



A highly efficient solvent system containing TODGA in room temperature ionic liquids for actinide extraction

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ABSTRACT

Extraction behavior of several actinide ions viz. Am^{3+} , Pu^{4+} and UO_2^{2+} was investigated using N,N,N',N' -tetra-*n*-octyl diglycolamide (TODGA) as extractant in three different room temperature ionic liquids (RTIL), viz. $\text{C}_4\text{mim}^+ \cdot \text{NTf}_2^-$, $\text{C}_6\text{mim}^+ \cdot \text{NTf}_2^-$, and $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ as the diluents. The solvent systems containing TODGA in the RTILs were found to result in higher distribution ratios for all the actinides (trivalent, hexavalent, tetravalent) as compared to that containing *n*-dodecane as the diluent. Moreover, the distribution ratio values of the metal ions at lower acidities were found to decrease with increasing feed nitric acid concentration. Extraction was found to be independent of the anion of the aqueous phase. Mechanism of extraction of the actinides was found to be different compared to *n*-dodecane, molecular diluent. Cation-exchange was found to be the mechanism of extraction followed in RTILs. Effect of carbon chain length of alkyl groups of the RTILs conclusively proved the mechanism of extraction of the actinides by TODGA. Nature of extracted species was also found to differ from *n*-dodecane. Stripping studies were carried out using complexing agents such as EDTA, DTPA in guanidine carbonate or a buffer mixture.

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1. Introduction

Room temperature ionic liquids (RTILs) have been used in a variety of investigations for diverse purposes like organic synthesis, catalysis, electrochemical purposes, etc., for more than a decade now [1–4]. Their properties, such as non-inflammability, non-measurable vapor pressure, high thermal stability, make them environmental friendly and suitable 'green' alternatives to the commonly known organic solvents. Moreover, physical characteristics such as water immiscibility, viscosity and polarity etc. are tunable depending on the cations and anions [5,6]. Though chemistry of main group elements are well studied in ionic liquids, there is a growing interest in understanding the chemistry of lanthanides and actinides in this interesting medium [7–9]. A more challenging application of RTIL has been in metal ion extraction which has interesting consequences in separation science [10–15]. Interesting revelations of these studies include insights into their extraction mechanism which are drastically different from those observed with the conventional solvent extraction of metal ions [16]. A recent review summarizes the application of ionic liquids in separation science involving advanced nuclear fuel cycle [17].

Some of the early work in this direction includes extraction of radio-caesium and radio-strontium from acidic radioactive wastes

[18,19]. Extraction of Cs(I) using a calix crown ether bis(2-propyloxy)calix[4]crown-6 (BPC6) in ionic liquids $\text{C}_n\text{mim}^+ \cdot \text{NTf}_2^-$ have been reported by Xu et al. [19]. They have proposed a dual exchange mechanism for the extraction of Cs by the calix-crown ether. Luo et al. [20] have reported a task specific ionic liquid containing an aza-crown ether fragment for recovery of fission products from aqueous phase. On the other hand, extraction of actinide ions is rather less studied and there are only a handful of reports are available in this area [14,21–23].

The ionic liquids are generally non-coordinating and if contacted with the aqueous phases containing the metal ions, no significant metal ion extraction is observed. The metal ion extractability in the ionic liquid medium can be increased by the addition of organic extractants capable of forming organophillic polar complexes with the metal ions stabilized in the RTIL phase. However, even when the metal ions form organophillic complexes in ionic liquid medium, the partitioning equilibria do not necessarily be the same with those found in conventional liquid–liquid extraction with molecular diluents. The equilibria depend largely on the combination of cations and anions. The organic ligand also plays an important role in determining the equilibria. There are various examples of application of the RTILs in separation of actinides, lanthanides and fission products in the literature. Comparable extraction behavior of U(VI) from nitric acid medium was reported by Giridhar et al. [21], employing tri-*n*-butyl phosphate (TBP) in *n*-dodecane and in $\text{C}_4\text{mim}^+ \cdot \text{PF}_6^-$ (1-*n*-butyl-3-methylimidazolium

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hexafluorophosphate) as the diluents. Cocalia et al. [14], reported identical extraction behavior and coordination of actinides in *n*-dodecane and $C_{10}mim^+ \cdot NTf_2^-$ (1-*n*-decyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide) diluents for dilakylphosphoric or dialkylphosphinic acids as the extractants. Ouadi et al. [22,23], reported task specific ionic liquids containing 2-hydroxybenzylamine and TBP moiety for the extraction of Am(III) and U(VI), respectively.

N,N,N',N'-tetraoctyl diglycolamide (TODGA) has been reported as one of the most promising extractants for 'Actinide Partitioning' [24–26] from High Level Waste (HLW) which requires the preferential extraction of trivalent actinides such as Am(III) and Cm(III) from moderate acidic feed conditions such as 3–4 M HNO_3 . The reported unusually high preference for trivalent actinides over the hexa- and tetra-valent actinides has been attributed to the favorable extraction of the trivalent actinide ions into reverse micelles formed in non-polar diluents constituted by four TODGA molecules [27]. Its solvent extraction properties for the actinides, lanthanides and fission products have been reported in detail using *n*-dodecane as the diluent [24].

Recently, the extraction behavior of trivalent lanthanides have been reported using TODGA in an RTIL diluent, viz. alkyl methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_nmim^+ \cdot NTf_2^-$) [28]. It was reported that the extraction of the lanthanides by TODGA was greatly enhanced in the presence of the RTIL. The extraction mechanism was also found to be different compared to that reported while using *n*-dodecane as the diluent. On the other hand, Shen et al., have investigated the extraction of uranyl ion using an analogous tetrabutyl diglycolamide and dimethyl dibutyl diglycolamide in ionic liquids [29]. However, in view of high water solubility of these diglycolamides, their extraction data have limited applications. We have also carried out studies involving the extraction of Am^{3+} using TODGA and a diglycolamide functionalized calixarene in ionic liquids such as $C_4mim^+ \cdot PF_6^-$, $C_6mim^+ \cdot PF_6^-$ and $C_8mim^+ \cdot PF_6^-$ [30]. However, studies with ionic liquids with PF_6^- counter anions have been reported to be unstable at moderate to high concentrations of nitric acid concentration [31] suggesting the need for carrying out studies with ionic liquids containing other types of counter anions such as NTf_2^- and Cl^- . Moreover, there is no systematic study carried out using the tri-, tetra- and hexa-valent actinides using TODGA in ionic liquids.

The present work reports the extraction of Am^{3+} , Pu^{4+} and UO_2^{2+} employing TODGA as the extractant in several $C_nmim^+ \cdot NTf_2^-$ as well as $C_nmim^+ \cdot Cl^-$ diluents where '*n*' varies from 4 to 8 and this is the first ever comparative extraction study of the tri-, tetra- and hexa-valent actinide ions using the TODGA – RTIL extraction system. Various factors like the kinetics of extraction, the effect of the feed nitric concentration, the effect of alkyl chain length, the mechanism of extraction, the nature of the extracted species, etc. have been investigated in detail.

2. Experimental

2.1. Materials

N,N,N',N'-tetraoctyl diglycolamide (TODGA) was synthesized by a previously reported procedure and was characterized by NMR, IR and elemental analysis [26]. Ionic Liquids ($C_nmim^+ \cdot NTf_2^-$, and $C_nmim^+ \cdot Cl^-$, where *n* = 4, 6, 8) were procured from Io-Li-Tec, Germany and were used as received. ^{241}Am , ^{233}U and Pu (mainly ^{239}Pu) tracers were purified from associated radiotracer impurities by ion-exchange methods described elsewhere [32]. Stock solutions of the radiotracers were made in dilute nitric acid after checking the purity by alpha spectrometry. All the other reagents were of AR grade and were used without further purification.

Assaying of ^{233}U and Pu was done by alpha-liquid scintillation counting using a toluene based scintillator cocktail whereas that of ^{241}Am was done by gamma counting using a NaI(Tl) well type scintillation counter.

2.2. Solvent extraction studies

The extractant solutions having the desired concentrations of TODGA in *n*-dodecane as well as in the ionic liquids as diluents were agitated with an equal volume of aqueous solutions spiked with the requisite radiotracers (^{241}Am , ^{233}U or ^{239}Pu) in a rotary thermostated water bath for an hour at 25.0 ± 0.1 °C. Usually, the organic solutions were pre-equilibrated with the aqueous phase prior to the actual experiments containing the radiotracers. The two phases were then centrifuged and assayed by taking suitable aliquots from the aqueous phase (before the phases were mixed and after the equilibration was over) followed by counting using a liquid scintillation counter. In view of viscosity of the ionic liquid phases, the distribution ratio (*D*) is calculated from the aqueous phase counts and is defined as [33]:

$$D = \frac{(C_i - C_f) \cdot \text{Volume of aqueous phase}}{C_f \cdot \text{Volume of organic phase}} \quad (1)$$

where C_i and C_f are the initial and final counts of the aqueous phase in the tubes. The data reported in this paper are average of triplicate measurements and the reproducibility in mass balance was $\pm 5\%$.

3. Results and discussion

3.1. Kinetics of extraction

One of the important parameters in the studies involving RTILs is the role of extraction kinetics. This is evident from the fact that the ionic liquids are usually high viscosity liquids and hence the mass transfer was expected to be slower than that expected in commonly employed organic diluents such as *n*-dodecane and kerosene. The kinetics of extraction of the actinides in different valency states, i.e., Am^{3+} , Pu^{4+} and UO_2^{2+} , were investigated using 1.0×10^{-2} M TODGA in $C_8mim^+ \cdot NTf_2^-$. The aqueous phase acidity was maintained at 1 M HNO_3 during the all the extraction kinetics experiments and the results are presented in Fig. 1. It is evident from the figure that the kinetics of extraction of Am(III) is faster compared to U(VI) and

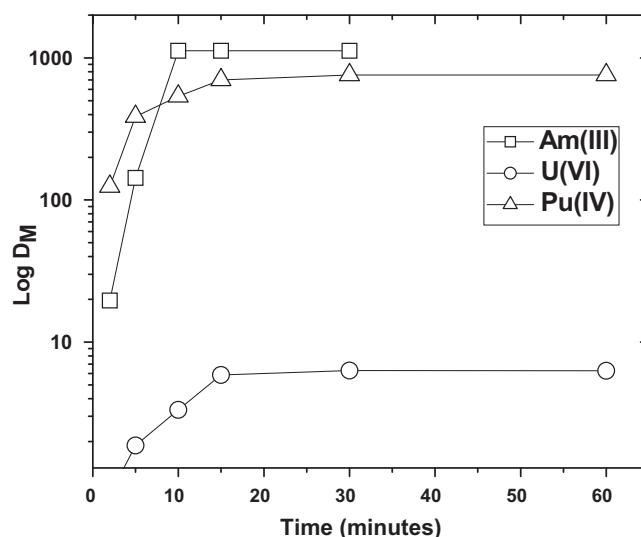
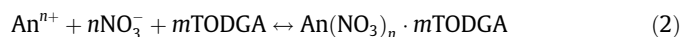


Fig. 1. Kinetics of extraction of U(VI), Pu(IV) and Am(III) using TODGA in $C_8mim^+ \cdot NTf_2^-$ as extractant; [TODGA] = 1.0×10^{-2} M, $[HNO_3]$ = 1 M.

Pu(IV). It took about 10 min to attain equilibrium extraction for Am(III) whereas for U(VI) and Pu(IV) the time taken to attain equilibrium was about 30 min. It is quite interesting to note that in the presence of *n*-dodecane as the diluent, 0.1 M TODGA was required for quantitative extraction of Am^{3+} [26] whereas in presence of $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ as the diluent, the concentration of TODGA required for quantitative extraction was significantly lower at 1.0×10^{-2} M. Therefore, with RTIL as the diluent there is a significant increase in the extractability of the actinides while TODGA was used as the extractant. Similar behavior with respect to enhancement of extraction performance of TODGA with respect to lanthanides was reported by Shimojo et al. [28].

3.2. Effect of aqueous phase acidity

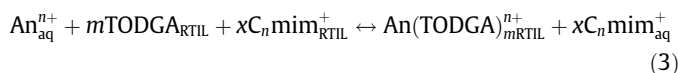
Aqueous phase acidity plays an important role in the extraction of actinides into neutral extractant like TODGA. In cases where *n*-dodecane was used as the diluent, the mass transfer of actinides takes place through a nitrate ion assisted complexation mechanism. The mechanism of actinide extraction in solvent systems containing *n*-dodecane as the diluent is given below:



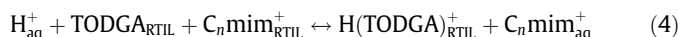
For this type of extraction mechanism, increasing the feed nitric acid concentration causes an increase in extraction of the actinides [26] due to an effective increase in nitrate ion concentration (which favors formation of neutral nitrate complex of the actinides) with increasing feed nitric acid concentration. Studies on the extraction of lanthanides have indicated that the mechanism of transfer of lanthanides into the TODGA–RTIL solvent system is entirely different [28]. Cation-exchange has been proved as the mechanism of transfer. For such an extraction mechanism, increasing aqueous phase acidity causes a decrease in the extraction of the actinides.

To understand the mechanism of mass transfer of actinides into the TODGA– $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ solvent system, we investigated the effect of aqueous phase nitric acid concentration on the extraction of the actinides. It is important to note that in the absence of TODGA, $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ itself showed negligible extraction of the actinides at very low acidity which was found to increase marginally with increasing feed acidity. On the other hand, the extraction behavior was entirely different in the presence of TODGA in studies carried

out at varying feed nitric acid concentration. As shown in Fig. 2, increasing the aqueous phase nitric acid concentration caused a sharp decrease in the extraction of the actinides where 1.0×10^{-2} M TODGA was employed with $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ as the diluent. The results suggested that the extraction of actinides by TODGA does not follow ion-pair extraction of the neutral nitrate complex of the actinides in RTIL as the diluent as found for the *n*-dodecane solvent system. Though TODGA is a neutral extractant, its extraction ability was found to decrease under highly acidic condition in RTILs as the diluent. Co-extraction of proton by TODGA in the RTIL diluent has been reported as a reason for such type of behavior [28]. The trend with respect to extractability of different oxidation states of actinides using TODGA as the extractant in $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ as the RTIL was: $\text{Am(III)} > \text{Pu(IV)} \gg \text{U(VI)}$. The trend was found to be similar for the molecular diluent, *n*-dodecane [25]. Apart from significantly higher *D* values with the RTILs as compared to extraction systems where *n*-dodecane was used as the diluent, the separation factor (S.F.) values (defined as the ratio of the distribution ratio values) appeared to be more favorable in the RTIL based solvent system as compared to the TODGA solvent containing *n*-dodecane as the diluent. For example, with $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ as the diluent, $\text{S.F.}_{\text{Am/U}} = 562$ at 0.5 M HNO_3 decreased sharply to 205 when 3 M HNO_3 was used as the feed. These values are still significantly higher as compared to the $\text{S.F.}_{\text{Am/U}} = 7.4$ for *n*-dodecane when 0.5 M HNO_3 was used as the aqueous phase. The impressive separation behavior of Am and U is attributed to significant enhancement in Am(III) extraction in RTIL medium as compared to that observed in U extraction. As is shown below, the extraction mechanism is free from any dependence of nitrate anion:



Though nitrate anion is not expected to have any effect on the extraction of the metal ions and hence the S.F. value, the decrease is attributed to the change in TODGA concentration at higher acidities due to extraction of nitric acid as per the following extraction equilibrium:



Further, as shown in Table 1, the $\text{S.F.}_{\text{Am/U}}$ values increases with increasing carbon chain length of the RTIL though the individual *D* values decreased. On the other hand, the $\text{S.F.}_{\text{Pu/U}}$ value remained nearly constant for the three RTILs used. The change in separation behavior is attributed to the different extent the metal ions are extracted in view of the aqueous solubility of the C_nmim^+ cations.

3.3. Mechanism of extraction

As discussed earlier, there is drastic enhancement of extraction of actinides by TODGA in the presence of the RTIL in comparison to *n*-dodecane, a molecular diluent. This is due to the fact the extraction of actinides by TODGA takes place by different mechanisms in *n*-dodecane and RTIL. In *n*-dodecane, the extraction of actinides from nitric acid medium takes place via solvation of neutral actinide-nitrate complex by TODGA (Eq. (2)). For such type of mechanism, concentration of nitrate ion plays an enhancing role and so the extraction increases with increasing nitric acid concentration. On the other hand, in RTIL based extraction of metal ions by neutral extractants there has been report of different types of extraction mechanism for different types of extractants. Dietz and Dzielawa [16], have reported that extraction of Cs^+ and Sr^{2+} by crown ethers in RTILs take place via a cation exchange mechanism where the metal-crown ether complex is exchanged for cation (C_nmim^+) of the RTIL. On the other hand, the mechanism of extraction of U(VI)

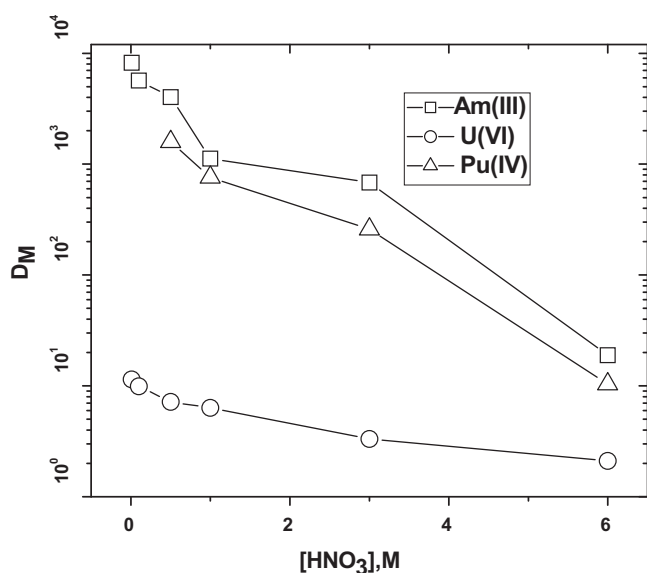


Fig. 2. Effect of feed nitric acid concentration on the extraction of actinides using TODGA in $\text{C}_8\text{mim}^+ \cdot \text{NTf}_2^-$ as extractant; $[\text{TODGA}] = 1.0 \times 10^{-2}$ M.

Table 1Comparative distribution ratio (*D*) and separation factor values (S.F.) of several actinide ions using room temperature ionic liquid and *n*-dodecane as the diluents.^a

Metal ion	<i>n</i> -Dodecane		$C_4mim^+ \cdot NTf_2^-$		$C_6mim^+ \cdot NTf_2^-$		$C_8mim^+ \cdot NTf_2^-$	
	<i>D</i>	S.F. ^b	<i>D</i>	S.F. ^b	<i>D</i>	S.F. ^b	<i>D</i>	S.F. ^b
Am ³⁺	157	31.3	871	116	760	130	682	205
Pu ⁴⁺	10.6	2.11	588	78.2	415	70.8	258	77.5
UO ₂ ²⁺	5.02	–	7.52	–	5.86	–	3.32	–

^a TODGA concentrations in *n*-dodecane solutions was 0.1 M while that in RTIL solutions was 1.0×10^{-2} M. Aqueous feed: 3 M HNO₃.^b Separation factor values are with respect to U.

by TBP in RTIL is similar to that observed in conventional organic diluents, i.e., solvation of the ion-pair as reported by Giridhar et al. [21]. However, the extraction of metal ions by CMPO in RTIL was reported to follow cation-exchange mechanism in another report [34]. Similar to the extraction mechanism reported for CMPO, the extraction mechanism for trivalent lanthanides has been reported to be that of cation-exchange type in RTIL with TODGA as the extractant [28].

In order to elucidate the extraction mechanism of actinides with TODGA in RTIL as the solvent, experiments were carried out to understand the effect of anions on the extraction of Am(III). For this purpose HNO₃ was replaced by H₂SO₄ as feed acid and extraction of Am(III) was carried out using TODGA as the extractant in *n*-dodecane and $C_8mim^+ \cdot NTf_2^-$ as the diluents. The trend of distribution coefficients in different diluents with varying concentration of H₂SO₄ is shown in Fig. 3. It is clear from the figure that extraction performance is significantly affected (as compared to those seen with HNO₃) for *n*-dodecane but it remains more or less unaffected in RTILs as the diluent. The trend for *n*-dodecane is expected keeping in mind the extraction mechanism of Am(III) for TODGA, where anion plays the role of counter-ion to form a neutral complex with Am(III) and thus the nature of the anion affects the extraction performance in a significant way. The absence of anion effect on the extraction performance of TODGA for Am(III) in RTILs as diluents suggested a different mechanism of extraction compared to *n*-dodecane which has been shown in Eq. (3). For the ion-exchange mechanism to be valid, the distribution-coefficient values for the actinide ions should decrease with increasing concentration of C_nmim^+ ion in the aqueous phase based on equilibrium shift. Hence, distribution studies of the actinides were carried out at different concentrations of C_nmim^+ in the aqueous phase employing water soluble $C_nmim^+ \cdot Cl^-$. As evident

from Figs. 4–6, the distribution coefficient of all the three actinides, viz, U(VI), Pu(IV) and Am(III) decreased with increasing C_nmim^+ concentration in the aqueous phase. This trend was similar for all three RTILs studied in the current study but distribution coefficient values were found to be independent of C_nmim^+ concentration for *n*-dodecane as diluent. Thus the extraction of actinides by TODGA in RTILs as diluent from nitric acid medium can be conclusively said to take place via cation-exchange mechanism analogous to that reported for lanthanides [28].

Further evidence of the above mentioned mechanism was found from variation of carbon chain length of alkyl group of the RTILs. Three different RTILs were tested as diluent for the extraction of actinides employing TODGA as the extractant, viz, *n*-butyl, *n*-hexyl and *n*-octyl. With increasing carbon chain length of the alkyl group, the hydrophobicity of the RTIL decreases causing a decrease in solubility of the diluent in aqueous solution. This decreasing solubility of the RTIL makes exchange of actinide ions for C_nmim^+ ion difficult causing a decrease in the distribution coefficient values of the actinides in TODGA. This trend was observed for all the three actinide ions at all the nitric acid concentrations as evident from Figs. 7–9. These data also support the extraction of actinides by TODGA in RTILs as diluent from nitric acid medium by a cation-exchange mechanism.

3.4. Nature of the extracted species

In order to determine the stoichiometry of the extracted complexes using the TODGA – RTIL solvent systems, slope analysis method was used where *D* values of the actinide ions were plotted as a function of the equilibrium concentration of TODGA at 3 M

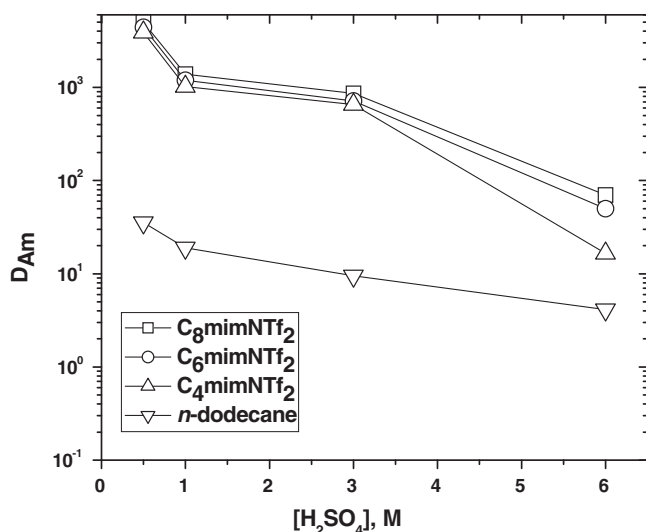


Fig. 3. Effect of H₂SO₄ concentration on the extraction of Am(III) by TODGA in different diluents: [TODGA] = 1.0×10^{-2} M.

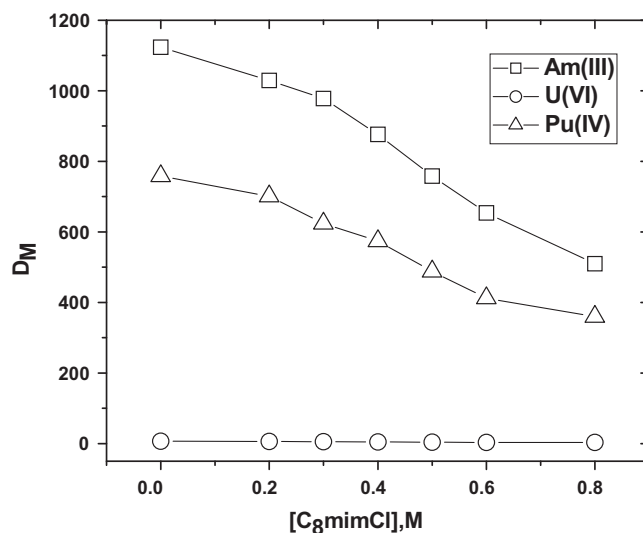


Fig. 4. Effect of *C*₈mimCl concentration on the extraction of actinides by TODGA in *C*₈mim⁺ · NTf₂[−]: [TODGA] = 1.0×10^{-2} M, [HNO₃] = 1 M.

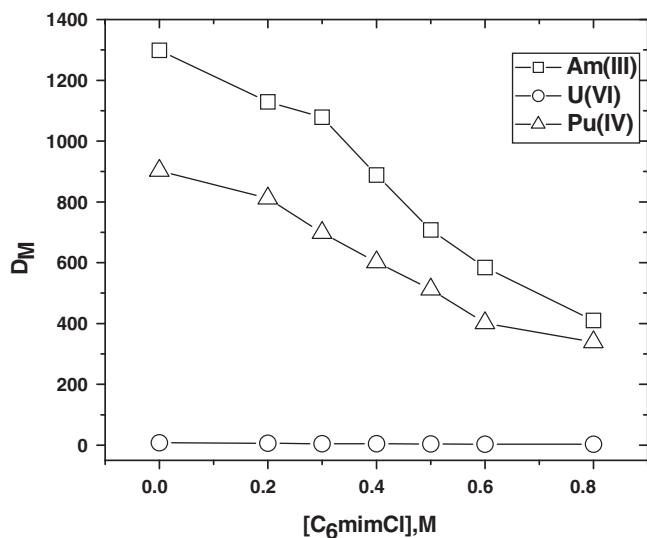


Fig. 5. Effect of C₆mimCl concentration on the extraction of actinides by TODGA in C₆mim⁺ · NTf₂⁻; [TODGA] = 1.0 × 10⁻² M, [HNO₃] = 1 M.

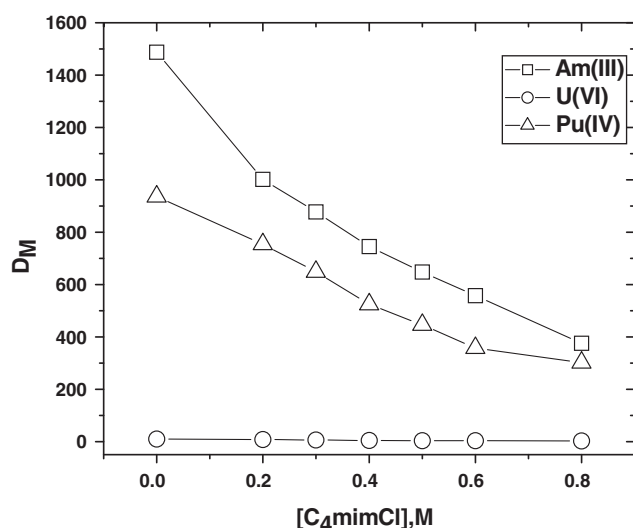


Fig. 6. Effect of C₄mimCl concentration on the extraction of actinides for TODGA in C₄mim⁺ · NTf₂⁻; [TODGA] = 1.0 × 10⁻² M, [HNO₃] = 1 M.

HNO₃ (Supplementary material). The natures of extracted species in *n*-dodecane as the diluent have been reported in previous reports [26,35,36]. Table 2 gives the slope values for the actinide extraction studies in the three RTILs, viz. C₄mim⁺ · NTf₂⁻, C₆mim⁺ · NTf₂⁻ and C₈mim⁺ · NTf₂⁻ using TODGA as extractant. As evident from the Table, Am(III) forms a mixture of di- and tri-solvate in all the three RTILs whereas in *n*-dodecane it was reported to be tetra solvate [25]. This is in sharp contrast to the tri-solvate species reported by Shimojo et al. [28] for the extraction of trivalent lanthanides using TODGA. U(VI) was found to form a mono-solvate in both *n*-dodecane as well as in the RTILs. On the other hand, Pu(IV) which forms a tri-solvate in *n*-dodecane was found to form a mixture of mono- and di-solvate in the RTILs. Thus when *n*-dodecane was replaced by the RTILs as the diluent, Am(III) and Pu(IV) formed different species whereas U(VI) formed a similar complex. Change of carbon chain length did not have any effect on the stoichiometry of the extracted complex. Thus, based on above discussions the extraction of actinides can be represented as below:

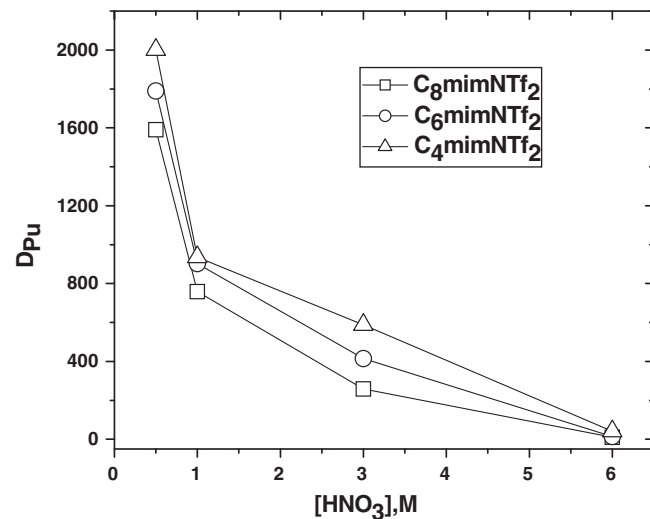


Fig. 7. Extraction of Pu(IV) by TODGA in C_nmim⁺ · NTf₂⁻ (n = 4, 6, 8) at different feed nitric acid concentrations.

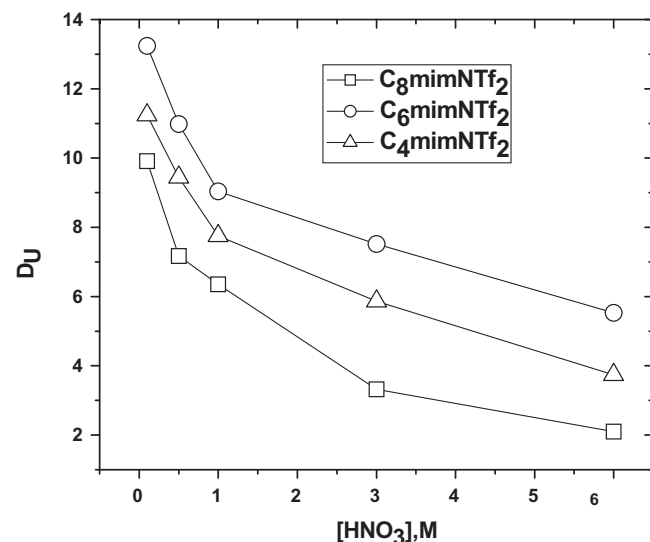
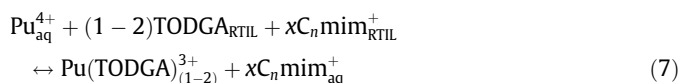
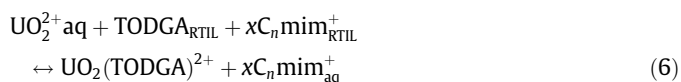
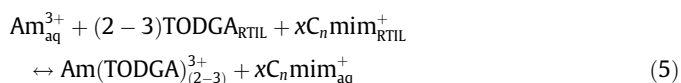


Fig. 8. Extraction of U(VI) by TODGA in C_nmim⁺ · NTf₂⁻ (n = 4, 6, 8) at different feed nitric acid concentrations.



where, *x* is anywhere between 0.5 and 1 for Am³⁺ ion extraction as found out from Figs. 4–6 (slopes of the same plots after replotting in log–log format). Similar behavior is expected for U and Pu extraction as well. Extraction of similar mixed species was reported in an earlier publication with molecular diluents [23]. This number of TODGA molecules associated with the extracted species indicates that the complexes may contain 2–3 molecules of water in the inner coordination sphere. This is in view of the fact that nitrate ion

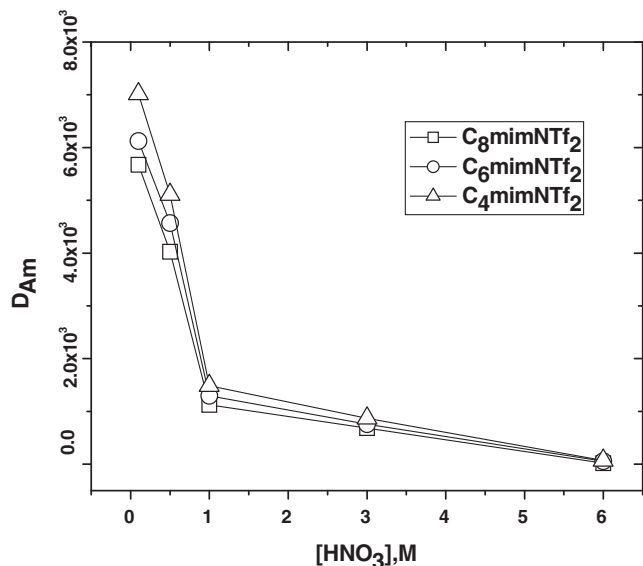


Fig. 9. Extraction of Am(III) by TODGA in $C_n\text{mim}^+ \cdot \text{NTf}_2^-$, ($n = 4, 6, 8$) at different feed nitric acid concentrations.

Table 2

Slope values of TODGA concentration variation studies for actinide ion extraction at 3 M HNO_3 .

An^{n+}	$C_8\text{mim}^+ \cdot \text{NTf}_2^-$	$C_6\text{mim}^+ \cdot \text{NTf}_2^-$	$C_4\text{mim}^+ \cdot \text{NTf}_2^-$
Am^{3+}	2.44 ± 0.09	2.51 ± 0.08	2.43 ± 0.08
UO_2^{2+}	0.99 ± 0.11	0.97 ± 0.07	0.85 ± 0.12
Pu^{4+}	1.39 ± 0.12	1.39 ± 0.13	1.41 ± 0.11

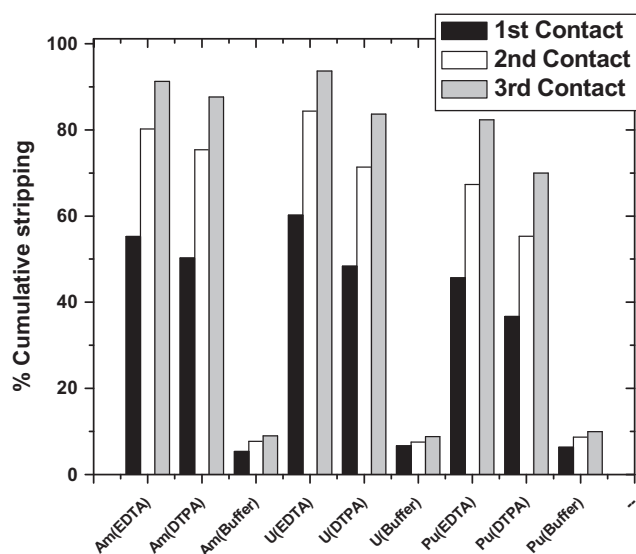


Fig. 10. Stripping studies of the actinide ions using 0.05 M EDTA + 1.0 M guanidine carbonate, 0.05 M DTPA + 1.0 M guanidine carbonate and buffer mixture (0.1 M citric acid + 0.4 M formic acid + 0.4 M hydrazine hydrate).

dependence on the extraction of the actinide ions was not observed. Fractional number of ligand molecules indicates extraction of mixed species. Similar species were reported for Am(III) extraction in our previous study using $C_n\text{mim}^+ \cdot \text{PF}_6^-$ as the ionic liquids. Lower number of ligand molecules in the extracted species as compared to the *n*-dodecane diluent system may be attributed to higher dielectric constant of the ionic liquid medium [37]. Similar lower number of

extracted species was also observed when higher dielectric constant diluents were employed [38,39].

3.5. Stripping studies

The stripping studies of the actinides were carried out using three strippants which have been employed by Nakashima et al. [40], for the stripping of the trivalent lanthanide ions from the CMPO – ionic liquid extracts. The results are presented in Fig. 10 and suggest that unlike the CMPO – RTIL extraction system, for which the buffer mixture of 0.1 M citric acid, 0.4 M formic acid and 0.4 M hydrazine hydrate was found to be the most efficient, was not good enough as a strippant for the TODGA – RTIL extraction system. This was partly due to the large concentration of nitric acid co-extraction and also due to weaker actinide extraction (as compared to the TODGA – RTIL extraction system) by the CMPO–RTIL system. As indicated in Fig. 10 and 0.05 M EDTA in 1.0 M guanidine carbonate appeared to be the most effective strippant for all the three metal ions and in three contacts, the cumulative % stripping were about 91%, 93% and 82% for Am, U and Pu, respectively. This also suggests that quantitative stripping is possible by suitable increasing the number of stripping stages.

4. Conclusions

Solvent Extraction studies of An^{n+} ions using TODGA as the extractant was carried out in different room temperature ionic liquid diluents. Invariably the extraction of the metal ions was much favoured in the RTIL system as compared to the conventional molecular diluents. However, the metal ion extraction was found to decrease with increasing feed nitric acid concentration. Mechanism of extraction of the actinides was found to be cation-exchange similar to those reported in several extraction systems involving RTILs as the diluent. Carbon chain length of alkyl group of the RTILs was found to play an important role on the extraction performance of TODGA and was also affected the separation factors. Nature of species was found to be different for the RTILs than those reported previously with *n*-dodecane. Though stripping of the metal ions appear difficult in view of significantly high *D* values in the entire range of acidity, use of complexing agents like EDTA and DTPA in guanidine carbonate appear promising.

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