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# New Ionic Liquid Based on the CMPO Pattern for the Sequential Extraction of U(VI), Am(III) and Eu(III)

Daria Ternova<sup>1,2,3</sup> · Ali Ouadi<sup>1,2</sup> · Valérie Mazan<sup>1,2</sup> · Sylvia Georg<sup>1,2</sup> · Maria Boltoeva<sup>1,2</sup> · Vitaly Kalchenko<sup>3</sup> · Stanislas Miroshnichenko<sup>3</sup> · Isabelle Billard<sup>4,5</sup> · Clotilde Gaillard<sup>6</sup>

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**Abstract** Extraction of U(VI), Eu(III) and Am(III) has been performed from acidic aqueous solutions (HNO<sub>3</sub>, HClO<sub>4</sub>) into the ionic liquid [C<sub>4</sub>mim][Tf<sub>2</sub>N] in which a new extracting task-specific ionic liquid, based on the CMPO unit {namely 1-[3-[2-(octylphenylphosphoryl)acetamido]propyl]-3-methyl-1H-imidazol-3-ium bis(trifluoromethane)sulfonamide, hereafter noted OctPh-CMPO-IL}, was dissolved at low concentration (0.01 mol·L<sup>-1</sup>). EXAFS and UV-Vis spectroscopy measurements were performed to characterize the extracted species. The extraction of U(VI) is more efficient than the extraction of trivalent Am and Eu using this TSIL, for both acids and their concentration range. We obtained evidence that the metal ions are extracted as a solvate (UO<sub>2</sub>(OctPh-CMPO-IL)<sub>3</sub>) by a cation exchange mechanism. Nitrate or perchlorate ions do not play a direct role in the extraction by being part of the extracted complexes, but the replacement of nitric acid for perchloric acid entails a drop in the selectivity between U and Eu. However, our TSIL allows a sequential separation of U(VI) and Eu/Am(III) using the same HNO<sub>3</sub> concentration and same nature of the organic phase, just by changing the ligand concentration.

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**Keywords** Ionic liquids · Solvent extraction · Uranyl · Europium(III) · Americium(III) · Carbamoylmethylphosphine oxide

## 1 Introduction

One of the first steps of spent nuclear fuel reprocessing is the extraction of U and Pu from the fission products and from the transuranic actinides and lanthanides through the PUREX flow-sheet. To this purpose, TBP (tributyl phosphate) is the extractant used, diluted in a hydrocarbon phase (kerosene, dodecane) at  $1.1 \text{ mol}\cdot\text{L}^{-1}$ . Then, the TRUEX process aims at an extraction of the transuranium elements (TRU) and lanthanide fission products remaining in the aqueous solution, using a mixture of  $0.2 \text{ mol}\cdot\text{L}^{-1}$  CMPO +  $1.2 \text{ mol}\cdot\text{L}^{-1}$  TBP [1]. In this part of the waste treatment, TBP is added as a diluent modifier in order to minimize third phase formation but it has no direct role in the TRU extraction. Consequently, the PUREX–TRUEX waste treatment is based on two different extractant mixtures, although one chemical, namely TBP, is common to both PUREX and TRUEX.

Ionic liquids (ILs) [2] have enabled many achievements in various areas such as carbon dioxide capture [3], lubricants [4], enzymatic reactions [5], polymerization [6] and pharmaceutical research [7]. In the specific case of metal extraction and separation [8–10], most of the time IL-based extraction systems (i.e., systems where the volatile organic solvent is replaced entirely by an IL, all other compounds being identical) exhibit superior extraction efficiency in comparison to traditional solvent extraction systems, as exemplified in the famous paper of Dai and co-workers [11]. It is now commonly accepted that extraction into such IL phases occurs, in most cases, through ion exchange, while some systems have also shown that extraction through ion-pairing may occur [12, 13]. The extraction of U(VI) by TBP diluted in ILs was thus examined and a different extraction mechanism was evidenced, as compared to the dodecane case [14]. However, the use of ILs instead of dodecane cannot be considered as a drastic improvement of U(VI) extraction, because there is no significant enhancement of the maximum U(VI) distribution ratio as compared to dodecane, excepting at very low acid concentration. Actually, in  $1.1 \text{ mol}\cdot\text{L}^{-1}$  TBP/dodecane, the maximum U(VI) distribution ratio equals ca. 20 for  $\text{HNO}_3 \sim 4 \text{ mol}\cdot\text{L}^{-1}$ , while for  $1.1 \text{ mol}\cdot\text{L}^{-1}$  TBP/[C<sub>4</sub>mim][Tf<sub>2</sub>N] the maximum distribution ratio reaches ca. 20 at  $\text{HNO}_3 = 6.5 \text{ mol}\cdot\text{L}^{-1}$  [15]. Similarly, keeping  $1.1 \text{ mol}\cdot\text{L}^{-1}$  TBP and changing to ammonium-based ILs does not give higher U(VI) distribution ratios, except in one case, while the nitric acid concentration for the maximum extraction can be significantly decreased from ca.  $4 \text{ mol}\cdot\text{L}^{-1}$  down to  $0.01 \text{ mol}\cdot\text{L}^{-1}$ , depending on the IL under study [16].

Turning to IL-based systems mimicking the TRUEX process, only two papers, from the same group [17, 18], have examined the extraction of Am(III) and Eu(III) using  $0.2 \text{ mol}\cdot\text{L}^{-1}$  CMPO +  $1.2 \text{ mol}\cdot\text{L}^{-1}$  TBP in [C<sub>4</sub>mim][Tf<sub>2</sub>N]. This limited set of data evidences a significant increase in  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  as compared to dodecane, but the most important point is that in [C<sub>4</sub>mim][Tf<sub>2</sub>N] adding TBP to CMPO leads to a decrease in the  $D_{\text{Eu}}$  values. Actually, it appears that replacing molecular solvents by this IL eliminates the third phase formation problem and that addition of TBP to the extraction mixture reduces the distribution ratio [17]. Therefore, other extraction experiments have been performed for U, Am and Eu using CMPO in [C<sub>4</sub>mim][Tf<sub>2</sub>N] in the absence of TBP [19]. As compared to the traditional TRUEX performances, higher extraction distribution ratios for U, Am and Eu have been obtained even with CMPO concentrations lower than  $0.2 \text{ mol}\cdot\text{L}^{-1}$ . This is

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very different from the IL homologue of the PUREX process and implies that the benefits that ILs can bring in terms of distribution ratio depend on the choice of the extractant.

The so called task-specific ionic liquids (TSILs) incorporate in their cations [20] and/or anions [21] a metal-complexing fragment and may be used as a replacement of the usual molecular extracting agents. This application is considered to be a further development in the evolution of IL-based metal extraction and separation strategy [22] and several papers have highlighted the benefits that TSILs bring to that field [23–25]. In particular, the extraction properties of trialkylphosphate derivatives of tetraalkylammonium cations bearing  $\text{Tf}_2\text{N}^-$  as a counter ion were reported. Such TSILs achieved distribution ratios for U(VI) two orders of magnitude higher than TBP in  $[\text{Me}_3\text{BuN}][\text{Tf}_2\text{N}]$  IL under the conditions of the PUREX process [26]. In the particular case of a TRUEX surrogate, to the best of our knowledge, only one study has appeared with a specific TSIL bearing the CMPO pattern, dissolved in  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  and in the absence of TBP [27]. However, comparisons with the traditional TRUEX extraction values are difficult because the TSIL-CMPO concentration is different ( $0.1 \text{ mol}\cdot\text{L}^{-1}$ ). Another functionalized CMPO ionic liquid (based on a  $[\text{C}_{14}\text{mim}][\text{PF}_6]$  pattern) was used by Turanov et al. [28] to extract uranium(VI) and Ln(III) in dichloroethane. In this case, the TSIL-CMPO was more efficient than CMPO, but to the detriment of the U/Eu selectivity.

As a conclusion of this brief literature review (see Table 1 for references and distribution ratios, chemical conditions and other information of relevance), it appears that the IL choice is also an important parameter. Beneficial aspects of the use of ILs (either as solvent or extractants) include higher distribution ratios, possibly at lower extractant concentration, changes in the acid concentration for maximizing the distribution ratio and reducing the number of additives.

In order to bring further insights into this question, we have been searching for an IL-based system capable of valuable U, Eu and Am extraction performances depending on acidic conditions. To this aim, and on the basis of the literature review discussed above, we focused on the CMPO related ILs and have synthesized a new CMPO based task-specific IL {1-[3-[2-(octylphenylphosphoryl)acetamido]propyl]-3-methyl-1H-imidazol-3-ium bis(trifluoromethane)sulfonimide, hereafter denoted OctPh-CMPO-IL} and tested its extraction ability towards U(VI), Am(III) and Eu(III) in  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ . The change in the nature of the metal and hence in ionic charge is expected to have important effects on their complexation in the IL phase [29] and on the extraction efficiency of the OctPh-CMPO-IL moiety. To gain more insights into the role of acid in the separation, we have also investigated a change in the aqueous phase composition, by use of either nitric or perchloric acid. Such a change is not trivial as it induces dramatic variations of the complexation constants between the metallic ion and the counter-anion of the acid in the aqueous phase [30], differences in the mutual solubilities of water, IL and acid [31], and finally possible changes of the complexation ability in the IL phase [32, 33].

## 2 Experimental

### 2.1 Chemicals

The ionic liquids 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide,  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  (99.5% purity), and 1-methyl-3-butylimidazolium chloride,  $[\text{C}_4\text{mim}][\text{Cl}]$

**Table 1** Literature data on the extraction of U(VI), Am(III) and Eu(III) using CMPO or FIL-CMPO extractants

Ligand	Extracting system	$D_U$	$D_{Am}$	$D_{Eu}$	SF U/Eu	References	
CMPO	0.2 mol·L <sup>-1</sup> CMPO + 1.2 mol·L <sup>-1</sup> TBP/dodecane	150	15			Mathur et al. [46]	
				22.6	15	Rout et al. [17, 18]	
					100	Sengupta et al. [51]	
		HCl 3 mol·L <sup>-1</sup> //0.2 mol·L <sup>-1</sup> CMPO + 1.2 mol·L <sup>-1</sup> TBP/dodecane		0			Sengupta et al. [52]
		0.2 mol·L <sup>-1</sup> CMPO + 10% isodecanol/dodecane	20	6		3.3	Sengupta et al. [53]
		0.05 mol·L <sup>-1</sup> CMPO/dichloroethane	72		0.44	164	Turanov et al. [28]
		0.05 mol·L <sup>-1</sup> CMPO/[C <sub>4</sub> mim][Tf <sub>2</sub> N]			643		Rout et al. [17]
		0.1 mol·L <sup>-1</sup> CMPO/[C <sub>4</sub> mim][Tf <sub>2</sub> N]	53	364	172	0.3	Mohapatra et al. [27]
		0.2 mol·L <sup>-1</sup> CMPO/[C <sub>4</sub> mim][Tf <sub>2</sub> N]				1142	Rout et al. [18]
		0.005 mol·L <sup>-1</sup> CMPO/[C <sub>4</sub> mim][Tf <sub>2</sub> N]	0.3				Sun et al. [19]
		0.03 mol·L <sup>-1</sup> CMPO/[C <sub>4</sub> mim][Tf <sub>2</sub> N]	30				Sun et al. [19]
		0.2 mol·L <sup>-1</sup> CMPO + 1.2 mol·L <sup>-1</sup> TBP/[C <sub>4</sub> mim][Tf <sub>2</sub> N]		905	352		Rout et al. [17, 18]
		0.05 mol·L <sup>-1</sup> CMPO + 1.2 mol·L <sup>-1</sup> TBP/[C <sub>4</sub> mim][Tf <sub>2</sub> N]		27			Rout et al. [17]
		0.02 mol·L <sup>-1</sup> CMPO + 1.2 mol·L <sup>-1</sup> TBP/[C <sub>4</sub> mim][Tf <sub>2</sub> N]		2.2			Rout et al. [17]
FIL-CMPO	0.1 mol·L <sup>-1</sup> TSIL-CMPO/[C <sub>4</sub> mim][Tf <sub>2</sub> N]	26.5	42	30	0.9	Mohapatra et al. [27]	
	0.05 mol·L <sup>-1</sup> TSIL-CMPO/dichloroethane	33		1.4	23.4	Turanov et al. [28]	
	0.01 mol·L <sup>-1</sup> OctPh-CMPO-IL/[C <sub>4</sub> mim][Tf <sub>2</sub> N]	70	0.18	0.18	390	This work	
	HClO <sub>4</sub> 3 mol·L <sup>-1</sup> //0.01 mol·L <sup>-1</sup> OctPh-CMPO-IL/[C <sub>4</sub> mim][Tf <sub>2</sub> N]	120		0.7	171	This work	

Data are given for 3 mol·L<sup>-1</sup> HNO<sub>3</sub> aqueous phase, unless specified (SF = separation factor)

(98% mass purity), were purchased from Solvionic (France). Nitric and perchloric acids were from Merck and Prolabo, respectively, and are of analytical grade.

CMPO (octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide) (98% purity) was purchased from Chemos GmbH (Germany). Dihydrated sodium citrate (99%) was purchased from Merck, and sodium trifluoroacetate (98%) was obtained from Alfa Aesar.

Uranium was introduced as either its UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or UO<sub>2</sub>(Tf<sub>2</sub>N)<sub>2</sub> salt, (Tf<sub>2</sub>N<sup>-</sup> stands for (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>), with initial aqueous concentration 1.2 × 10<sup>-5</sup> mol·L<sup>-1</sup> (HNO<sub>3</sub>) or 1.9 × 10<sup>-5</sup> mol·L<sup>-1</sup> (HClO<sub>4</sub>). Similarly, europium was introduced as its Eu(III) nitrate/Tf<sub>2</sub>N<sup>-</sup> salt, at an initial concentration of 5.4 × 10<sup>-5</sup> mol·L<sup>-1</sup> (HNO<sub>3</sub>) or 3.5 × 10<sup>-5</sup> mol·L<sup>-1</sup> (HClO<sub>4</sub>). The <sup>241</sup>Am(III) solution was prepared from an acidic aqueous solution [HNO<sub>3</sub>] = 1 mol·L<sup>-1</sup>, the final Am(III) concentration was about 10<sup>-7</sup> mol·L<sup>-1</sup>. Owing to

the very high nitrate concentration in the Am(III) stock solution, it is not possible to prepare any Am(III) aqueous phase without a large  $\text{NO}_3^-/\text{Am(III)}$  ratio, therefore no study could be made in perchloric acid solution free of nitrate ions.

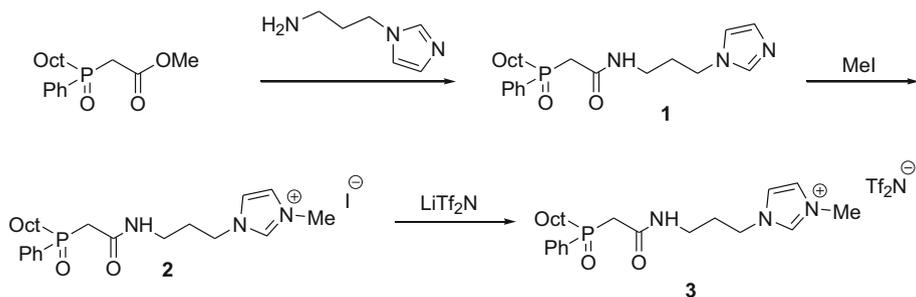
## 2.2 Synthesis of OctPh-CMPO Ionic Liquid

The procedure for the synthesis of the OctPh-CMPO ionic liquid, further denoted as OctPh-CMPO-IL, and the structure of the precursors are summarized in Scheme 1. Briefly, the key substance 2-(octylphenylphosphinyl)-*N*-[3-(1*H*-imidazol-1-yl)propyl]-acetamide **1** was obtained through acylation of 1*H*-imidazol-1-propylamine with the methyl ester of (octylphenylphosphinyl) acetic acid (ratio of reagents 1:2, 105 °C, 72 h, vacuum sealed ampoule). Then imidazole **1** was methylated with iodomethane (reagents ratio 1:1.5 in dichloromethane solution, room temperature, 12 h). Thus, iodide of octylphenyl-*N*-[3-(1*H*-methylimidazoliumpropyl)]carbamoylmethylphosphine oxide **2** was obtained in quantitative yield. The corresponding OctPh-CMPO-IL **3** (yield 70%) was synthesized by reacting **2** with  $\text{LiTf}_2\text{N}$  in aqueous solution followed by extraction with chloroform.

$^1\text{H}$  NMR spectra were recorded using a Bruker AC-300 spectrometer,  $^{31}\text{P}$  NMR was recorded using a Bruker Avance series 400 MHz spectrometer.

### 2.2.1 2-(Octylphenylphosphinyl)-*N*-[3-(1*H*-imidazol-1-yl)propyl]-acetamide **1**

A mixture of 2-(octylphenylphosphinyl)-acetic acid methyl ester (10 g, 0.0322 mol) and 1*H*-imidazol-1-propylamine (7.7 mL, 0.0644 mol) was heated in a closed Pyrex ampule at 105 °C for 72 h. The ampule was opened and the solvent was removed under vacuum. The viscous yellow residue was recrystallized from hexane to give the amide as a white solid, m.p. 47–49 °C (yield 10 g, 77.5%).  $^{31}\text{P}$  NMR (400.131 MHz,  $\text{CDCl}_3$ ):  $\delta$  38.19;  $^1\text{H}$  NMR (300.130 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.84 (t, 3H,  $^3J_{\text{H-H}} = 7.0$  Hz,  $\text{CH}_3$ ), 1.21–1.61 (m, 12H,  $\text{CH}_2$ ), 1.83 (q, 2H,  $^3J_{\text{H-H}} = 6.6$  Hz  $\text{CH}_2\text{-CH}_2\text{-NHC(O)}$ ), 1.87–2.18 (m, 2H,  $\text{P-CH}_2\text{-CH}_2$ ), 3.11 (d, 2H,  $\text{PCH}_2$ ,  $^2J_{\text{P-H}} = 12.1$  Hz); 3.29 (qv, 2H,  $^3J_{\text{H-H}} = 6.4$  Hz,  $\text{CH}_2\text{-NH-C(O)}$ ), 3.84 (t, 2H,  $J$  7.15 Hz,  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-NHC(O)}$ ), 6.87 (s, 1H,  $\text{C}^5\text{H}$  in Im); 6.91 (s, 1H,  $\text{C}^4\text{H}$  in Im); 7.03 (s, 1H,  $\text{NH}$ ); 7.45 (s, 1H,  $\text{N=CH-N}$ ); 7.47–7.77 (m, 5H,  $\text{C}_6\text{H}_5\text{P}$ ).



**Scheme 1** Synthesis of OctPh-CMPO-IL

### 2.2.2 1-[3-[2-(Octylphenylphosphoryl)acetamido]propyl]-3-methyl-1H-imidazol-3-ium bis(trifluoromethane)sulfonimide **3**

To a solution of 2-(octylphenylphosphinyl)-*N*-[3-(1H-imidazol-1-yl)propyl]-acetamide **1** (3.5 g, 8.67 mmol) in dichloromethane (20 mL) the iodomethane (1.85 g, 0.013 mol) was added at room temperature. The mixture was stirred at room temperature for 12 h. Then the volatile compounds were evaporated under vacuum and the resulting oil was washed with dry Et<sub>2</sub>O (twice, 15 mL). The residual ether was removed under reduced pressure. The viscous compound **2** (yield 4.73 g, 100%) was used for the next stage without purification.

To a solution of imidazolium iodide **2** (4.73 g, 8.67 mmol) in water (50 mL) at room temperature was added the lithium bis(trifluoromethane)sulfonamide salt (3.75 g, 13 mmol). The mixture was stirred at room temperature for 12 h. The product was extracted with dichloromethane (twice, 100 mL), the extract was washed with water (7 times, 50 mL), dried with sodium sulfate and evaporated under vacuum. The resulting ionic liquid **3** (oil) was dried in high vacuum to give 4.36 g (yield 72%). <sup>31</sup>P NMR (400.1316 MHz, CDCl<sub>3</sub>): δ 39.23; <sup>1</sup>H NMR (300.130 MHz, CDCl<sub>3</sub>); <sup>1</sup>H NMR (300.130 MHz, CDCl<sub>3</sub>): δ 0.79 (t, 3H, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, CH<sub>3</sub>), 1.07–1.40 (m, 12H, CH<sub>2</sub>), 1.40–1.51 (m, 2H, P–CH<sub>2</sub>–CH<sub>2</sub>), 1.91 (m, 2H, CH<sub>2</sub>–CH<sub>2</sub>–NHC(O)), <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz), 3.06 (m, 2H, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, CH<sub>2</sub>–NH–C(O)), 3.11 (d, 2H, PCH<sub>2</sub>, <sup>2</sup>J<sub>P-H</sub> = 12.1 Hz) 3.78 (s, 3H, CH<sub>3</sub>-N), 4.04 (m, 2H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–NHC(O)), 7.21 (s, 1H, C<sub>5</sub>H in Im); 7.35 (s, 1H, C<sub>4</sub>H in Im); 7.42 (s, 1H, NH); 7.33–7.53 (m, 3H, *m* and *p*-C<sub>6</sub>H<sub>5</sub>P); 7.56–7.68 (m, 2H, *o*-C<sub>6</sub>H<sub>5</sub>P), 8.92 (s, 1H, N=CH–N).

## 2.3 Sample Preparation for Extraction Experiments

All aqueous solutions were prepared with ultra-pure water ( $\omega = 18 \text{ M}\Omega\text{-cm}$ ). The IL was carefully dried under reduced pressure before sample preparation following a previously published procedure [34]. The OctPh-CMPO ionic liquid was introduced by weight, at a concentration of  $0.013 \text{ mol}\cdot\text{L}^{-1}$  (extraction curves) or  $0.00614 \text{ mol}\cdot\text{L}^{-1}$  (addition of [C<sub>4</sub>mim][Cl]). Samples were stirred overnight to insure complete dissolution of the compound.

## 2.4 Extraction as a Function of Initial Acid Concentration

All extraction experiments have been performed at  $t = (22 \pm 2) \text{ }^\circ\text{C}$ . Equal volumes of IL and aqueous phases were first pre-equilibrated by mechanical shaking for 3 h. Then an aliquot of the metal stock solution was added. Mechanical shaking was then applied for an additional 3 h, and finally samples were centrifuged before phase separation. Kinetics experiments were made at three different acidities in HNO<sub>3</sub> that showed that the equilibrium was reached for a 3-h contact time (see Supplementary Material Fig. S1).

The uranium and europium distribution ratio,  $D_U$  and  $D_{Eu}$ , were measured by ICP-MS determination of the metal amount in the aqueous phase prior and after the extraction protocol. Then,  $D_M$  was calculated on the basis of:

$$D_M = \frac{[M]_{\text{aq,init}} - [M]_{\text{aq,eq}}}{[M]_{\text{aq,eq}}} \quad (1)$$

In this case, the experimental uncertainty on  $D$  values amounts to ca. 5%.

For the determination of the americium distribution ratio,  $D_{Am}$ ,  $\gamma$ -counting was performed using a Eurisis high purity germanium detector equipped with the ITech

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Instruments InterWinner 6.0 software. The  $\gamma$ -line at 59.5 keV was examined for  $^{241}\text{Am}$ . Both aqueous and IL phases were measured. The peak surface ratio readily gives the distribution ratio. Owing to auto-absorption of photons below 100 keV, especially in the IL phases, the uncertainty on  $D_{\text{Am}}$  is equal to ca. 15%.

## 2.5 Extraction at Fixed Initial Acidity and as a Function of $[\text{C}_4\text{mim}][\text{Cl}]$

$D_{\text{U}}$  was measured as a function of the aqueous initial concentration of  $[\text{C}_4\text{mim}][\text{Cl}]$  at two nitric acid concentrations, 0.3 and 2.24 mol·L<sup>-1</sup>. The initial uranium concentrations were respectively  $5.9 \times 10^{-5}$  and  $4.6 \times 10^{-5}$  mol·L<sup>-1</sup>, while the OctPh-CMPO-IL concentration was held to 0.006 mol·L<sup>-1</sup>.

## 2.6 EXAFS and UV-Visible Spectroscopy Measurements

Spectroscopic measurements were made on the ionic liquid phases obtained by liquid-liquid extraction of uranium(VI) following the previous protocol. Due to the technical detection limit, the initial uranium concentration was held at 0.006 mol·L<sup>-1</sup>. As a consequence, the OctPh-CMPO-IL concentration was held at 0.26 mol·L<sup>-1</sup>. The acidity of the aqueous phases was chosen as representative from the extraction curve, 1 and 6 mol·L<sup>-1</sup> HClO<sub>4</sub> or 6 mol·L<sup>-1</sup> HNO<sub>3</sub>.

EXAFS measurements were carried out at the ROBL beamline, ESRF (Grenoble, France) at ambient temperature (19 °C), using a double crystal Si(111) monochromator. Analysis were made at the uranium L<sub>III</sub> (17,166 eV) edge in the fluorescence mode using a 13-element germanium detector. The monochromator energy was calibrated with an yttrium metal foil (17,038 eV). Data were extracted using ATHENA software [35] and their analysis was carried out with the FEFFIT code [36], using phase and backscattering amplitude functions generated with the FEFF 8.1 code [37]. 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 Å. The  $k$ -range used was 3.0–15 Å<sup>-1</sup>. The amplitude reduction factor ( $S_0^2$ ) was held constant at 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 ( $O_{\text{ax}}$ ) was held constant at two. The multiple scattering paths of the axial oxygens were included in the fit by constraining its effective path-length to twice the values of the corresponding U –  $O_{\text{ax}}$  distance.

After EXAFS, the three samples were analyzed by UV-Vis spectroscopy at room temperature (19 °C), with a Varian Cary 100 spectrophotometer using a quartz cell (optical path length 1 cm) and pure  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  as reference.

## 2.7 Other Measurements

Acid concentration was determined in the aqueous phase by classical titration procedures (Schott, Titroline). Uncertainty is equal to 1%.

The  $\text{Tf}_2\text{N}^-$  and  $\text{C}_4\text{mim}^+$  concentrations in the aqueous phase (no metallic ion added) as a function of  $[\text{HNO}_3]$  and  $[\text{HClO}_4]$  was determined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR, according to an experimental protocol developed by our group [38]. Uncertainties are in the range of 5% for  $[\text{Tf}_2\text{N}]$  anions and 10% for imidazolium cations.

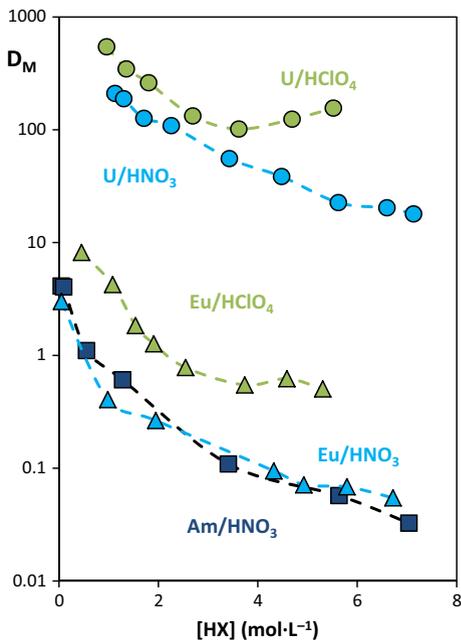
## 3 Experimental Results

### 3.1 Extraction

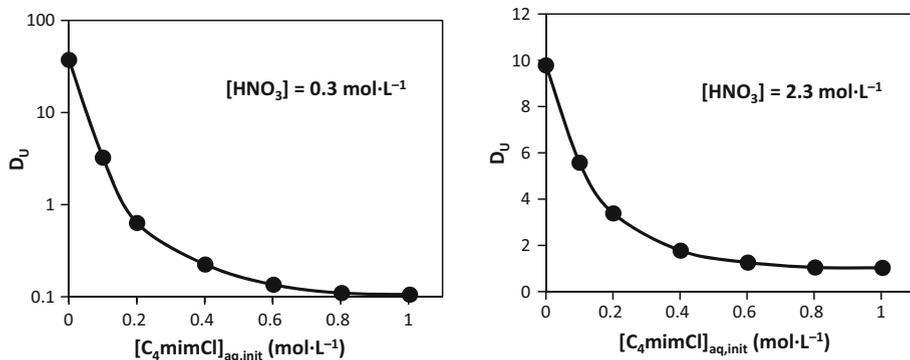
Figure 1 displays the metal distribution ratios (U, Eu and Am) as a function of the acid ( $\text{HNO}_3$  and  $\text{HClO}_4$ ) concentration in the aqueous phase, for an IL phase composed of  $0.01 \text{ mol}\cdot\text{L}^{-1}$  OctPh-CMPO-IL dissolved in  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  (Table 2). In the absence of extractant, it has been already observed that uranium is not extracted into the  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  phase, even at the highest  $\text{HNO}_3$  concentration [39, 40]. Similarly, we have checked this without extractant: Am(III) and Eu(III) are not extracted in the presence of  $\text{HNO}_3$  nor is U(VI) significantly extracted in the presence of  $\text{HClO}_4$  (see Fig. S2). Also, one of our previous works showed that Am(III) is not extracted into  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  from highly acidic  $\text{HClO}_4$  aqueous solutions [41]. We assume an identical behavior on that point for Eu(III) and Am(III) and, therefore, we consider the extraction data presented hereafter to be solely due to the presence of the OctPh-CMPO-IL.

All the distribution ratios (U, Eu and Am) display a continuous decrease with concentration of  $\text{HNO}_3$ . In contrast, using perchloric acid,  $D_{\text{U}}$  decreases until  $[\text{HClO}_4] \approx 3 \text{ mol}\cdot\text{L}^{-1}$  and then increases as a function of acid concentration (boomerang shape) while the  $D_{\text{Eu}}$  values level off at high acidity. Similar features of the distribution ratio have already been observed by several groups in many systems: the decrease has been obtained for U(VI)/ $\text{HNO}_3$ //Cyanex-272/ $[\text{C}_1\text{C}_{10}\text{im}][\text{Tf}_2\text{N}]$  [42]; leveling off is found for U(VI)/ $\text{HNO}_3$ //malonamide/ $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  [39] while numerous examples of a boomerang-like behavior can be found in the literature, for example Pu(IV)/ $\text{HNO}_3$ //malonamide// $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  [17] (see [10] for a review of such experimental data). However, the replacement of nitric acid by perchloric acid entails an increase of the distribution ratios for

**Fig. 1** Variation of the distribution ratio for the five extraction systems studied in this work. Symbols correspond to experimental data, while dotted lines are guides for the eye:  $[\text{U(VI)}] = 1.2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  ( $\text{HNO}_3$ ) or  $1.9 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  ( $\text{HClO}_4$ ),  $[\text{Eu(III)}] = 5.4 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  ( $\text{HNO}_3$ ) or  $3.5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  ( $\text{HClO}_4$ ),  $[\text{Am(III)}] = 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ , and  $[\text{OctPh-CMPO-IL}] = 0.013 \text{ mol}\cdot\text{L}^{-1}$







**Fig. 2** Variation of the uranium distribution ratio as a function of the aqueous  $\text{C}_4\text{mimCl}$  concentration, for  $[\text{HNO}_3] = 0.3 \text{ mol}\cdot\text{L}^{-1}$  and  $[\text{HNO}_3] = 2.3 \text{ mol}\cdot\text{L}^{-1}$ . Left hand figure:  $[\text{U(VI)}] = 5.9 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{HNO}_3] = 0.3 \text{ mol}\cdot\text{L}^{-1}$ , and  $[\text{OctPh-CMPO-IL}] = 6.14 \text{ mmol}\cdot\text{L}^{-1}$ ; right hand figure:  $[\text{U(VI)}] = 4.567 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ,  $[\text{HNO}_3] = 2.245 \text{ mol}\cdot\text{L}^{-1}$ , and  $[\text{OctPh-CMPO-IL}] = 6.14 \text{ mmol}\cdot\text{L}^{-1}$

**Table 3** Variation of the uranium distribution ratio as a function of the  $\text{C}_4\text{mimCl}$  aqueous concentration, for  $[\text{HNO}_3] = 0.3 \text{ mol}\cdot\text{L}^{-1}$  and  $[\text{HNO}_3] = 2.3 \text{ mol}\cdot\text{L}^{-1}$

$[\text{HNO}_3] = 0.3 \text{ mol}\cdot\text{L}^{-1}$	$[\text{C}_1\text{C}_4\text{mimCl}] \text{ (mol}\cdot\text{L}^{-1})$	$D$	$[\text{HNO}_3] = 2.3 \text{ mol}\cdot\text{L}^{-1}$	$[\text{C}_1\text{C}_4\text{mimCl}] \text{ (mol}\cdot\text{L}^{-1})$	$D$
	1.0040	0.10		1.0040	1.03
	0.8032	0.11		0.8032	1.05
	0.6024	0.131		0.6024	1.26
	0.4016	0.221		0.4016	1.77
	0.2008	0.631		0.2008	3.38
	0.1004	3.23		0.1004	5.57
	0	37.20		0	9.78

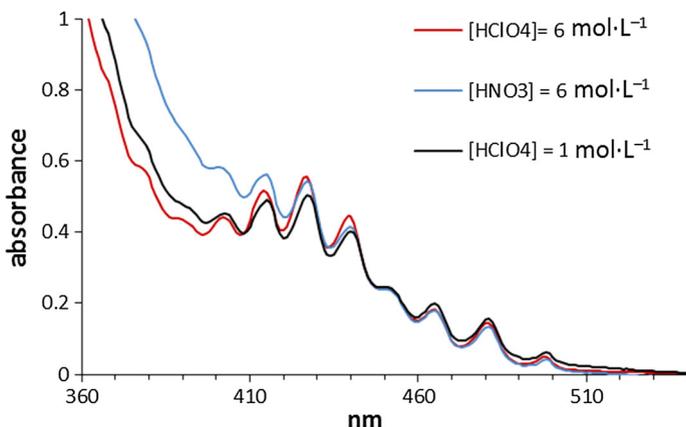
Data are displayed in Fig. 2

### 3.3 Final Acid and IL Ions Concentrations

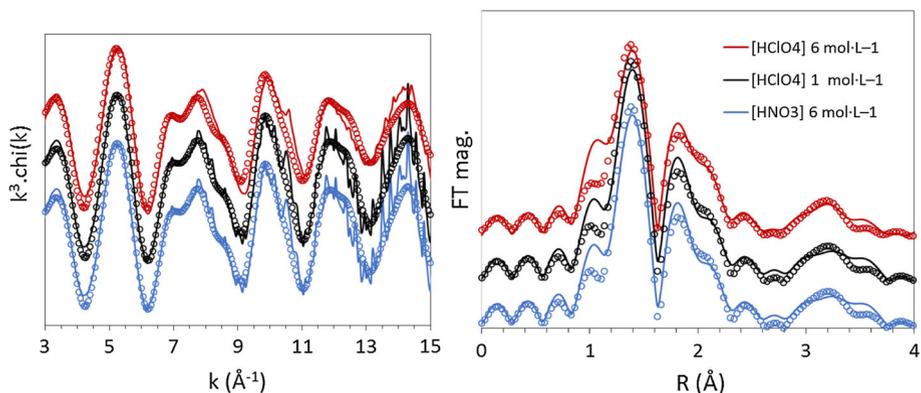
We have checked the equilibrium IL ion concentrations in the aqueous phase and the proton concentration in the IL phase, as a function of the acid nature and concentration.

It is known that CMPO extracts nitric acid in molecular solvents such as  $\text{CMPO}\cdot\text{HNO}_3$  or  $\text{CMPO}(\text{HNO}_3)_2$  [43]. In our case, the presence of  $13 \text{ mmol}\cdot\text{L}^{-1}$  of CMPO or OctPh-CMPO-IL in the IL phase (Fig. 5) does not change the acid uptake as compared to that in the absence of ligand. This is most probably due to the low concentration of ligand used in this work. This also shows that the ligand protonation, if any, is not measurable under our experimental conditions. More precisely, the measurement of the proton uptake by the IL phase as a function of the ligand concentration (comparison between OctPh-CMPO-IL and CMPO), for  $\text{HNO}_3 = 0.2 \text{ mol}\cdot\text{L}^{-1}$  (Fig. S3) shows that in the range of ligand concentration used in our work ( $< 0.03 \text{ mol}\cdot\text{L}^{-1}$ ), the protonation of OctPh-CMPO-IL is similar to that of CMPO and remains negligible.

Figure 6 shows the  $\text{C}_4\text{mim}^+$  and  $\text{Tf}_2\text{N}^-$  ions concentrations in the aqueous phase at equilibrium as a function of the acid's nature and initial concentration, in the presence of



**Fig. 3** UV-vis spectra of IL phases of U(VI)/HX//OctPh-CMPO-IL/[C<sub>4</sub>mim][Tf<sub>2</sub>N], HX being 6 mol·L<sup>-1</sup> HNO<sub>3</sub> or 1 mol·L<sup>-1</sup> and 6 mol·L<sup>-1</sup> HClO<sub>4</sub>. Samples were also analyzed by EXAFS



**Fig. 4** Uranium L<sub>3</sub> edge EXAFS spectra (left) and their corresponding Fourier transforms (right) of the three samples obtained by extraction with OctPh-CMPO-IL in [C<sub>4</sub>mim][Tf<sub>2</sub>N] from HNO<sub>3</sub> or HClO<sub>4</sub> aqueous phases. Lines represent data and dots represent fits. For sake of clarity, spectra are shifted along the y-axis

13 mmol·L<sup>-1</sup> of ligand. Note that these experiments were made using CMPO, and as the cation of the OctPh-CMPO-IL is bulky and contains a rather hydrophobic part, we expect similar results for OctPh-CMPO-IL. The fact that the cation and IL anion solubilities are not equal has already been observed in different systems [38, 44] and has been discussed in detail [45].

## 4 Discussion

First, our study shows that the extraction of uranium(VI) is larger than the extraction of Am(III) and Eu(III) using OctPh-CMPO-IL in [C<sub>4</sub>mim][Tf<sub>2</sub>N], no matter the acid and concentration range (see Fig. 1). This tendency is in line with observations made in the classical CMPO + TBP/dodecane system [46] (see Table 1 for values at 3 mol·L<sup>-1</sup>

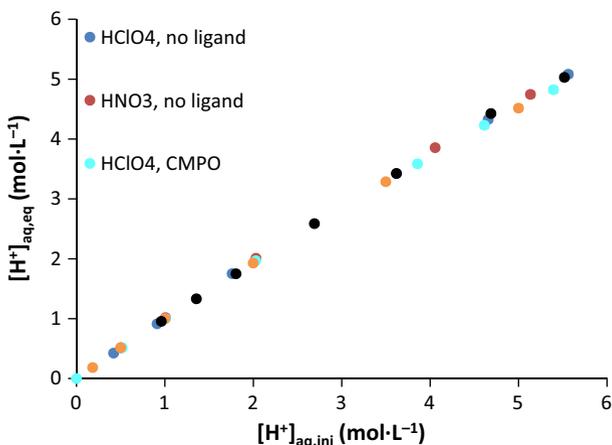
**Table 4** EXAFS fit results,  $N$  being the coordination number,  $R$  the interatomic distance and  $\sigma^2$  the Debye–Waller factor

Aqueous phase composition	Path	$N$	$R$ (Å)	$\sigma^2$ (Å <sup>2</sup> )	$E_0$ (eV)	$R_{\text{factor}}$	System
[HNO <sub>3</sub> ] = 6 mol·L <sup>-1</sup>	O <sub>ax</sub>	2*	1.77	0.001	4.3	0.03	[UO <sub>2</sub> (OctPh-CMPO-IL) <sub>3</sub> ]
	O <sub>eq</sub>	5.8	2.39	0.009			
	C	2.9	3.52	0.002			
	P	2.9	3.61	0.008			
[HClO <sub>4</sub> ] = 1 mol·L <sup>-1</sup>	O <sub>ax</sub>	2*	1.77	0.002	4.4	0.03	[UO <sub>2</sub> (OctPh-CMPO-IL) <sub>3</sub> ]
	O <sub>eq</sub>	6.0	2.39	0.009			
	C	3.0	3.51	0.003			
	P	3.0	3.60	0.008			
[HClO <sub>4</sub> ] = 6 mol·L <sup>-1</sup>	O <sub>ax</sub>	2*	1.78	0.002	3.4	0.03	[UO <sub>2</sub> (OctPh-CMPO-IL) <sub>3</sub> ]
	O <sub>eq</sub>	6.1	2.40	0.009			
	C	3.0	3.49	0.004			
	P	3.0	3.64	0.009			

The \* indicates parameters fixed during the fit.  $E_0$  is the shift in energy and  $R_{\text{factor}}$  indicates the goodness of the fit according to [36]:  $N \pm 20\%$ ,  $R \pm 0.01$  Å,  $\sigma^2 \pm 10^{-3}$  Å<sup>2</sup>

**Fig. 5** Influence of the presence of a ligand (CMPO or OctPh-CMPO-IL) on the acid uptake by the IL phase:

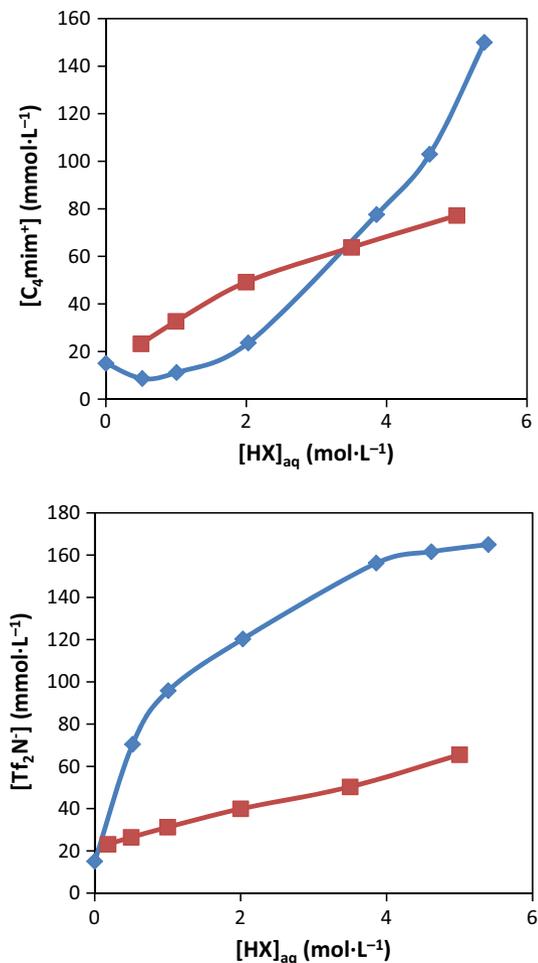
[CMPO]<sub>IL</sub> = [OctPh-CMPO-IL]<sub>IL</sub> = 13 mmol·L<sup>-1</sup>



HNO<sub>3</sub>), and this was explained on the basis of the effective charge of ions (+ 3 for Am and Eu, + 3.2 for U(VI)). Mohapatra et al. [27] observed the opposite trend in CMPO/[C<sub>4</sub>mim][Tf<sub>2</sub>N] and in a TSIL-CMPO/[C<sub>4</sub>mim][Tf<sub>2</sub>N] mixture, where the TSIL was composed of a C<sub>1</sub>C<sub>12</sub>mim<sup>+</sup> cation functionalized with a CMPO function and a Tf<sub>2</sub>N<sup>-</sup> counter-anion. According to these authors, both CMPO and their TSIL-CMPO diluted in [C<sub>4</sub>mim][Tf<sub>2</sub>N] lead to lower  $D_U$  values as compared to  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  (HNO<sub>3</sub> up to 3 mol·L<sup>-1</sup>).

Second, the general trend as HNO<sub>3</sub> increases is a decrease in  $D_U$ ,  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  values using our extractant, while in 0.2 mol·L<sup>-1</sup> CMPO + 1.2 mol·L<sup>-1</sup> TBP/dodecane,  $D_U$  steadily increases while  $D_{\text{Am}}$  increases up to ca. 1.5 mol·L<sup>-1</sup> and slightly decreases above 1.5 mol·L<sup>-1</sup> HNO<sub>3</sub> [47].

**Fig. 6** Concentrations of the IL ions  $C_4mim^+$ , (top) and  $Tf_2N^-$  (bottom) in acidic solutions: results for  $HNO_3$  in red and  $HClO_4$  in blue. Ligand concentration:  $13\text{ mmol}\cdot\text{L}^{-1}$  (CMPO)



Third, at  $3\text{ mol}\cdot\text{L}^{-1}$  acid, the  $D_U$  value we obtained is two orders of magnitude lower than the  $D_U$  value of the traditional TRUEX system ( $0.2\text{ mol}\cdot\text{L}^{-1}$  CMPO +  $1.2\text{ mol}\cdot\text{L}^{-1}$  TBP/dodecane) [47] but the extractant concentration is ca. 15 times lower in our case, and we did not use TBP. Furthermore, the U/Eu selectivity we obtain is far larger than the one reached with extraction systems using molecular solvents or IL.

The nature of the acid ( $HNO_3$  or  $HClO_4$ ) composing the aqueous phase has a direct impact on the distribution ratios and on the extraction selectivity between U(VI) and Eu(III)/Am(III). Moreover, in our system, the shape of the U(VI) extraction curve is different between the two acids. So the acid, and more specifically the acid anion, must play a role in the ion's separation.

Obviously, the extraction features in our system are very different from that of ( $0.2\text{ mol}\cdot\text{L}^{-1}$  CMPO +  $1.2\text{ mol}\cdot\text{L}^{-1}$  TBP/dodecane) and of most of the other systems studied so far with ILs, if not for all.

We now consider the possible stoichiometries of the U(VI) extracted species in  $HNO_3$  medium in order to get some insights into the extraction mechanism. On the basis of data

displayed in Figs. 3, 4 and Table 4, the extracted uranium species are identical in  $6 \text{ mol}\cdot\text{L}^{-1}$   $\text{HNO}_3$  and  $\text{HClO}_4$  ( $1 \text{ mol}\cdot\text{L}^{-1}$  and  $6 \text{ mol}\cdot\text{L}^{-1}$ ) and are thus ascribed to  $[\text{UO}_2(\text{OctPh-CMPO-IL})_3]$ . Written as such on purpose, the charge of this entity is not specified because, as pointed above, EXAFS and UV-Vis are not sensitive to the outer coordination spheres that may contain the ions responsible for the entity's charge. Anyway, the extracted species does not contain  $\text{NO}_3^-$  or  $\text{ClO}_4^-$  in its first coordination sphere. This has already been observed for several U(VI) extracted species in IL-based extraction systems, such as TBP/ $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  [15] and CMPO/ $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  [48]. In the case of  $\text{HClO}_4$ , this is in line with the non-complexing ability of  $\text{ClO}_4^-$  towards U(VI) [49]. In the case of  $\text{HNO}_3$ , in contrast, the aqueous speciation of uranium is well documented with evidence for the formation of two nitrate-complexes  $\text{UO}_2(\text{NO}_3)^+$  and  $\text{UO}_2(\text{NO}_3)_2$  [50]. Consequently, we can imagine two possibilities: either  $\text{UO}_2(\text{NO}_3)^+$  and  $\text{UO}_2(\text{NO}_3)_2$  are extracted but the OctPh-CMPO-IL ligand expels the nitrate moieties from the first coordination sphere or only  $\text{UO}_2^{2+}$  is extracted. In both cases, the TSIL-CMPO fills the first coordination sphere totally. We consider the second possibility to be more probable because extraction of nitrate complexes would involve an increase in  $D$  as a function of  $\text{HNO}_3$ , which is not experimentally observed. Conversely, the hypothesis of  $\text{UO}_2^{2+}$  as the unique extracted species is in line with a decrease in  $D$  as  $\text{HNO}_3$  increases: as the nitrate complexes are formed, extraction is diminished. Finally, the addition of the  $\text{C}_4\text{mim}^+$  cation in the aqueous phase through the dissolution of  $[\text{C}_4\text{mim}][\text{Cl}]$  induces a decrease in the  $D_{\text{U}}$  values (see Fig. 2), at high and low nitric acid concentration, which is indicative of a cation exchange mechanism.

The trend observed for U(VI) is identical to those for Am(III) and Eu(III), that is, a decrease of extraction as the  $\text{HNO}_3$  concentration increases. It seems thus reasonable to conclude that nitrate ions do not directly bind to Am(III) and Eu(III) and that these trivalent species are also extracted in a cationic form  $[\text{M}(\text{OctPh-CMPO-IL})_4]^{3+}$  {Ln(III) and An(III) coordination sphere can be filled with 8 or 9 atoms}.

The data in  $\text{HClO}_4$  medium appear to contrast with the  $\text{HNO}_3$  case at first sight. Actually, neither the decrease in  $D_{\text{U}}$  as a function of  $\text{HClO}_4$  in the range  $0\text{--}3.8 \text{ mol}\cdot\text{L}^{-1}$  nor the increase in  $D_{\text{U}}$  above  $\text{HClO}_4 = 3.8 \text{ mol}\cdot\text{L}^{-1}$  can be ascribed to aqueous complexation because no perchlorate-U(VI) complexes are known in this range of acid concentration [49]. A qualitative explanation has thus to be found in another specific behavior of the perchloric acid system. According to Fig. 5, the  $\text{H}^+$  equilibrium concentration is not modified as a function of the acid or the presence of ligand so this is not a clue to the origin of the boomerang shape of the  $D_{\text{U}}$  with variation in  $\text{HClO}_4$  concentration. The data in Fig. 6 show that the IL cation and anion solubilities in water are very different between the  $\text{HNO}_3$  and  $\text{HClO}_4$  media. Moreover, for the  $\text{HClO}_4$  medium, the  $\text{Tf}_2\text{N}^-$  solubility displays a plateau above ca.  $3.8 \text{ mol}\cdot\text{L}^{-1}$ , and thus correlates with the change in curvature of the variation of  $D_{\text{U}}$ . So this is probably the parameter governing the  $D_{\text{U}}$  variations although we are not able to give a quantitative analysis.

On a wider perspective, the ligand we developed displays quite interesting features. Used at a concentration of only  $13 \text{ mmol}\cdot\text{L}^{-1}$ , Eu(III) and Am(III) remain in the aqueous phase at  $\text{HNO}_3 = 4 \text{ mol}\cdot\text{L}^{-1}$  while uranyl is extracted with a  $D_{\text{U}} \approx 46$ . This extraction ratio compares favorably with the one obtained for the "Purex type" system  $1.1 \text{ mol}\cdot\text{L}^{-1}$  TBP/dodecane, showing that our TSIL may be efficient for uranyl/An(III) partitioning.

Am(III), Eu(III) and U(VI) distribution ratios depend directly on the ligand concentration, as a function of  $[\text{OctPh-CMPO-IL}]^3$  for U(VI) and  $[\text{OctPh-CMPO-IL}]^4$  for Am(III) and Eu(III). So, in the latter case, a slight increase of OctPh-CMPO-IL concentration

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would render the extraction of Am(III) and Eu(III) noticeable. The multiplication of the ligand concentration by a factor 5 (i.e.,  $0.05 \text{ mol}\cdot\text{L}^{-1}$ ) would lead to a  $D$  increase proportional to  $[\text{ligand}]^4$ , and thus to  $D_{\text{Am}}$  and  $D_{\text{Eu}} \sim 100$  at  $\text{HNO}_3 = 3 \text{ mol}\cdot\text{L}^{-1}$ . This is a far better performance than those obtained with other TSIL-CMPOs for a smaller ligand concentration (see Table 1). This opens the road to a new strategy for the sequential separation of U(VI), Am(III) and Eu(III) by using the same organic phases: first, a separation of U(VI) using the OctPh-CMPO-IL at low concentration and second, increasing the OctPh-CMPO-IL concentration to extract Am(III) and Eu(III), both steps being performed at the same nitric acid concentration. Then, ion back-extraction can be performed by contact with an aqueous solution of  $[\text{C}_4\text{mim}][\text{Cl}]$ , an inexpensive IL.

## 5 Conclusion

Extraction of uranium(VI), europium(III) and americium(III) was studied using a newly synthesized TSIL (OctPh-CMPO-IL) dissolved in the ionic liquid  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ . A small amount of this ligand allows a noticeable extraction of U(VI). The extraction decreases as the acid concentration ( $\text{HNO}_3$  or  $\text{HClO}_4$ ) increases, and the nature of the acid has an influence on the separation factor between U(VI) and Eu(III). Metal ions are extracted via a cation exchange mechanism, the metal ions being extracted as a solvate  $[\text{M}(\text{OctPh-CMPO-IL})_x]^{+a}$  ( $x = 3$  for U(VI), probably 4 for M(III)). It is proposed that the OctPh-CMPO-IL TSIL may be used for a sequential separation of U(VI) and then of An(III) or Ln(III).

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