HNO}_3$  concentration lead to an increase of the mole fraction of extracted uranyl species as disolvates.

To explore the effect of hydrophobic  $\text{Tf}_2\text{N}^-$  anions on the U(VI) extraction behavior in this classical extraction system, we added  $\text{LiTf}_2\text{N}$  salt in the aqueous phase. The effect of the initial aqueous  $\text{HNO}_3$  concentration on the U(VI) extraction is shown in Fig. 7 for  $[\text{LiTf}_2\text{N}] = 0.01 \text{ M}$ . It can be seen that  $D_U$  values drop with the increase of the aqueous  $\text{HNO}_3$  concentration. This is probably caused by the TODGA molecules uptake by  $\text{HNO}_3$  (Eq. (1)) and  $\text{HTf}_2\text{N}$ , causing a decrease in the free  $\text{Tf}_2\text{N}^-$  and TODGA concentrations.

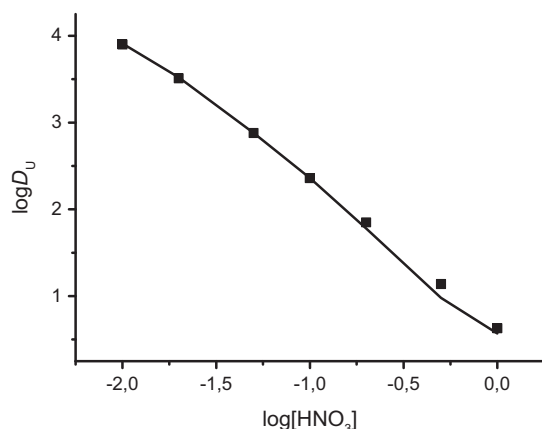
The initial TODGA concentration is equal to the sum of concentrations of extracted species:

$$[L]_o = [L]_{(\text{org})} + [(\text{HTf}_2\text{N})L]_{(\text{org})} + [(\text{HNO}_3)L]_{(\text{org})} + 2[(\text{UO}_2)(\text{Tf}_2\text{N})_2(L)_2]_{(\text{org})} \quad (19)$$

The equation above can be transformed into Eq. (20), when  $[(\text{UO}_2)(\text{Tf}_2\text{N})_2(L)_2]_{(\text{org})} \ll [L]_o$ :

$$[L]_o = [L]_{(\text{org})} + K_{\text{HTf}_2\text{N}}[L]_{(\text{org})}[\text{H}^+][\text{Tf}_2\text{N}^-] + K_{\text{HNO}_3}[L]_{(\text{org})}[\text{H}^+][\text{NO}_3^-] \\ = [L]_{(\text{org})}(1 + K_{\text{HTf}_2\text{N}}[\text{H}^+][\text{Tf}_2\text{N}^-] + K_{\text{HNO}_3}[\text{H}^+][\text{NO}_3^-]) \quad (20)$$

where  $K_{\text{HTf}_2\text{N}}$  and  $K_{\text{HNO}_3}$  are the  $\text{HTf}_2\text{N}$  and  $\text{HNO}_3$  conditional extraction constants. Hence, the relationship between  $D_U$  and the aqueous  $\text{HNO}_3$  concentration, for constant initial TODGA concentration and aqueous  $\text{LiTf}_2\text{N}$  concentration, can be written as:



**Fig. 7.** Effect of the initial  $\text{HNO}_3$  concentration in the aqueous phase containing 0.01 M  $\text{LiTf}_2\text{N}$  on the extraction of U(VI) with 0.01 M solutions of TODGA in 1,2-dichloroethane. The solid line is the calculated values from Eq. (22).

$$D_U = K_{\text{ex}}[\text{Tf}_2\text{N}^-]^2 [L]_o^2 (1 + K_{\text{HTf}_2\text{N}}[\text{H}^+][\text{Tf}_2\text{N}^-] + K_{\text{HNO}_3}[\text{H}^+][\text{NO}_3^-])^{-2} \quad (21)$$

Assuming that  $K_{\text{HTf}_2\text{N}}[\text{H}^+][\text{Tf}_2\text{N}^-] \gg K_{\text{HNO}_3}[\text{H}^+][\text{NO}_3^-]$ , the relationship between  $D_U$  and  $[\text{H}^+]$  concentration can be expressed as:

$$D_U = K_{\text{ex}}[\text{Tf}_2\text{N}^-]^2 [L]_o^2 (1 + K_{\text{HTf}_2\text{N}}[\text{H}^+][\text{Tf}_2\text{N}^-])^{-2} \quad (22)$$

We thus can calculate  $D_U$  in the  $[\text{HNO}_3]$  range from 0.01 to 1 M using the  $K_{\text{ex}}$  and  $K_{\text{HTf}_2\text{N}}$  values ( $K_{\text{HTf}_2\text{N}} = 14,100$  is taken from Ref. [36]). A satisfactory agreement between the calculated and experimental data is obtained (Fig. 7).

In summary, U(VI) is extracted with TODGA in DCE from aqueous nitric acid solutions as  $(\text{UO}_2)(\text{TODGA})(\text{NO}_3)_2$  and  $(\text{UO}_2)(\text{TODGA})_2(\text{NO}_3)_2$ , while the presence of  $\text{LiTf}_2\text{N}$  in the aqueous phase leads to the extraction of  $(\text{UO}_2)(\text{TODGA})_2(\text{Tf}_2\text{N})_2$  species (Table 1). In both cases the metal ion extraction occurs via a common solvation mechanism.

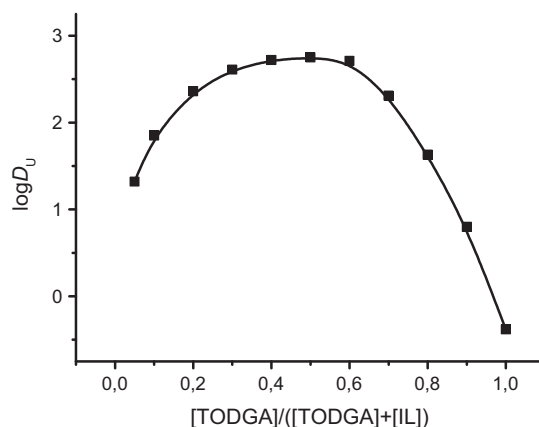
### 3.5. Extraction of Uranium(VI) with TODGA and $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ from $\text{HNO}_3$ solutions

Let us turn now to the most complex extraction system. Each phase is a three components solution: (i) the aqueous phase is composed of uranium(VI) dissolved in nitric acid; (ii) the organic phase is composed of TODGA and IL dissolved in DCE. Equilibria reactions such as metal distribution, nitric acid uptake with TODGA and distribution of hydrophobic IL anions should be considered.

In order to evidence a possible synergistic effect between the neutral organic ligand and the ionic liquid, the molar fraction of TODGA in  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ , ( $R = [\text{TODGA}]/([\text{TODGA}] + [\text{IL}])$ ), ranges from 0.05 to 1. The total concentration of these two organic solutes in DCE,  $[\text{TODGA} + \text{IL}]$ , was kept constant at a value of 0.1 M.

As can be seen in Fig. 8, the addition of  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  to TODGA/DCE solutions leads to a significant enhancement of U(VI) extraction. This graph can be divided in three sections. In the first one, from  $R = 0.05$  to 0.4 ( $[\text{IL}] > [\text{TODGA}]$ ), U(VI) extraction increases smoothly as the  $[\text{IL}]$  decreases. It should be noted that in the absence of TODGA,  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  alone does not extract U(VI) under the considered chemical conditions ( $\log D_U < -2$ ). Then, between  $R = 0.4$  and 0.6,  $D_U$  remains high and almost constant. Finally, above  $R = 0.6$  ( $[\text{TODGA}] > [\text{IL}]$ )  $D_U$  decreases as the  $[\text{TODGA}]$  increases.

The most probable explanation for the synergistic effect observed between TODGA and IL is the participation of IL anions in the formation of extracted uranium(VI) species. Indeed, the



**Fig. 8.** Extraction of U(VI) with mixtures of TODGA and  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  in 1,2-dichloroethane from 1 M  $\text{NH}_4\text{NO}_3$  aqueous solutions containing 0.1 M  $\text{HNO}_3$ .  $([\text{TODGA}] + [\text{C}_4\text{mim}][\text{Tf}_2\text{N}]) = 0.1 \text{ M}$ . The solid line is guide for the eye.



uranium(VI) complexes  $\text{UO}_2(\text{L})_s(\text{Tf}_2\text{N})_x$  are more hydrophobic than those formed with nitrate ions.

In synergistic systems, a plot of metal  $D$  values versus the mole fraction of each extractant agent in a mixture for a constant total concentration exhibits a maximum corresponding to the composition of a synergistic complex. In our case, the maximum value of  $D_{\text{U}}$  is observed for a TODGA mole fraction of 0.5 (Fig. 8), which is consistent with 1:1 M ratio of TODGA and  $\text{Tf}_2\text{N}^-$  anions in the extracted U(VI) complex.

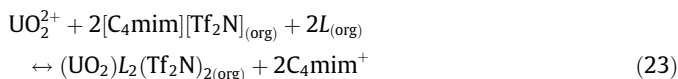
The variation of  $D_{\text{U}}$  as a function of the TODGA concentration in the organic phase containing 0.1 M  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  is shown in Fig. 6b and c. The variation of  $\log D_{\text{U}}$  vs.  $\log [\text{L}]_0$  is linear with a slope of 2 when  $[\text{H}^+] = 0.1 \text{ M}$  (Fig. 6b). This means that in low acidic aqueous phase, U(VI) is extracted with TODGA as disolvate species, i.e. two TODGA molecules are required to extract one uranyl ion in DCE. On the other hand, a non-integer slope is observed for the U (VI) extraction from 3 M  $\text{HNO}_3$  solutions (Fig. 6c). This issue can result from the formation of a mixture of mono- and disolvate extracted species (1:1 and 1:2). This may probably be explained by the competitive interactions of TODGA with  $\text{HNO}_3$  at high acidity and the decrease of  $D_{\text{Tf}_2\text{N}}$  (Fig. 2).

The effect of the  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  organic phase concentration on the U(VI) extraction is shown in Fig. 9. The plot of  $\log D_{\text{U}}$  versus  $\log [\text{IL}]$  is linear with a slope of 2 when  $[\text{H}^+] = 0.1 \text{ M}$  (Fig. 9a). This result supports the idea that the extraction mechanism at work here is similar to the one occurring for the  $\text{LiTf}_2\text{N}/\text{TODGA}/\text{DCE}$  system, the extracted species  $\text{UO}_2(\text{TODGA})_2(\text{Tf}_2\text{N})_2$  being also the same. According to these data, we can infer that the  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  ionic liquid acts as a source of hydrophobic anions in the synergistic extraction system. For U(VI) extraction from 1 M  $\text{HNO}_3$  aqueous solutions, the plot of  $\log D_{\text{U}}$  versus  $\log [\text{IL}]$  is linear with a slope of 2 when  $[\text{IL}] < 0.03 \text{ M}$  (Fig. 9b). This slope diminishes with a further increase of IL concentration. It can be due to the decrease of the free extractant concentration in the organic phase, as a result of the  $\text{HTf}_2\text{N}$  uptake by TODGA molecules.

In order to determine the nature of the extracted metallic species, we investigated the extraction of U(VI) with mixtures of TODGA and  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  into 1,2-dichloroethane from  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_4\text{NO}_3$  aqueous solutions (Fig. 5).  $D_{\text{U}}$  values fall with the increase of aqueous  $\text{HNO}_3$  or  $\text{HCl}$  concentration (Fig. 5b and c) as in  $\text{U(VI)}/(\text{H}_2\text{O} + \text{LiTf}_2\text{N})/\text{TODGA}/\text{DCE}$  (Fig. 7), but not when the aqueous  $\text{NO}_3^-$  concentration increases (Fig. 5d) for a given acidity. Thus, the IL synergistic effect becomes smaller when the aqueous  $\text{HNO}_3$  concentration increases (Fig. 5). This can be explained by the extraction of both  $(\text{UO}_2)(\text{TODGA})_s(\text{Tf}_2\text{N})_2$  and  $(\text{UO}_2)(\text{TODGA})_s(\text{NO}_3)_2$  complexes at high aqueous nitric acid con-

centration. The extraction of mixed  $(\text{UO}_2)(\text{TODGA})_s(\text{Tf}_2\text{N})(\text{NO}_3)$  species is also possible.

The extraction of U(VI) ions from aqueous acidic media into organic phases containing TODGA and  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  can be described on the base of the following equilibrium:



The corresponding extraction equilibrium constant,  $K'_{\text{ex}}$  is:

$$K'_{\text{ex}} = \frac{[\text{UO}_2\text{L}_2(\text{Tf}_2\text{N})_{2(\text{org})}][\text{C}_4\text{mim}^+]^2}{[\text{UO}_2^{2+}][\text{IL}]_{(\text{org})}^{-2}[\text{L}]_{(\text{org})}^{-2}} = D_{\text{U}}[\text{C}_4\text{mim}^+]^2[\text{IL}]_{(\text{org})}^{-2}[\text{L}]_{(\text{org})}^{-2} \quad (24)$$

It is necessary to note that the concentration of  $\text{C}_4\text{mim}^+$  in the equilibrium aqueous phase is not equal to twice the U(VI) concentration in the organic phase in the equilibrium (Eq. (23)). It is determined by the IL solubility in the aqueous phase under given chemical conditions. Introducing the equation for the IL partition between the organic diluent and the aqueous solution (Eqs. (7) and (24)) becomes:

$$K'_{\text{ex}} = D_{\text{U}}[\text{Tf}_2\text{N}^-]^{-2}[\text{L}]_{(\text{org})}^{-2}K_{\text{RA}}^{-2} \quad (25)$$

and taking into account the interaction of TODGA with  $\text{HTf}_2\text{N}$  and  $\text{HNO}_3$ :

$$K'_{\text{ex}} = D_{\text{U}}[\text{Tf}_2\text{N}^-]^{-2}[\text{L}]_{(\text{org})}^{-2}K_{\text{RA}}^{-2}(1 + K_{\text{HTf}_2\text{N}}[\text{H}^+][\text{Tf}_2\text{N}^-] + K_{\text{HNO}_3}[\text{H}^+][\text{NO}_3^-])^2 \quad (26)$$

Although the nitric acid dependence of the uranium(VI) extraction is completely different for U(VI)/ $\text{HNO}_3$ /(TODGA+ $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ )/DCE and U(VI)/ $\text{HNO}_3$ /(TODGA/DCE extraction systems (Fig. 5), it can be explained by a solvation mechanism for both extraction systems (Eqs (16) and (23)).

The relationship between  $K'_{\text{ex}}$  and  $K_{\text{ex}}$  can be expressed as:

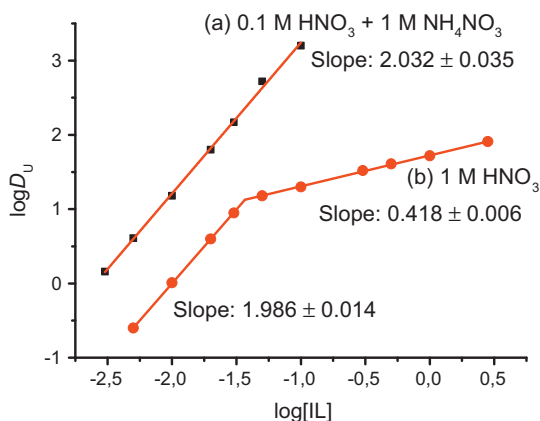
$$K'_{\text{ex}} = K_{\text{ex}}K_{\text{RA}}^{-2} \quad (27)$$

The Eq. (27) shows that the increase of  $K_{\text{RA}}$  for ILs with long alkyl chain attached to  $\text{C}_n\text{mim}^+$  cation should result in a decrease of  $K'_{\text{ex}}$ , i.e. in a decrease of the U(VI) extractability and a weakening of the synergistic effect. Actually, in the case of U(VI) extraction from 0.1 M  $\text{HNO}_3$  solutions with 0.05 M TODGA into 1,2-dichloroethane containing 0.1 M of  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ , [di-2-ethylhexyl-mim][ $\text{Tf}_2\text{N}$ ] or  $[\text{C}_{12}\text{mim}][\text{Tf}_2\text{N}]$ ,  $\log D_{\text{U}}$  values were measured as 3.2, 1.35 and 0.14, respectively.

The comparison of extraction constant values for  $(\text{UO}_2)_2\text{L}_2(\text{Tf}_2\text{N})_2$  ( $\log K_{\text{ex}} = 12.42$ ) and  $(\text{UO}_2)_2\text{L}_2(\text{NO}_3)_2$  ( $\log K_{\text{U(2)}} = 3.31$ ) complexes with those for  $(\text{HTf}_2\text{N})\cdot\text{TODGA}$  ( $\log K_{\text{HTf}_2\text{N}} = 4.15$  [36]) and  $(\text{HNO}_3)\cdot\text{TODGA}$  ( $\log K_{\text{HNO}_3(1)} = -0.204$ ) shows that the extraction ability of TODGA towards U(VI) and towards acids follows the increase of the counter-ions hydrophobicity (Table 1). Therefore, we conclude that the observed synergistic effect is due to an increase of the U (VI) extracted complexes hydrophobicity.

The experimental extraction data of the present study do not allow us to characterize the exact structure (the nature and the numbers of ligands) of the uranyl extracted species. Further spectroscopic and modelling studies will provide helpful information about the postulated metal extracted complexes and the extraction mechanism.

To evaluate the performance of synergistic extraction system for other metals, the distribution of Fe(III), Cr(III), Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Sr(II), with 0.05 M TODGA and 0.1 M  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  in DCE from 1 M  $\text{HNO}_3$  solutions was determined. A negligible extraction of all metals (M) except Pb (II) and Sr(II) was observed as  $D_{\text{M}}$  values are lower than 0.01. For Pb(II) and Sr(II),  $D$  values are 2.02 and 2.20, respectively. The



**Fig. 9.** Effect of the  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  concentration in 1,2-dichloroethane containing 0.05 M TODGA on the extraction of U(VI) from 1 M  $\text{NH}_4\text{NO}_3$  containing 0.1 M  $\text{HNO}_3$  (a) and 1 M  $\text{HNO}_3$  (b) solutions.

**Table 3**

Distribution ratio of U(VI) ( $[U(VI)]_{aq, init} = 5 \cdot 10^{-6}$  M) and separation factors  $D_U/D_M$  ( $M = Fe(III), Cr(III), Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II)$  and  $Sr(II)$ ,  $[M]_{aq, init} = 5 \cdot 10^{-4}$  M). Organic phase: 0.05 M TODGA and 0.1 M  $[C_4mim][Tf_2N]$  in DCE. Aqueous phase: 1 M  $HNO_3$ .

$D_{U(VI)}$	$D_{U(VI)}/D_M$ $M = Fe(III), Cr(III), Al(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)$	$D_{U(VI)}/D_{Pb(II)}$	$D_{U(VI)}/D_{Sr(II)}$
18.1	>1800	8.96	8.23

separation factor values ( $D_U/D_M$ ) for the metals ions are: >1800 (U(VI)/M), 8.96 (U(VI)/Pb(II)) and 8.23 (U(VI)/Sr(II)) (Table 3). Thus, the proposed synergistic system co-using TODGA and  $[C_4mim][Tf_2N]$  can be used for an efficient separation of U(VI) from several metal ions in aqueous nitric acid media.

#### 4. Conclusion

The addition of a small amount of a hydrophobic ionic liquid to an organic phase containing a neutral organic extractant is a way to do a more efficient liquid–liquid extraction of metal ions. The present study demonstrates for the first time a considerable synergistic effect for U(VI) extraction from an aqueous nitric acid media into a 1,2-dichloroethane containing TODGA and  $[C_4mim][Tf_2N]$ . This effect is associated with the high hydrophobicity of the IL anions, which participate in the formation of U(VI) extracted species. The partition of  $Tf_2N^-$  anions between the organic and aqueous phases is the major factor governing the extractability of U(VI) ions in the TODGA – IL synergistic system. We show that taking this feature into account, the extraction of U(VI) with mixtures of TODGA and  $[C_4mim][Tf_2N]$  in 1,2-dichloroethane can be described as a common solvation extraction mechanism like U(VI) extraction from  $HNO_3$  solutions with only TODGA as an extractant. The proposed synergistic system co-using TODGA and  $[C_4mim][Tf_2N]$  can be used for an efficient separation of U(VI) from several metal ions in aqueous nitric acid media.

Further spectroscopic and modelling studies on the extraction of U(VI) with TODGA in the presence of hydrophobic ionic liquids into an organic diluent will allow us to confirm the postulated extracted complexes and the mechanism of extraction.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2016.03.004>.

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