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Extraction of actinides by tertiary amines in room temperature ionic liquids: evidence for anion exchange as a major process at high acidity and impact of acid nature†

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Extraction of U(vi) and Pu(iv) using several tri-alkylamines such as tri-*n*-butylamine (TBA), tri-*n*-hexylamine (THA), tri-*n*-octylamine (TOA), and tri-iso-octylamine (TiOA) in room temperature ionic liquids, [C_{*n*}mim]-[Tf₂N] (where *n* = 4, 6 or 8), was investigated from nitric acid as well as hydrochloric acid medium. In the absence of the amines, the extraction results indicated an increase in the extraction of both U(vi) and Pu(iv) as a function of the acid concentration which was attributed to the extraction of probable anionic species such as UO₂X₃[−], UO₂X₄^{2−}, PuX₅[−] and PuX₆^{2−} (where X = Cl[−] or NO₃[−]) according to an anion-exchange mechanism involving Tf₂N[−] ions. The presence of amines in the ionic liquid enhances the extraction of the metal ions with increased HCl concentration, especially in the case of UO₂²⁺, but the amines appear to be almost inefficient in HNO₃ medium. This is ascribed to the protonation/association of amines *via* solubilization of H⁺ and NO₃[−] ions in the ionic liquid phase in the case of nitric medium, while hydrochloric acid does not solubilize in ionic liquid, and thus the amine remains efficient. Modeling of the extraction data in HCl medium for U(vi) and Pu(iv) in the presence of amines has been performed and confirmed the anion exchange mechanism.

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1. Introduction

Extraction of actinides from nitric acid feeds has been one of the major challenges and such separation methods find applications in radioactive waste management. Usually, for feeds containing low concentrations of acid (in the pH range) one employs acidic extractants such as TTA (2-thenoyltri-fluoroacetone), HD2EHP (di-2-ethylhexylphosphoric acid), Cyanex 272, *etc.* while those containing moderate concentrations of nitric acid (*i.e.*, from 1 to 3 M) require solvating type neutral extractants such as TBP (tri-*n*-butyl phosphate), CMPO (carbamoyl methylene phosphine oxide), TODGA (*N,N,N',N'*-tetra-*n*-octyldiglycolamide), *etc.*^{1–3} On the other hand, some radioactive wastes contain actinide ions at rather high concentrations of acid (>3 M) and in such cases amines are usually used as the extractants.¹

Ionic liquids (IL) have gained considerable attention in recent years for metal ion extraction such as actinides/lanthanides^{3–5} and transition elements.⁶ Due to their negligible vapour pressure, non-inflammability and wide liquid range, ILs have been considered as possible 'green' alternatives to conventional molecular diluents. Several important features have been the signature of IL based extraction systems, especially for metal ion extraction which include usually higher extraction and improved separation efficiency as compared to the molecular diluents.^{3–5} As a consequence, ILs have been used for the extraction of actinide ions by many research groups using the above mentioned extractants.

Owing to the growing interest in the recovery of actinides, especially uranium, from various streams including lean solutions and wastes, a large number of publications are available on the recovery of uranium from such feeds using ILs. The extraction of UO₂²⁺ has been investigated in IL using TBP,^{7,8} Cyanex 272,⁹ CMPO,^{10–12} TODGA¹³ and malonamides.¹⁴ Other examples related to either less common actinides and/or ligands, such as amines, can also be found. Zuo *et al.*,¹⁵ carried out studies on the extraction of Th⁴⁺ using a primary amine N1923 (dialkyl methylamine where the alkyl groups range from C₉H₁₉ to C₁₁H₂₃) in [C₈mim][PF₆] which indicated a reverse micellar mechanism and efficient separation of Th⁴⁺ from rare earth elements. There are other reports in which ILs containing quaternary ammonium cation such as Aliquat 336

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(A336) have been used for the extraction of metal ions,^{16,17} including UO_2^{2+} ion extraction.¹⁸ These studies, however, have not given any information on the mechanism of extraction. Though these extraction systems may not find immediate applications for the separation of actinides in a plant scale, the basic solvent extraction data showed many interesting features making these studies quite relevant.

From this wealth of studies, several drawbacks of the IL based extraction methods have been identified and then have been tentatively fought. For example, ILs with PF_6^- as the counter anion display large viscosities and show considerable degradation at high concentrations of nitric acid.¹⁹ These limitations can be easily countered by using ILs containing other favorable counter anions such as NTf_2^- which have considerably lower viscosities²⁰ and are water-stable. Similarly, aqueous solubility of the cationic component of the ILs, which is a consequence of the cation-exchange mechanism acknowledged at low acidities, is more common with ILs containing smaller alkyl groups such as *n*-butyl. The aqueous solubility of the cationic component of ILs can be made insignificant by opting bulkier alkyl groups such as *n*-octyl or *n*-decyl or by use of fluorinated ILs. Unfortunately, with these methods, the overall extraction efficiency is drastically decreased, rendering the solution quite inefficient.^{8,21} Provided the cation exchange mechanism occurring at low acidity is changed to the solvation mechanism at high acidities, performing extraction under high acidic conditions would thus be an elegant way to counter (cationic) pollution of the aqueous phase. However, there is still some debate on the relative importance of anionic exchange and extraction of neutral species at high acidities.^{22,23}

Therefore, in the present study, the extraction mechanism of UO_2^{2+} and Pu^{4+} from acidic feed conditions using several tri-alkylamines such as tri-*n*-butylamine (TBA), tri-*n*-hexylamine (THA), tri-*n*-octylamine (TOA), and tri-iso-octylamine (TiOA) was investigated in several ILs, $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$, where $n = 4, 6$ or 8 . Pu^{4+} was chosen because there is also a need to understand the extraction behavior of this important actinide ion under moderate to high acidic conditions. This has significant implications in the simultaneous recovery of U and Pu, including applications in spent nuclear fuel reprocessing. Simulation of the solvent extraction data in the presence of amine was also performed (HCl medium) for validation of the extraction mechanism. The simulation results have shown the extraction of negatively charged species through an anion exchange mechanism.

2. Experimental

2.1. Reagents and radiotracers

Suprapur nitric and hydrochloric acids (Merck) were used for preparing the dilute acid solutions. Ionic liquids (>99%) were purchased from Iolitec, Germany and were used as received. The trialkylamines (>99%) were procured from Sigma Aldrich and were used without further purification. All the other reagents were of AR grade.

²³³U, purified from its daughter products following an ion exchange method,²⁴ was used as the stock solution. Pu (mainly

²³⁹Pu) was used from the laboratory stocks after confirming its radiochemical purity. The purity of Pu was checked by α spectrometry using a Si-surface barrier detector and also by confirming the absence of ²⁴¹Am by gamma ray spectrometry. Pu^{4+} was prepared by addition of a few drops of a dilute NaNO_2 solution (50 mM) to a Pu solution taken in 1 M HNO_3 which was subsequently extracted using a 0.5 M solution of TTA (2-thenoyltrifluoroacetone) in xylene. The extracted Pu^{4+} was stripped using 8 M HNO_3 . The back extracted tracer solution was subsequently washed three times with xylene (to ensure removal of dissolved TTA in the aqueous solution) and was preserved as the stock solution of Pu^{4+} . The stability of the oxidation state was insured due to the strongly complexing medium.

2.2. Distribution studies

The amine solutions in ILs were prepared by prolonged ultrasonification which resulted in clear single phase solutions. Leak tight Pyrex tubes with one mL of the IL phase containing requisite tri-alkylamine was allowed to be vortexed in a thermostated water bath at $25 \pm 0.1^\circ\text{C}$ for about an hour with equal volume of the aqueous phase containing the radiotracer in the desired acid concentration. This time was found sufficient to reach the equilibrium condition. The equilibration time was optimized by carrying out extraction kinetics experiments (*vide infra*). The tubes were subsequently centrifuged for about 5 minutes to enable clear phase separation. After centrifugation, both the phases were separated and assayed radiometrically. ²³⁹Pu and ²³³U were assayed using an alpha liquid scintillation counting system (Hidex, Finland) coupled to a multi-channel analyzer using a toluene-based extractive scintillator cocktail (SRL, Mumbai) containing 0.7% (w/v) PPO (2,5-diphenyloxazole), 0.03% (w/v) POPOP (1,4-di-[2-(5-phenyloxazolyl)]-benzene), and 10% (v/v) HD2EHP (di(2-ethylhexyl) phosphoric acid) which acted as the extractant. The distribution ratio, D_M , was defined as the ratio of the activity per unit volume in the organic phase to that in the aqueous phase. Typically, the concentration of Pu^{4+} was in the range of 10^{-6} – 10^{-7} M while that of UO_2^{2+} was in the range of 10^{-5} – 10^{-6} M. Amines were introduced in the IL phases at 1% (v/v). Such a procedure is adopted for the sake of sample preparation convenience, which corresponded to 42.0 mM TBA, 29.6 mM THA, 22.9 mM TOA and 23.1 mM TiOA. All the extraction experiments were carried out in duplicate with a precision of $\pm 5\%$ of standard deviation.

2.3. Acid uptake

Acid uptake in the IL phase (in the absence and in the presence of amines) was determined in the range 1–6 M of initial acid concentration by titration of the aqueous phase after equilibration with the respective IL phases. The IL phases were first equilibrated with aqueous phase containing required acid, followed by contacting the IL phase with deionized water (pH 7). Subsequently, this back extracted acid was titrated using phenolphthalein indicator with standard NaOH solution. Uncertainties in the H^+ titrations were within 5% (no amine) or 10% (with amine). All experiments have been performed at room temperature.

2.4. Measurements of C_8mim^+ and Tf_2N^- solubilities

Ion concentrations in the aqueous phase have been measured by NMR, so in this case only, deuterated water (99%) and deuterated hydrochloric acid, DCL, (analytical grade, Sigma Aldrich) have been used. Equal volumes of the acidic aqueous phase and of the pure IL phase (no ligand added) have been contacted in a mechanical shaker for three hours. Then, phases have been separated by centrifugation and aliquots of the aqueous equilibrated phase have been measured by NMR. The standard used in 1H -NMR was dihydrated sodium citrate $C_6H_5Na_3O_7 \cdot 2H_2O$ (Merck, >98%), for IL cation determination. The standard used in ^{19}F -NMR was sodium trifluoroacetate (Alfa Aesar, >98% purity), for Tf_2N^- determination. The NMR protocol is identical to that detailed elsewhere.²⁵ Data are presented as supplementary materials (ESI†).

3. Results and discussion

3.1. Acid uptakes and amine protonation in ionic liquids

Acid uptake by the organic phase is one of the key features of extraction, as this may impact both the aqueous speciation and the possibilities of ion exchange. Although many ILs are hydrophobic enough to generate biphasic systems when contacted with acidic aqueous solutions, they are known to accept rather high water and acid contents in their bulk. For example, HNO_3 enters the $[C_4mim][Tf_2N]$ phase up to ca. 6%, in the range of initial acidic concentration 1–6 M.^{25,26} By contrast, HCl does not solubilize in $[C_4mim][Tf_2N]$, with acid uptake below the titration uncertainty.^{25,26} Therefore, acid uptakes by the pure IL phases (no ligand, no metal ion) have been measured as a function of acid nature (HNO_3 , HCl) and acid concentration. Typical results for $[C_8mim][Tf_2N]$ (HCl) are shown in Fig. 1.

In the three ILs investigated, it is observed that HCl solubilization is negligible, while HNO_3 solubilization is significant,

Fig. 1 H^+ equilibrium value in the aqueous phase, $[H^+]_{aq,eq}$ as a function of initial HCl value for $[C_8mim][Tf_2N]$. Solid line: linear fit.

as about 5–6% HNO_3 is extracted into the IL phase ($n = 4$ and $n = 10$).²⁵ The acid extraction data was also determined in the presence of amines, but the data was similar to pure IL phase within the measured uncertainty due to low amine concentrations used. The solubilization data indicate that the amines/IL solution contacted with HCl solution may behave differently than those with HNO_3 . This property has significant effect on the extraction of UO_2^{2+} and Pu^{4+} by these amines, and will be discussed in the following sections.

3.2. Extraction of actinides in the absence of amines

We now turn to extraction of metallic ions, as a function of acid nature and amount. The distribution ratio (D) values were measured as a function of HNO_3 and HCl concentrations in the absence of amines and the results are listed in Table 1. As a typical example, D values for UO_2^{2+} and Pu^{4+} from HNO_3/H_2O towards pure $[C_8mim][Tf_2N]$ (in the absence of ligand) are shown in Fig. 2. The extraction of UO_2^{2+} is insignificant in the acid range from 1–6 M HNO_3 . On the other hand, extraction of Pu^{4+} increases with HNO_3 concentration. Close examination of the data of Table 1 lead to the following comments. Even at high acid concentration (HCl or HNO_3) and whatever the IL used, UO_2^{2+} extraction is always below 0.1 and can be considered as not negligible only at 6 M acidities ($D > 0.1$). For UO_2^{2+} extraction, no real difference can be detected between HNO_3 and HCl, and no significant difference is observed from one IL to the other, which may be ascribed, in part, to the rather low D values measured. By contrast, Pu^{4+} extraction from nitric acid medium is efficient, with all values above 1 and up to 3 at $[HNO_3] = 6$ M, while HCl leads to lower Pu^{4+} distribution ratios, ranging from <0.1 to 0.8 at $[HCl] = 6$ M.

Though the extraction of UO_2^{2+} and Pu^{4+} from HCl medium (in the absence of any extractant) is reported here for the first time, their extraction from HNO_3 medium has been reported by several research groups. In the case of UO_2^{2+} , our value $D_{U(VI)} = 0.184$ in $[C_8mim][Tf_2N]$, $[HNO_3] = 6$ M is in line with data collected at $[HNO_3] = 5$ M in $[C_8mim][Tf_2N]$ ($D_{U(VI)} = 0.135$).²⁷ Similarly, $D_{Pu(IV)}$ values equal to 1.6 ($[C_4mim][PF_6]$, $[HNO_3] = 5$ M)²⁸ or 7.8 ($[C_8mim][PF_6]$, $[HNO_3] = 5$ M),²⁹ have been obtained. Although these data are based on slightly different ILs and chemical conditions, they are in line with our measurements. By contrast to this work, Rout *et al.*,³⁰ reported higher extraction of Pu^{4+} by $[C_nmim][Tf_2N]$ from 1–5 M HNO_3 with $D_{Pu(IV)}$ values equal to 6.6 ($n = 4$) and 37.5 ($n = 8$). On the other hand, Patil *et al.*³¹ reported the extraction of the Pu metal ion to a much lower extent for the same chemical conditions, but in line with the data obtained in the present work. Relatively large $D_{Pu(IV)}$ values reported by Rout *et al.*^{28,30} could be attributed partly to liquid scintillation counting errors, particularly relevant at higher acidities, which are due to quenching in case of dioxane based scintillator cocktail or inefficient extraction in case of an extractive scintillator cocktail. It may be noted that the toluene based extractive scintillator cocktail requires the addition of a particular amount of a complexing agent such as di-2-ethylhexylphosphoric acid.

Table 1 Distribution of UO_2^{2+} and Pu^{4+} from varying concentrations of acid in the absence of amines

[Acid], M	Distribution ratio of UO_2^{2+}						Distribution ratio of Pu^{4+}					
	[C ₄ mim][Tf ₂ N]		[C ₆ mim][Tf ₂ N]		[C ₈ mim][Tf ₂ N]		[C ₄ mim][Tf ₂ N]		[C ₆ mim][Tf ₂ N]		[C ₈ mim][Tf ₂ N]	
	HNO ₃	HCl	HNO ₃	HCl	HNO ₃	HCl	HNO ₃	HCl	HNO ₃	HCl	HNO ₃	HCl
1	0.001	0.002	0.001	0.001	0.001	0.001	0.004	0.009	0.014	0.010	0.020	0.016
3	0.008	0.001	0.011	0.002	0.012	0.003	0.396	0.004	1.06	0.004	1.28	0.006
4	0.026	0.004	0.034	0.009	0.041	0.017	1.30	0.008	2.02	0.010	2.31	0.011
6	0.136	0.060	0.179	0.153	0.184	0.418	2.70	0.148	2.93	0.380	3.00	0.807

In order to understand our extraction data, it has to be recalled that actinide ions such as UO_2^{2+} and Pu^{4+} form anionic species in HCl medium (for example, UO_2Cl_3^- , $\text{UO}_2\text{Cl}_4^{2-}$, PuCl_5^- , PuCl_6^{2-}) as well as HNO_3 medium (for example, $\text{Pu}(\text{NO}_3)_5^-$ and $\text{Pu}(\text{NO}_3)_6^{2-}$) at moderate to high concentrations of the acids.²⁷ In ionic liquid medium where the diluent itself is constituted of a cation and an anion, such anionic complexes can be partitioned even in the absence of the extractant molecules, according to:

The extraction mechanism above is of the anion-exchange type and has been observed in some systems^{14,32} but not so well-documented, particularly in the case of actinides. In order to validate the general extraction mechanism as in eqn (1), experiments were carried out as a function of LiNTf_2 concentration in the aqueous phase at a fixed acid concentration. As expected, the addition of NTf_2^- in to the aqueous phase suppresses the metal ion extraction, supporting eqn (1) as the appropriate extraction mechanism. Slopes of the plots of $\log D_M$ vs. $\log[\text{Tf}_2\text{N}^-]$ for UO_2^{2+} extraction from 6 M HCl and Pu^{4+} extraction from 6 M HNO_3 were found to be close to -2 (Fig. 3),

suggesting extraction of $[\text{UO}_2\text{Cl}_4]^{2-}$ and $[\text{Pu}(\text{NO}_3)_6]^{2-}$ as per the following equations:

3.3. Extraction of actinides in the presence of amines

It is well-known that the anionic species involved in eqn (2) and (3) above are not favorably extracted towards pure molecular solvents, because they only accept neutral species in their bulk. Therefore, an extracting agent is required in order to extract these metal ions through neutral complexes. When using IL, as shown in the above section, extraction occurs even in the absence of extractant, but in the systems under investigation in this work, the distribution ratio are nonetheless rather low. We, therefore, considered amines as possible extracting agents. The extraction data of UO_2^{2+} from HCl medium by the four amine ligands dissolved in ILs were measured and data obtained for 6 M HCl are summarized in Table 2. Comparison with data displayed in Table 1 shows that addition of any of the amines is beneficial to uranium extraction, with $D_{\text{U(VI)}}$ values in the

Fig. 2 Extraction of actinides by $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$ (in the absence of ligand). Solid lines are guide for the eye only.

Fig. 3 Distribution ratio of actinide ions by pure $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$ in the presence of varying concentration of $\text{Li}\cdot\text{NTf}_2$ salt; Pu^{4+} slope: -1.83 ± 0.09 ; UO_2^{2+} slope: -1.79 ± 0.25 .

Table 2 Distribution of UO_2^{2+} by amines/ILs; aqueous phase: 6 M HCl; organic phase: 42 mM tri-*n*-butylamine, 30 mM tri-*n*-hexyl amine, 23 mM tri-*n*-octyl amine and 23 mM tri-iso-octyl amine

Amine	RTIL	$D_{\text{U(VI)}}$	$D_{\text{Pu(IV)}}$
Tri- <i>n</i> -butyl amine	$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.09	5.38
	$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.57	
	$[\text{C}_8\text{mim}][\text{NTf}_2]$	6.50	
Tri- <i>n</i> -hexyl amine	$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.09	3.34
	$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.40	
	$[\text{C}_8\text{mim}][\text{NTf}_2]$	4.29	
Tri- <i>n</i> -octyl amine	$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.08	1.94
	$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.31	
	$[\text{C}_8\text{mim}][\text{NTf}_2]$	2.56	
Tri-iso-octyl amine	$[\text{C}_4\text{mim}][\text{NTf}_2]$	0.08	2.07
	$[\text{C}_6\text{mim}][\text{NTf}_2]$	0.32	
	$[\text{C}_8\text{mim}][\text{NTf}_2]$	3.26	

presence of amine always larger than in its absence. This conclusion also applies for Pu^{4+} extraction. However, differences are small in some cases and extraction of UO_2^{2+} from 6 M HCl increases with increase in the alkyl chain length of the IL ($[\text{C}_n\text{mim}][\text{TF}_2\text{N}]$) from butyl to hexyl with all the four amines (Fig. 4). For subsequent studies, only $[\text{C}_8\text{mim}][\text{TF}_2\text{N}]$ was employed as it gives superior distribution values.

The kinetics for the extraction of UO_2^{2+} by amines (TBA, THA and TOA) dissolved in $[\text{C}_8\text{mim}][\text{TF}_2\text{N}]$ was investigated and the results are shown in Fig. 5. Results reveal that the extraction equilibria are reached within 15 min of equilibration for all the three amines. It should be noted that the distribution behavior and kinetics for extraction with TiOA was similar to that of TOA. As reported in several studies involving the ILs, relatively slower extraction kinetics is attributed to the higher viscosity of the ILs as compared to molecular diluents²² although chemical effects

Fig. 5 Distribution ratio of UO_2^{2+} as a function of time. Ligand: 1% v/v tertiary amine/ $[\text{C}_8\text{mim}][\text{TF}_2\text{N}]$; aqueous phase: 6 M HCl.

have been evidenced in some cases.³³ Though the kinetics studies were performed with all the four amines, for simplicity of the system in the present work, we focused rest of the study with TBA in $[\text{C}_8\text{mim}][\text{TF}_2\text{N}]$.

Effect of HCl concentration on UO_2^{2+} and Pu^{4+} extraction was investigated and the results are shown in Fig. 6. The D value for UO_2^{2+} increases sharply after 3 M HCl. Increase in Pu^{4+} extraction is also pronounced above 3 M HCl. These distribution values should be ascribed, for the main part, to the presence of TBA, although the pure IL also contributes to the metal extraction as discussed above. In particular, $D_{\text{U(VI)}}$ is equal to 6.5 at the highest HCl concentration used in this work in the presence of TBA, to be compared to $D_{\text{U(VI)}} = 0.42$ without it. Similarly, $D_{\text{Pu(IV)}}$ values amount to 5.38 and 0.81 with and without TBA, respectively ($[\text{HCl}] = 6 \text{ M}$). This contribution of the

Fig. 4 Effect of alkyl group of $[\text{C}_n\text{mim}][\text{TF}_2\text{N}]$ on extraction of UO_2^{2+} . Aqueous phase: 6 M HCl; organic phase: 1% v/v of the tertiary amine in RTIL. Solid lines are guide for the eye only.

Fig. 6 Distribution behaviour of UO_2^{2+} and Pu^{4+} in HCl medium by tri-*n*-butylamine/ $[\text{C}_8\text{mim}][\text{TF}_2\text{N}]$. [Amine]: 1% v/v (42 mmol L^{-1}).

ligand is also confirmed by the experiments performed at a fixed acidity (6 M HCl) and variable ligand concentration (Fig. 7), where the distribution ratio for UO_2^{2+} and Pu^{4+} in the absence of amine have been plotted for comparison purposes. By contrast, extraction data in HNO_3 medium evidence a rather limited effect of TBA : $D_{\text{U(VI)}} = 0.28$ and 0.18 with and without the ligand respectively, for 6 M HNO_3 ($D_{\text{Pu(IV)}} = 3.39$ and 3.00 , same chemical conditions). This demonstrates that the nature of the acid is a key to the extraction efficiency by the TBA. The most obvious difference between HNO_3 and HCl media is the amount of H^+ dissolving in the IL phase, from 0% (HCl) (this work) to about 6% (HNO_3).²⁵ However, this difference in H^+ values induces other differences that we suspect to be the rationale for the observed change in extraction efficiencies between HCl and HNO_3 media. In the case of HCl media (ESI[†]), the equilibrium concentrations of C_8mim^+ and Tf_2N^- ions in the aqueous phase are very low. Also, the difference between the two amounts only to a few mM: a value an order of magnitude smaller than the amine concentration used in this work. Consequently, this implies that Cl^- ions do not transfer significantly to the IL phase either. By contrast, it has been shown previously that in HNO_3 media and $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ or $[\text{C}_{10}\text{mim}][\text{Tf}_2\text{N}]$, solubilization of the Tf_2N^- ions in the aqueous phase is more important, in the range of 100 ($n = 4$) to 50 mM ($n = 10$), while the C_4mim^+ or $\text{C}_{10}\text{mim}^+$ solubilities are at least 20 mM lower than that of Tf_2N^- . Interpolation of these data for $n = 8$ implies a transfer of NO_3^- ions to the IL phase, in amounts of the order the H^+ transfer (5–6%), which is above the amine amount. In addition, HNO_3 is known to associate significantly above 3 M,³⁴ which would also allow

transfer of HNO_3 neutral entities to the IL phase. During extraction, whatever the acid used, plenty of H^+ ions may interact with the amine to form a protonated amine, R_3NH^+ , which is the potential extracting agent for U(VI) and Pu(IV) . However, in HNO_3 media, the competition with amine- HNO_3 association in the IL phase renders the amine moiety inefficient, thus leading to a difference in the metal ion extraction between HCl and HNO_3 media. In other words, solubilization of ~5–6% HNO_3 is sufficient to react with 1% amines, and therefore, amines are not free to participate in extraction of actinides.

Ligand stoichiometry of the extracted species was determined for both UO_2^{2+} and Pu^{4+} from 6 M HCl by slope analysis (Fig. 7). The corrections in the distribution ratios were made by subtracting the D_{M} values of UO_2^{2+} and Pu^{4+} by the pure IL at 6 M HCl. Results indicated the extraction of predominantly 1 : 1 (metal to ligand) species. This suggests that the extracted species contain one amine molecule. Furthermore, the dependence of UO_2^{2+} and Pu^{4+} extraction as a function of Tf_2N^- added concentration in the aqueous phase (Fig. 8) was found closer to 1 than 2 as indicated in the absence of the amines (*vide supra*). These results confirm the following extraction equilibria, involving one amine (as discussed above) and either one or two IL anions, depending on the charge of the envisioned extracted species: K_{Pu5}

Fig. 7 Ligand variation studies to determine stoichiometry of the extracted species. Aqueous phase: 6 M HCl; organic phase: tri-*n*-butylamine/ $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$; experimental data: Pu^{4+} slope: -1.25 ± 0.08 ; UO_2^{2+} slope: -1.39 ± 0.11 . Upper horizontal line: $D_{\text{U(VI)}}$ in the absence of amine; lower horizontal line: $D_{\text{Pu(IV)}}$ in the absence of amine.

Fig. 8 Distribution ratio of actinide ions by 1% v/v tri-*n*-butyl amine/ $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$; aqueous phase: 6 M HCl containing varying concentration of $\text{Li} \cdot \text{NTf}_2$ salt; Pu(IV) slope: -1.32 ± 0.13 ; U(VI) slope: -1.21 ± 0.18 .

where, K_{Mx} is the conditional extraction constant ($\text{M} = \text{U}$ or Pu ; $x = 3, 4, 5, 6$ accordingly and indicates the number of chloride ions involved). It should be noted that similar experiments could not be performed in HNO_3 medium (unlike those in HCl medium) due to poor extraction of UO_2^{2+} and Pu^{4+} in the nitric acid solution.

3.4. Modeling of actinides extraction data in the presence of amines

Considering the low UO_2^{2+} and Pu^{4+} extraction efficiency of the amines in HNO_3 medium, we performed data fitting only for the UO_2^{2+} and Pu^{4+} extraction data recorded for TBA in HCl medium. A general extraction model has previously been developed³⁵ and has proven to very satisfactorily describe liquid–liquid extraction of actinides and other metallic elements towards IL phases. In view of modeling the data of this work, we therefore rely on this model, together with the specific experimental data on Tf_2N^- and C_8mim^+ solubility in $\text{H}_2\text{O}/\text{HCl}$ medium. Details of the mathematical treatment and software procedures can be found elsewhere.³⁴ The basic assumptions of the calculations are: (i) successive complexation of actinide with Cl^- in the aqueous phase, (ii) extraction may concern any of the possible chlorocomplexes: UO_2^{2+} , UO_2Cl^+ , UO_2Cl_2 , $[\text{UO}_2\text{Cl}_3]^-$ and $[\text{UO}_2\text{Cl}_4]^{2-}$ for U and Pu^{4+} , PuCl^{3+} , $[\text{PuCl}_2]^{2+}$, $[\text{PuCl}_3]^+$, PuCl_4 , $[\text{PuCl}_5]^-$ and $[\text{PuCl}_6]^{2-}$ for Pu , (iii) extraction of positively charged species proceeds solely by the transfer of C_8mim^+ to the aqueous phase to compensate the charge, as no H^+ is present in the IL phase (see above), and extraction of negatively charged species implies transfer of Tf_2N^- anions to comply with the electro-neutrality principle, (iv) metal extraction in the absence of extracting agent simply adds to the extraction in the presence of extracting agent, and (v) the effective ligand concentration is constant, whatever are the chemical conditions. In the calculations, whenever known, the successive complexation constants have been fixed to their published thermodynamical values.³⁶ This corresponds to formation of UO_2Cl^+ ($K_1 = 1.48$) and UO_2Cl_2 ($K_2 = 0.08$), and also the formation of PuCl^{3+} ($K_1 = 63.1$). The other successive complexation constants are not known, although experiments detailed in section 3.1 clearly demonstrate that negatively charged $\text{U}(\text{vi})$ and $\text{Pu}(\text{iv})$ complexes do exist in the solution and are extracted, even in the absence of amine. Therefore, in the model, the unknown successive complexation constants were included in the overall extraction conditional constants, in order to maintain the number of unknown parameters to a reasonable value.

Another important point of the calculations concerns the increase of C_8mim^+ solubility as a function of HCl concentration (ESI^+). This trend is in line with previous data obtained for $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$.²⁶ It is important to point here that these data have been obtained in the absence of metal (U or Pu) and in the absence of TBA, thus evidencing a primary effect of the HCl concentration onto the equilibrium concentrations in the

aqueous phase. These values cannot be significantly modified owing to the very low metal concentration and were thus considered as equilibrium values in the calculations.

The collected experimental data correspond to three different chemical conditions: (i) $[\text{R}_3\text{N}] = 42 \text{ mM}$, variable HCl concentration, (ii) $[\text{HCl}] = 6 \text{ M}$, variable R_3N concentration, and (iii) $[\text{R}_3\text{N}] = 42 \text{ mM}$, $[\text{HCl}] = 6 \text{ M}$, variable LiTf_2N concentration. Adding LiTf_2N salt to acidic solutions in such biphasic systems has been shown to lead to a very complex interplay between all ions from the two phases, leading to intricate ion exchanges.²⁵ In particular, the IL solubility product is highly dependent on the initial acidity, owing to the solubility of HTf_2N in the IL phase. As a consequence, the added amount of Tf_2N^- is not equal to the equilibrium amount of this ion, while the latter, that was not measured, would be needed in the calculation, instead of the former. We thus excluded from the fits the last series of data. Another consequence of this effect is that the slope analysis that has been performed (Fig. 3, 7 and 8) is distorted as compared to reality, in a way that cannot be easily quantified. The slopes thus derived are just indicative of the process at work and do not provide a quantitative basis.

First, various trials have been performed in order to understand and evaluate the contributions of the individual extractions of the species present in the aqueous phase. For both $\text{U}(\text{vi})$ and $\text{Pu}(\text{iv})$ data, assuming extraction of any of the positively charged species leads to a decrease in the D values as a function of HCl , which is in disagreement with the experimental trend. This decrease is mainly due to the large impact of the C_8mim^+ values onto the extraction conditional constants but also to the fact that by increasing the HCl value, positively charged species are eventually transformed into a neutral or negatively charged species and thus, disappear from the speciation. As a consequence, in a second step, we considered only extraction of the neutral and negatively charged species. For each metal, the data D vs. HCl and D vs. $[\text{TBA}]$ have been fitted together. Table 3 gathers the conditional extraction constants, K_{Mx} , and the stoichiometric coefficients for the ligand, p_{Mx} , corresponding to the dotted lines in Fig. 6 and the fitted lines in Fig. 7. For $\text{U}(\text{vi})$, the conditional extraction constant for $[\text{UO}_2\text{Cl}_3]^-$ is lowered to zero whatever its starting values. Imposing extraction of $[\text{UO}_2\text{Cl}_4]^{2-}$ alone gives a very good fit (Fig. 6 and 7), with a ligand stoichiometry equal to 1.4, in excellent agreement with the result derived from the slope analysis (Fig. 7). Allowing extraction of UO_2Cl_2 in addition to that of $[\text{UO}_2\text{Cl}_4]^{2-}$ does not improve the quality of the fit. It may be noted that the extraction

Table 3 Values of the fitting parameters for $\text{Pu}^{4+}/\text{HCl}/[\text{TBA}]/[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$ and $\text{UO}_2^{2+}/\text{HCl}/\text{TBA}/\text{C}_8\text{mim} \cdot \text{Tf}_2\text{N}$. Values in parenthesis correspond to uncertainties for a 5% increase in χ^2 values

Metal ion	K_{Mx}	p_{Mx}	χ^2
UO_2^{2+}	$3 \times 10^{-5} (\pm 1 \times 10^{-5})$ $x = 4$	$4.4 (\pm 0.2)$ $x = 4$	0.025
Pu^{4+}	$3 \times 10^{-6} (\pm 1 \times 10^{-5})$ $x = 6$	$0.8 (\pm 0.6)$ $x = 6$	0.31

of $[\text{UO}_2\text{Cl}_4]^{2-}$ was already evidenced in the absence of TBA (section 3.2). Similarly, for $\text{Pu}(\text{vi})$, the conditional extraction constant for $[\text{PuCl}_5]^-$ is lowered to zero by the fitting procedure whatever the conditions. A very good fit is obtained with extraction of $[\text{PuCl}_6]^{2-}$ alone (Fig. 6 and 7) with a ligand stoichiometry equal to 0.80. This value is somehow different from that obtained with the slope analysis method but the uncertainty on this value is quite high (see Table 3, where errors on the parameter values are calculated for an increase of 5% of the χ^2 value). This may be ascribed, in part, to the limited number of experimental data points available. Allowing the extraction of PuCl_4 , in addition to that of $[\text{PuCl}_6]^{2-}$, does not improve the quality of the fit. These modeling results are in line with the general model previously proposed.²² In particular, they confirm the role of anion exchange at high acidity, which was not considered in another publication.²³

4. Conclusions

Our results show that in the absence of extracting agent, in both HCl and HNO_3 media, for both $\text{U}(\text{vi})$ and $\text{Pu}(\text{iv})$, extraction proceeds at high acidic conditions according to an anion exchange mechanism, involving the NTf_2^- anion of the IL. Although these results are limited in terms of ILs nature and chosen metal, they seem to indicate that anion exchange is unavoidable. Addition of amines does not significantly hampers the anion exchange mechanism, which is still occurring without any significant contribution of neutral species. Again, these results are limited in terms of investigated systems but they indicate that ILs strongly favor charged species rather than neutral ones. Therefore, in order to tackle the problem of pollution of the aqueous phase at high acidities, a possibility would be to use sacrificial anions, in a way similar to the attempts already made with some success with sacrificial cations at low acidities.³⁷ Another idea would be to use IL based on low cost anions instead of the NTf_2^- . For example, trihexyl-(tetradecyl)phosphonium chloride ($\text{P}_{66614}\text{Cl}$) is a water-immiscible IL. On a very different perspective, one should try to understand why amines are almost inefficient in HNO_3 medium, while they are efficient in HCl . This may be due to partial protonation of the amine in the IL phase, because HNO_3 solubilizes in IL phase while HCl does not. Additional experiments along these lines are under progress in our laboratories.

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