Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 6970

www.rsc.org/dalton

PAPER

A highly efficient solvent system containing functionalized diglycolamides and an ionic liquid for americium recovery from radioactive wastes†

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Received 7th December 2011, Accepted 23rd March 2012
DOI: 10.1039/c2dt12364a

Three room temperature ionic liquids (RTILs), *viz.* $C_4mim^+\cdot PF_6^-$, $C_6mim^+\cdot PF_6^-$ and $C_8mim^+\cdot PF_6^-$, were evaluated as diluents for the extraction of Am(III) by *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA). At 3 M HNO_3, the D_{Am}-values by 0.01 M TODGA were found to be 102, 34 and 74 for $C_4mim^+\cdot PF_6^-$, $C_6mim^+\cdot PF_6^-$ and $C_8mim^+\cdot PF_6^-$, respectively. The extraction of Am(III) decreased with increasing feed acidity for all three diluents, indicating an ion exchange mechanism for the extraction. The stoichiometry of the extracted species suggested that two TODGA molecules were associated with Am(III) during the extraction for all three RTILs and the conditional extraction constants have been determined. The D_M-values for different metal ions followed the order: 75 (Am(III)) > 30.7 (Pu(IV)) > 3.9 (Np(IV)) > 1.19 (Pu(VI)) > 0.52 (U(VI)) > 0.12 (Cs(I)) > 0.024 (Sr(II)). The distribution behaviour of Am(III) was also studied with a recently synthesized calix[4]arene-4DGA (C4DGA) extractant dissolved in $C_8mim^+\cdot PF_6^-$. Using this extractant diluent combination, the D_{Am}-value was 194 at 3 M HNO_3 using 5×10^{-5} M C4DGA, suggesting a very high distribution coefficient at very low extractant concentrations. The stoichiometry of the extracted species containing Am was found to be 1 : 2 (M : L) in $C_8mim^+\cdot PF_6^-$. The thermodynamics of the extraction was also studied for both extractants in $C_8mim^+\cdot PF_6^-$. The use of RTILs gives rise to significantly improved extraction properties than the commonly used *n*-dodecane and an unusual increase in separation factor values was seen for the first time which can lead to selective separation of Am from wastes containing a mixture of U, Pu and Am.

1. Introduction

Nuclear energy is gaining an important role in worldwide increasing energy demand. During reprocessing of nuclear fuel, the strategy followed is partitioning of minor actinide and long lived fission products followed by transmutation. The exploration of various separation routes has been driven by the need for technology to successfully process the large quantity of high level nuclear wastes. Solvent extraction is a widely used technique for selective separation in addition to pre-concentration of metal ions in biphasic water–organic solvent systems. Extractants such as CMPO (carbamoyl methyl phosphine oxide), malonamide, TRPO (trialkyl phosphine oxide), DIDPA (diisodecyl phosphoric acid) and DGA (diglycolamide) are well known for the extraction of trivalent actinides from a moderately acidic medium.[1–5] Use of CMPO leads to the generation of large amounts of secondary waste, while malonamide-based extractants are prone to third phase formation.[6] In this context diglycolamide-based extractants are found to be environmentally benign and do not form a third phase. Among the diglycolamide-based extractants TODGA (*N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide) was found to be one of the most promising extractants for the separation of trivalent actinides from a moderately acidic aqueous feed.[7,8] Further, a recent study has indicated that a mixture of $CyMe_4BTBP$ and TODGA can be used for direct extraction of the trivalent actinides which is termed as 1-cycle SANEX (selective actinide extraction) process.[9]

It has been reported that the extraction mechanism with TODGA involves reverse micelle formation with four TODGA molecules,[10] which results in unusually high extraction coefficients for the trivalent actinide ions as compared to the tetra- and hexavalent actinide ions.[8] The usual extraction tendency for actinide ions with the common ‘actinide partitioning’ reagents such as CMPO, malonamides, *etc.*, is that tetravalent ions are more extracted than the hexavalent ions, which in turn are more extracted than the trivalent actinide ions. As diluents have a very important role in the formation of reverse micelles, the extraction trends and also the species extracted vary significantly with the nature of the diluent. To exclude diluent effects, the ligating sites can be grouped together on a molecular platform. Since four diglycolamide molecules are required for complexation, calix[4]arene is the ideal platform. It is known

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2dt12364a

that calixarenes appended with actinide specific ligating sites such as CMPO give rise to more efficient metal ion binding and extraction based on a co-operative complexation mechanism.[11] We have synthesized diglycolamide functions preorganized at the C-pivot and trialkylphenyl platforms resulting in good extraction efficiencies of Eu^{3+} and Am^{3+}.[12] In addition, the performance of a tripodal diglycolamide in solvent extraction and supported liquid membrane studies was evaluated by us for actinide extraction.[13] However, very little work has been reported thus far dealing with diglycolamide-functionalized calixarenes.

Room temperature ionic liquids (RTILs) have aroused increasing interest for their promising role as alternative diluent medium in synthesis,[14–17] separation[18–22] and electrochemistry[23,24] as a result of their unique chemical and physical properties.[25–29] These solvents exhibit several properties that make them attractive as a potential basis for 'green' separation processes, among them negligible vapour pressure, a wide liquid range, non flammable, tunable viscosity and miscibility and good thermal and radiation stability. Even minor structural variation, either in cationic or anionic moieties, can produce significant changes in their physicochemical properties.[30] This tenability is obviously offering vast opportunities for the design of ionic liquid-based separation systems, and also poses formidable challenges to separation scientists. Significant studies have been reported on the extraction of Sr^{2+} from acidic nitrate media by dicyclohexano-18-crown-6,[31] uranyl ion by a CMPO–TBP (tri-n-butyl phosphate) mixture,[32] Ag^+ by calix[4]arenes[33] and Eu^{3+} by 2-thenoyltrifluoroacetone (TTA) from a perchlorate acid medium[34] by various water immiscible *N*,*N*′-dialkyl imidazolium-based ionic liquids. Odinets *et al.* synthesized a novel class of functionalized ionic liquids with grafted CMPO moieties for actinides and rare earth elements recovery.[35] Attempts were also made to understand the mechanism of metal ion transfer and complexation of metal ions in ionic liquids.[36–38] Recent reports deal with the use of TODGA for the extraction of alkali metal, alkaline earth metal and lanthanide ions with room temperature ionic liquids.[39,40] However, to our knowledge, the extraction of actinide ions using TODGA in room temperature ionic liquids is unprecedented.

The present work deals with the extraction of Am(III) under acidic feed conditions using TODGA in three commercially available room temperature ionic liquids, *viz.* $C_4mim^+{\cdot}PF_6^-$, $C_6mim^+{\cdot}PF_6^-$ and $C_8mim^+{\cdot}PF_6^-$ (C_nmim^+ = 1-alkyl-3-methylimidazolium). Extraction of Am(III) was also carried out using calix[4]arene-4-diglycolamide (abbreviated hence forth as C4DGA) in $C_8mim^+{\cdot}PF_6^-$, which displayed a reasonably good solubility of the extractant, favourable kinetics of extraction and reasonably high distribution ratio values. The stoichiometry of the complexes was determined for both the TODGA–RTIL as well as the C4DGA–RTIL extraction systems. The thermodynamic parameters, such as the change in enthalpy, entropy and Gibb's free energy during the extraction of the complexes, were also calculated for both ligands. Finally, a highly favourable separation behaviour of Am from U and Pu was observed when the C4DGA–RTIL extraction system was used leading to possible separation of Am from radioactive wastes containing U, Pu and Am for possible applications in neutron sources, smoke detectors, *etc.*

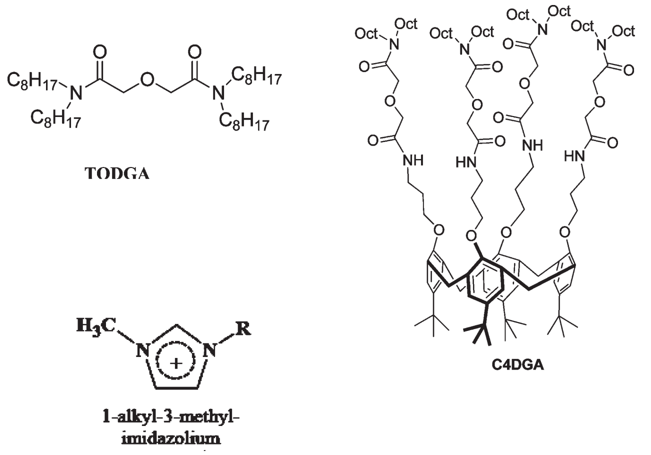


Fig. 1 Structural formula of TODGA, C4DGA and C_nmim^+.

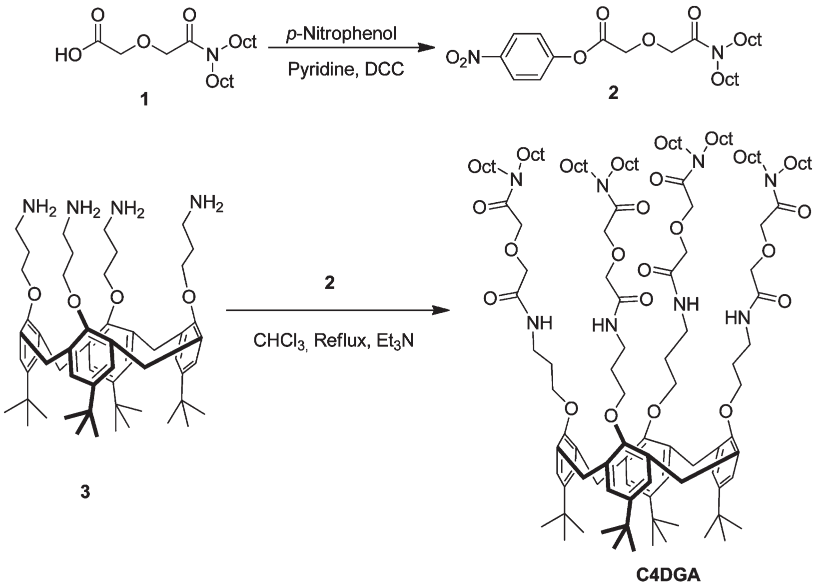
2. Experimental

2.1 Materials

TODGA (Fig. 1) was obtained from Thermax Ltd, Pune, India. The extractant was characterized by NMR, HPLC and GC-MS. The synthesis of calix[4]arene-based DGA extractant C4DGA is summarized in Scheme 1. Room temperature ionic liquids were purchased from Iolitec, Germany and were used as received. The dynamic viscosity and density of the ionic liquids were measured using an Anton Paar equipment (Model No. SVM 3000). All reagents were of AR grade and were used without further purification.

2.1.2 Synthesis of *p*-nitrophenol activated DGA (2). A solution of *N*,*N*-dioctyldiglycolic acid (**1**) (2.00 g, 5.6 mmol), *p*-nitrophenol (0.81 g, 5.7 mmol), and DCC (1.22 g, 5.8 mmol) in pyridine (60 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was dissolved in *n*-hexane, filtered and the filtrate was washed with 4% $NaHCO_3$ solution (2 × 50 mL). The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2–MeOH, 98 : 2) to afford *p*-nitrophenol activated DGA (**2**) (2.16 g, 81%) as a light yellow oil. ^{1}H NMR: δ 0.81–0.93 (m, 6H, CH_3), 1.14–1.38 (m, 20H, $CH_3(CH_2)_5$), 1.45–1.60 (m, 4H, NCH_2CH_2), 3.18 and 3.31 (t, 2H J = 7.5 Hz, NCH_2), 4.37 (s, 2H, OCH_2), 4.58 (s, 2H, OCH_2), 7.33 (d, 2H, J = 9.0 Hz, ArH), 8.28 (d, 2H, J = 9.0 Hz, ArH); ^{13}C NMR: δ 14.3, 22.8, 29.5, 31.9, 60.1, 68.2, 69.4, 122.5, 125.5, 126.3, 145.9, 169.1; HRMS: *m*/*z* 479.3130 $(M + H)^+$, calculated: 479.3121.

2.1.3. Synthesis of C4DGA. A mixture of cone tetrakis-(aminopropoxy)calix[4]arene (**3**)[41] (0.45 g, 0.5 mmol) and **2** (1.20 g, 2.5 mmol) and triethylamine (0.25 g, 2.5 mmol) in chloroform (50 mL) was refluxed overnight. The crude reaction mixture was successively washed with 2 M NaOH solution (3 × 50 mL), 1 M HCl (3 × 50 mL), and water (2 × 50 mL). The organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2–MeOH, 96 : 4) to afford calix[4]arene 4-DGA (1.10 g, 71%) as a dense oil. ^{1}H NMR: δ 0.81–0.93 (m, 24H, CH_3), 1.07 (s, 36H, *t*-Bu), 1.17–1.35 (m, 80H, $CH_3(CH_2)_5$), 1.43–1.60



Scheme 1

(m, 16H, NCH$_2$CH_2), 2.25 (pentet, 8H, J = 6.0 Hz, OCH$_2$CH_2), 3.04–3.16 (m, 12H, ArCH$_2$Ar and NCH$_2$), 3.27 (t, 8H, J = 7.5 Hz, NCH$_2$), 3.46 (t, 8H, J = 6.0 Hz, NHCH$_2$), 3.89 (t, 8H, J = 6.0 Hz, ArOCH$_2$), 4.09 (s, 8H, OCH$_2$CO), 4.27 (s, 8H, OCH$_2$CO), 4.34 (d, 4H, J = 12.0 Hz, ArCH$_2$Ar), 6.75 (s, 8H, ArH), 7.97–8.07 (m, 4H, NH); ^{13}C NMR: δ 14.3, 22.9, 27.1, 29.5, 31.6, 32.0, 34.0, 36.7, 46.3, 47.0, 60.1, 133.9, 144.8, 153.5, 168.4, 170.0; MS: m/z 2234.7 $(M + H)^+$, calculated: 2234.8.

2.2 Radiotracers

^{241}Am tracer was purified by ion exchange methods prior to use and its purity was checked by both alpha as well as gamma ray spectrometry. ^{241}Am was assayed by a NaI(Tl) scintillation detector using 60 keV gamma ray. ^{239}Np ($t_{1/2}$ = 2.3 d) tracer was prepared by irradiation of natural U (as uranyl nitrate hexa hydrate) in a reactor at a thermal neutron flux of 1×10^{13} neutrons cm^{-2} s^{-1} followed by the purification method reported by us in an earlier publication.[42] Plutonium tracer (mainly ^{239}Pu) was purified from ^{241}Am and the ^{233}U tracer was purified from ^{229}Th using standard ion-exchange methods reported before.[43] ^{85,89}Sr and ^{137}Cs were obtained from BRIT (Board of Radiation and Isotope Technology), India and were used after checking their radiochemical purity. The valency of Np was adjusted to the +4 state by using hydroxylamine hydrochloride as the holding reductant. The valency of Pu was adjusted to the +4 state by using NaNO$_2$ and ammonium metavanadate as the holding oxidant, while the conversion of Pu to the +6 state was achieved using AgO as the oxidizing agent.[44] The radiometric assay of ^{233}U and Pu was done by alpha-liquid scintillation counting using the Ultima Gold scintillator cocktail, while that of ^{85,89}Sr, ^{137}Cs and ^{239}Np was performed by gamma ray counting using a NaI(Tl) scintillation counter. Alpha-spectrometry was carried out using a silicon surface barrier detector.

2.3 Distribution studies

The distribution studies were carried out by equilibrating the organic phase, containing the required concentration of the extractants in room temperature ionic liquids, as well as the aqueous phase, with required feed acidity, spiked with ^{241}Am tracer, with a phase ratio of 1 : 1 in a thermostated water bath at 25 ± 0.1 °C. The tubes were centrifuged for 5 min to enable phase separation. After centrifugation, both phases were separated and assayed radiometrically. 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 americium was in the range of 10^{-6}–10^{-7} M. The thermodynamic parameters were calculated from temperature variation studies carried out in the temperature range of 20–40 °C. The experiments were carried out in duplicate with a precision of ±5%.

3. Results and discussion

The room temperature ionic liquids used in the present study did not extract Am(III) in the absence of TODGA (Table 1). Similar behaviour was reported by Shimojo *et al.*[39] in their studies on lanthanide extraction using a different set of ionic liquids. In the presence of TODGA as the extractant, however, a sharp increase in the D_M-values was observed. The distribution ratio values obtained with 0.01 M TODGA in RTILs are significantly higher than those obtained with TODGA in *n*-dodecane as the organic phase (<0.1). Similar enhancements in the distribution ratio values were reported with RTILs for Sr(II) extraction using crown ethers,[45,46] for Cs(I) extraction using calix-crown ligands[47,48] and for actinide extraction using a CMPO and TBP mixture.[22,49] The extractability of Am(III) in the ionic liquids with TODGA as the extractant was found to be $C_4mim^+\cdot PF_6^- > C_8mim^+\cdot PF_6^- > C_6mim^+\cdot PF_6^-$. Shimojo *et al.*, on the other hand, have shown that the extraction of Eu(III) with

Table 1 D_{Am}-values without and with 0.01 M TODGA, time to attain equilibrium D_{Am}-values, and physical parameters of the ionic liquids

	Equilibrium D_{Am}				
RTIL	No TODGA	0.01 M TODGA	Time to attain equilibrium (min)	Dynamic viscosity (mPa s)	Density (g cm^{-3})
$C_4mim^+{\cdot}PF_6^-$	<0.01	102	60	250.86	1.366
$C_6mim^+{\cdot}PF_6^-$	<0.01	34	60	308.48	1.290
$C_8mim^+{\cdot}PF_6^-$	<0.01	74	180	694.19	1.235

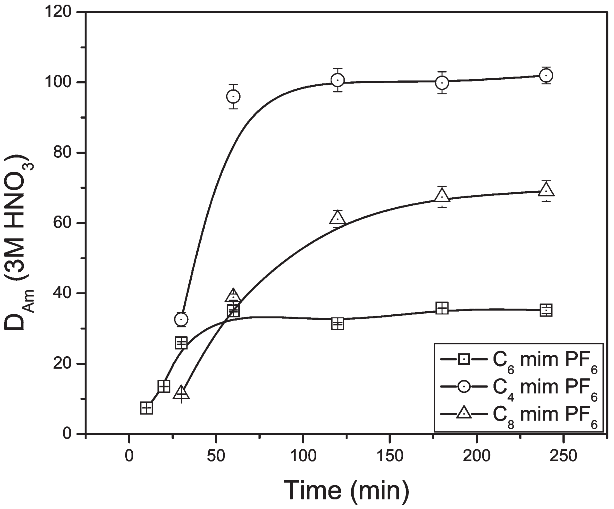


Fig. 2 Extraction kinetics of americium from 3 M HNO_3 feed into 0.01 M TODGA in $C_n mim^+{\cdot}PF_6^-$ ($n = 4, 6, 8$).

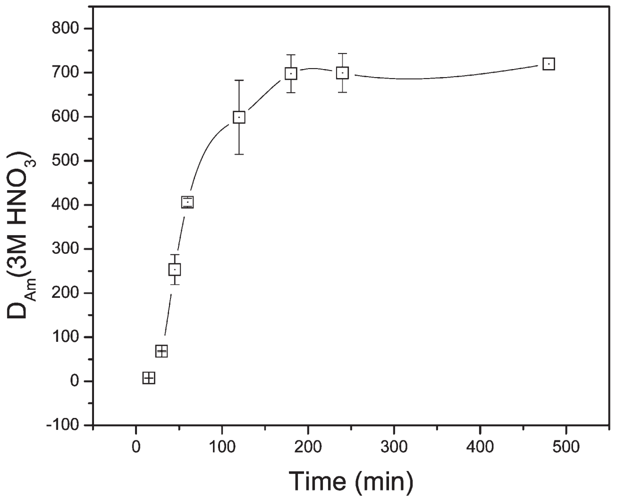


Fig. 3 Extraction kinetics of americium from 3 M HNO_3 feed into 0.001 M C4DGA in $C_8mim^+{\cdot}PF_6^-$.

TODGA decreased with increase of the alkyl chain length.[39] They have also reported that 10^{-4} M TODGA is capable of extracting Eu(III), a trivalent lanthanide ion of comparable ionic radius as Am(III), when the aqueous phase acidity was 0.01 M. In the present case, a distribution coefficient value of ~2500 was obtained for Am(III) with 0.01 M TODGA in $C_4mim^+{\cdot}PF_6^-$ from a feed containing 0.01 M HNO_3, which is significantly lower than that reported by Shimojo *et al.* for Eu(III). Higher extraction of Eu(III) as compared to Am(III) has been reported previously using TODGA as the extractant.[7,8]

3.1 Extraction kinetics

In order to get information on the attainment of the extraction equilibrium, the extraction kinetics was investigated. The kinetics of Am(III) extraction was reported to be fast when TODGA in *n*-dodecane was used as the solvent system.[8] In the present study, the Am(III) extraction kinetics was studied from a 3 M HNO_3 feed solution using 0.01 M TODGA in $C_n mim^+{\cdot}PF_6^-$ with an organic to aqueous volume ratio of 1. The ligand concentration was kept at 1×10^{-2} M, which is about 10 times less than the usual concentration employed for actinide ion extraction in the *n*-dodecane system. Fig. 2 represents the extraction kinetics of americium with TODGA into $C_n mim^+{\cdot}PF6^-$. In case of $C_4mim^+{\cdot}PF_6^-$, a sharp increase in D_{Am}-value was observed up to 60 min, while beyond that a plateau was observed with a distribution ratio of ~100. Similar observations were made in case of $C_6mim^+{\cdot}PF_6^-$ where the D_{Am}-value increased with the equilibration time followed by a plateau beyond 60 min with a consistent D_{Am}-value of ~35. On the other hand, for $C_8mim^+{\cdot}PF_6^-$, the D_{Am}-value increased gradually up to 180 min, followed by a plateau with a D_{Am}-value of ~70 showing the slowest kinetics among the three RTILs. The observed slower kinetics in all the cases as compared to the conventional diluents like *n*-dodecane can be attributed to the high viscosity of the ionic liquids. Table 1 shows that the dynamic viscosity of $C_8mim^+{\cdot}PF_6^-$ is almost twice that of the other two RTILs employed in the present work. As a consequence, $C_8mim^+{\cdot}PF_6^-$ showed the slowest kinetics among the three RTILs investigated, though the butyl and the hexyl derivatives exhibited a nearly similar extraction kinetics.

The extraction kinetics was also studied using 0.001 M C4DGA in $C_8mim^+{\cdot}PF_6^-$ (Fig. 3) under identical feed conditions. The concentration of C4DGA was kept 10 times lower than that employed with TODGA as the extractant due to the fact that four diglycolamide moieties are present in C4DGA to make it a superior extractant than TODGA. The distribution ratio of Am(III) increased sharply up to 180 min with a value of about 700 followed by a plateau with $D_{Am} \sim 700$. Though the viscosity of the resulting organic phase is comparable with that used with TODGA, the slower kinetics may also be due to the conformational rigidity of the C4DGA ligand.

3.2 Effect of the number of ligating sites and a substituent on the calix[4]arene

The effect of the number of ligating sites and a substituent on the calix[4]arene extractant was also investigated using

Table 2 Extraction of Am(III) with the diglycolamide functionalized calix[4]arenes from 3 M HNO_3 using 5×10^{-4} M extractant in $C_8mim^+ \cdot PF_6^-$

Extractant	D_{Am}
C4DGA	194 ± 2
C2DGA[50]	0.692 ± 0.021
C2DGA-Bu[50]	0.233 ± 0.065

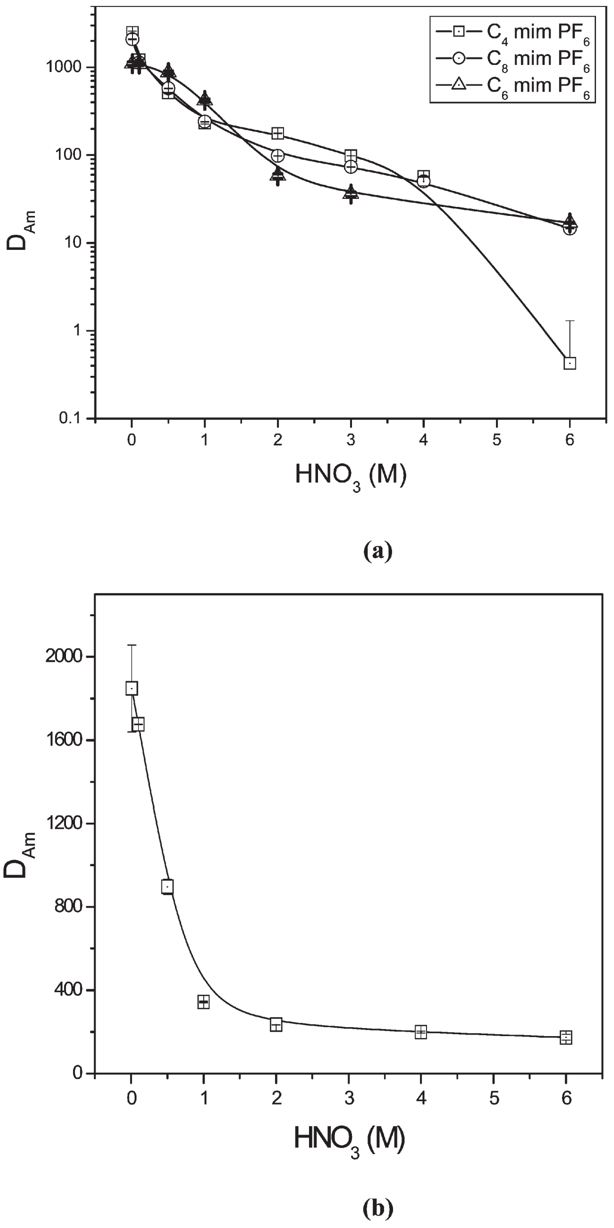
$C_8mim^+ \cdot PF_6^-$ as the diluent. For comparison purpose, the concentration of the calix-2DGA (abbreviated as C2DGA and C2DGA-Bu[50]) ligands was taken as 5×10^{-4} M and the results of Am(III) extraction from 3 M HNO_3 feed solutions are listed in Table 2. The equilibration time was fixed at 3 h, similar to that used for the C4DGA as mentioned above. The results showed a significantly lower extraction of Am(III) with the C2DGA compounds, clearly indicating that the C4DGA is far more effective for metal ion extraction. This is in line with our previous observations on the extraction behaviour of the three calix[4]arene DGA compounds in *n*-dodecane as the organic diluent.[50]

3.3 Effect of the feed acidity

Fig. 4(a) shows the dependence of the distribution ratio of Am(III) with the change in the feed nitric acid concentration. For all the RTILs, an increase in the feed nitric acid concentration led to a decrease in the distribution ratio values. Though a sharp fall was observed in the lower acidity region, plateau like profiles were noticed at higher acidities (beyond 3 M HNO_3). Similar to the trend mentioned above, the highest D_{Am}-value (2502) was obtained at 0.01 M HNO_3 with $C_4mim^+ \cdot PF_6^-$ as the diluent, while the lowest D_{Am}-value (1104) was obtained under identical conditions with $C_6mim^+ \cdot PF_6^-$ as the diluent. A drastic decrease in the D_{Am}-value was observed in the latter case by changing the feed acidity from 0.01 M HNO_3 (D_{Am} = 1104) to 2 M HNO_3 (D_{Am} = 58) followed by a moderate decrease in the D_{Am}-value with a further increase of the feed acidity. A similar trend was also noticed in case of $C_8mim^+ \cdot PF_6^-$ as the diluent, where the D_{Am}-value decreased from 2092 (0.01 M HNO_3) to 241 (1 M HNO_3), followed by a moderate decrease upon further increase of the feed acidity.

The variation of the D_{Am}-value with the feed acidity was studied using 7×10^{-4} M C4DGA in $C_8mim^+ \cdot PF_6^-$ as the organic phase with phase ratio 1 : 1. The equilibration time was kept at 3 h to assure complete equilibration. Also in this case, the D_{Am}-value decreased with increasing aqueous feed acidity (Fig. 4(b)). The D_{Am}-value was found to be 1847 at 0.01 M HNO_3, which decreased drastically up to 1 M HNO_3 with a D_{Am}-value of 343 with much lower subsequent decrease upon further increase in the aqueous phase acid concentration.

The decrease in the D_{Am}-values with increasing feed acidity is entirely opposite to the trend observed with the extraction of actinides with diglycolamide extractants such as TODGA in diluents like *n*-dodecane. The extraction profiles obtained in the present study indicate that the extraction mechanism is not ion-pair type as in case of the conventional diluents such as *n*-dodecane. On the contrary, an ion-exchange mechanism is responsible for the extraction of americium from nitric acid feed to the ionic liquid phase. At higher acidity, due to the availability of large amounts of H^+, it competes with the metal ions in the ion-exchange process resulting in substantially lower D_{Am}-values. Extraction of nitric acid was investigated by equilibrating the ionic liquid solutions with 3 M HNO_3 and the results suggested 7.3, 8.1 and 8.6% extraction of the acid using the butyl, hexyl and octyl derivatives of the ionic liquids using 1.0×10^{-2} M TODGA as the extractant.



(a)

(b)

Fig. 4 Extraction behavior of americium from different feed acidities into (a) 0.01 M TODGA in $C_nmim^+ \cdot PF_6^-$ (n = 4, 6, 8) and (b) 7×10^{-4} M C4DGA in $C_8mim^+ \cdot PF_6^-$.

3.4 Effect of the TODGA concentration

The extraction of Am(III) with varying TODGA concentration was also investigated in the three RTILs and the results are presented in Fig. 5(a). An increase in Am(III) extraction with increasing TODGA concentration in the ionic liquids was

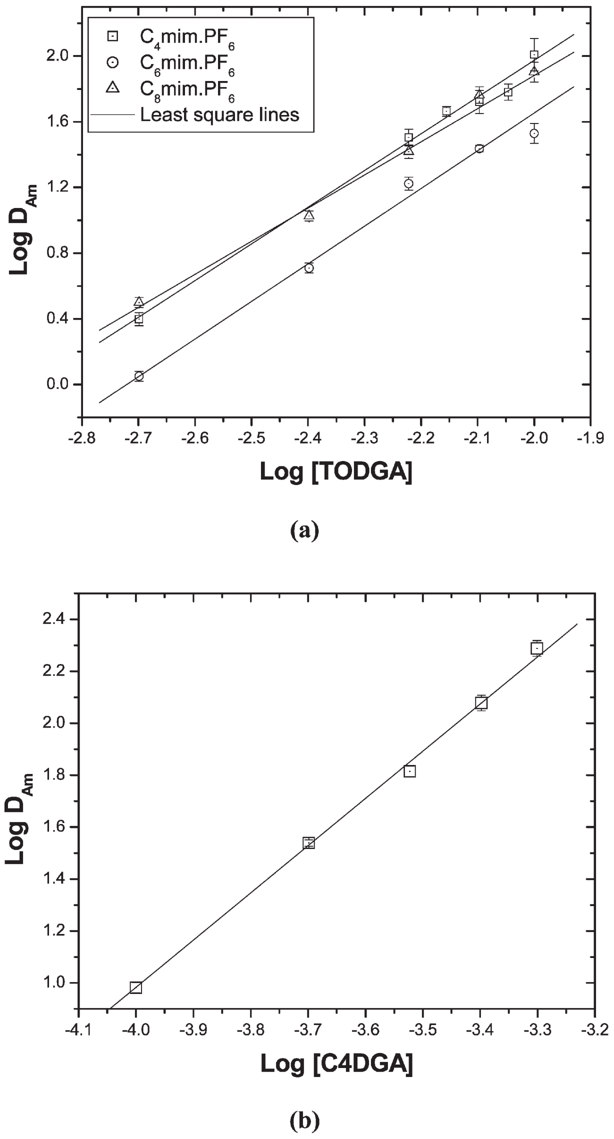


Fig. 5 Distribution ratio of americium at (a) varying TODGA concentrations from 3 M HNO_3 feed into $C_n mim^+ \cdot PF_6^-$ (n = 4, 6, 8) and (b) varying C4DGA concentrations from 3 M HNO_3 feed into $C_8 mim^+ \cdot PF_6^-$.

observed. This indicates that TODGA is participating in the extraction process by being part of the extracted species (*vide infra*). A similar increase in Am(III) extraction was also observed with C4DGA in $C_8 mim^+ \cdot PF_6^-$ as the diluent (Fig. 5(b)). Shimojo *et al.* reported a similar increase in the extraction of lanthanide ions with TODGA in ionic liquids.[39] It was of interest to understand the nature of the extracted species and the number of TODGA molecules involved in the metal ion extraction.

3.5 Extraction mechanism and extraction constants

In view of the above observations, the extraction of Am(III) using TODGA in ionic liquids can be best represented by an ion-exchange mechanism as per the following equation.

$$\begin{aligned} &\mathrm{Am^{3+}}_{\mathrm{aq}} + n\mathrm{TODGA}_{\mathrm{IL}} + 3\mathrm{C}_n\mathrm{mim^+}_{\mathrm{IL}} \\ &\quad \leftrightarrow \mathrm{Am(TODGA)}_n{}^{3+}{}_{\mathrm{IL}} + 3\mathrm{C}_n\mathrm{mim^+}_{\mathrm{aq}} \end{aligned} \quad (1)$$

The species with the subscripts 'aq' and 'IL' refer to those in the aqueous phase and in the room temperature ionic liquid phase, respectively. A strong influence of hydrogen ion on Am(III) extraction can be explained on the basis of a competing equilibrium reaction as follows:

$$\begin{aligned} &\mathrm{H^+}_{\mathrm{aq}} + \mathrm{TODGA}_{\mathrm{IL}} + \mathrm{C}_n\mathrm{mim^+}_{\mathrm{IL}} \\ &\quad \leftrightarrow \mathrm{H \cdot TODGA^+}_{\mathrm{IL}} + \mathrm{C}_n\mathrm{mim^+}_{\mathrm{aq}} \end{aligned} \quad (2)$$

Formation of adducts of TODGA with nitric acid is well reported[8] and could be attributed to be the reason for a sharp decrease in the D_{Am} values with increasing acidity. In case of molecular diluents like *n*-dodecane, though $HNO_3 \cdot$TODGA adduct also gets extracted, the effect of decreasing D_{Am} with acidity leading to a plateau is seen only at higher acidities.[8] On the other hand, the increasing trend with increasing acidity seen at lower acidities is due to increasing nitrate ion concentration (nitrate ion is part of the extracted species). In case of room temperature ionic liquids, the decrease in D_{Am} with increasing acid concentration is seen in the entire range of acidity (Fig. 4) which corroborates the fact that the extracted species does not contain nitrate ion and the ion-exchange mechanism as indicated above is prevailing. A similar ion-exchange extraction mechanism was reported for the extraction of lanthanide ions using TODGA.[39] If D_{Am} is the distribution ratio, $P_{\mathrm{C}_n\mathrm{mim+}}$ represents the partition coefficient and K_{Am} the equilibrium constant for the extraction of americium, then it can be written that

$$\begin{aligned} K_{\mathrm{Am}} = {}&([\mathrm{Am(TODGA)}_n{}^{3+}]_{\mathrm{IL}}\ [\mathrm{C}_n\mathrm{mim^+}]_{\mathrm{aq}}{}^3)/([\mathrm{Am^{3+}}]_{\mathrm{aq}} \\ &[\mathrm{TODGA}]_{\mathrm{IL}}{}^n\ [\mathrm{C}_n\mathrm{mim^+}]_{\mathrm{IL}}{}^3) \end{aligned} \quad (3)$$

Or, substituting D_{Am} for the term $[\mathrm{Am(TODGA)}_n{}^{3+}]_{\mathrm{IL}}/[\mathrm{Am^{3+}}]_{\mathrm{aq}}$ one obtains

$$K_{\mathrm{Am}} = D_{\mathrm{Am}}/([\mathrm{TODGA}]^n \cdot P_{\mathrm{C}_n\mathrm{mim+}}) \quad (4)$$

Taking the logarithm and rearranging:

$$\log D_{\mathrm{Am}} = \log K_{\mathrm{Am}} + \log P_{\mathrm{C}_n\mathrm{mim+}} + n \log[\mathrm{TODGA}] \quad (5)$$

A plot of logD_{Am} *vs.* the concentration of TODGA or C4DGA should result in straight lines with a slope '*n*', *i.e.* the number of TODGA or C4DGA molecules associated with the complex formed during the extraction and the intercept represents $\log K_{\mathrm{Am}} + \log P_{\mathrm{C}_n\mathrm{mim+}}$.

On the basis of eqn (5), a slope analysis was conducted as a function of the equilibrium concentration of a ligand in $C_n mim^+ \cdot PF_6^-$ (n = 4, 6, 8) and used to determine the fundamental stoichiometry of the Am^{3+}–diglycolamide complex formed in 3 M HNO_3 feed. Fig. 5(a) represents the variation in the log D_{Am} value with the TODGA concentration. In case of TODGA in $C_4 mim^+ \cdot PF_6^-$, the slope is 2.23 ± 0.07, while in case of the ionic liquid with n-hexyl and n-octyl derivatives, TODGA concentration dependencies of 2.29 ± 0.06 and 2.02 ± 0.07 were obtained. Fractional slope values (Fig. 5(a)) indicated extraction of mixed species of 1 : 2 as well as 1 : 3 M : L compositions. Extraction of mixed species has previously been reported in case of molecular diluents.[7,8] However, Shimojo *et al.*, reported extracted species with 1 : 3 stoichiometry for lanthanide ion extraction using $C_n\text{mim}^+\cdot\text{NTf}_2^-$ as the ionic liquid medium.[39] The extraction of americium with TODGA can thus be expressed as

$$\text{Am}^{3+}{}_{\text{aq}} + 2\text{–}3\text{TODGA}_{\text{IL}} + 3C_n\text{mim}^+{}_{\text{IL}} \leftrightarrow \text{Am(TODGA)}_2{}^{3+}{}_{\text{IL}} + 3C_n\text{mim}^+{}_{\text{aq}} \quad (6)$$

A similar study was carried out to determine the stoichiometry of the complex formed by americium with C4DGA in $C_8\text{mim}^+\cdot\text{PF}_6^-$. The log D_{Am} *vs.* log[C4DGA] plot (Fig. 5(b)) yielded a slope value of 1.8 ($\chi^2 = 0.9979$) indicating the extraction both ML and ML_2 type of species from 3 M HNO_3 with the latter being present predominantly in the ionic liquid phase. Though this is rather unusual in view of the large coordination number feasible with 24 coordinating atoms present around the metal ion, a similar extracted species was reported in our earlier studies involving a tripodal diglycolamide ligand.[13] The extraction of Am(III) with C4DGA can be represented as

$$\text{Am}^{3+}{}_{\text{aq}} + 2\text{C4DGA}_{\text{IL}} + 3C_n\text{mim}^+{}_{\text{IL}} \leftrightarrow \text{Am(C4DGA)}_2{}^{3+}{}_{\text{IL}} + 3C_n\text{mim}^+{}_{\text{aq}} \quad (7)$$

From eqn (3), $[C_n\text{mim}^+]_{\text{aq}}$ and $[C_n\text{mim}^+]_{\text{IL}}$ can be regarded as constant (the aqueous phase is saturated with $C_n\text{mim}^+\cdot\text{PF}_6^-$ salt) and, therefore, the conditional extraction constant K'_{Am} can be given as:

$$K'_{\text{Am}} = [\text{Am}\cdot\text{L}_2{}^{3+}]_{\text{IL}}/[\text{Am}^{3+}{}_{\text{aq}}]\ [\text{L}]_{\text{IL}}{}^2 \quad (8)$$

where L represents the extractant (TODGA or C4DGA when the two ligand molecules are assumed to be present in the extracted species). Substituting D_{Am} for the term $[\text{Am}\cdot\text{L}_2{}^{3+}]_{\text{IL}}/[\text{Am}^{3+}]_{\text{aq}}$, one obtains

$$K'_{\text{Am}} = D_{\text{Am}}/[\text{L}]_{\text{IL}}{}^2 \quad (9)$$

$$\log D_{\text{Am}} = \log K'_{\text{Am}} + 2\log[\text{L}]_{\text{IL}} \quad (10)$$

The K'_{Am}-value is calculated from the intercept of a plot of log *D* *vs.* $\log[\text{TODGA}]_{\text{IL}}$ at a constant nitric acid concentration. K'_{Am} was calculated for americium with TODGA in $C_n\text{mim}^+\cdot\text{PF}_6^-$ (n = 4, 6, 8) and C4DGA in $C_8\text{mim}^+\cdot\text{PF}_6^-$. The complex formation equilibrium in an ionic liquid can be described by the following equations.

$$\text{Am}^{3+}{}_{\text{IL}} + 2\text{L}_{\text{IL}} = [\text{Am}\cdot\text{L}_2]^{3+}{}_{\text{IL}} \quad (11)$$

$$K_{\text{form}} = [\text{Am L}_2{}^{3+}]_{\text{IL}}/[\text{Am}^{3+}]_{\text{IL}}\ [\text{L}]_{\text{IL}}{}^2 \quad (12)$$

$$K_{\text{form}} = K'_{\text{Am}}[\text{Am}^{3+}]_{\text{aq}}/[\text{Am}^{3+}]_{\text{IL}} \quad (13)$$

$$K_{\text{form}} = K'_{\text{Am}}/P_{\text{Am}} \quad (14)$$

where P_{Am} is the partition coefficient of Am^{3+} defined as the ratio of $[\text{Am}^{3+}]_{\text{IL}}$ to $[\text{Am}^{3+}]_{\text{aq}}$. Table 3 lists the extraction constants (K'_{Am}) of americium for TODGA as well as C4DGA in $C_n\text{mim}^+\cdot\text{PF}_6^-$. As indicated in Table 1, the P_{Am} values are <0.01 suggesting that the K_{form} values are approximately two orders of magnitude higher as compared to the extraction constants.

Table 3 Extraction (K'_{Am}) constants of americium(III) from 3 M HNO_3 at 298.15 K

Ligand	Diluent	Log K'_{Am}
1×10^{-2} M TODGA	$C_4\text{mim}^+\cdot\text{PF}_6^-$	6.45 ± 0.18
	$C_6\text{mim}^+\cdot\text{PF}_6^-$	6.24 ± 0.13
	$C_8\text{mim}^+\cdot\text{PF}_6^-$	5.92 ± 0.17
5×10^{-4} M C4DGA	$C_8\text{mim}^+\cdot\text{PF}_6^-$	8.26 ± 0.15

Note: The log K'_{Am} values were obtained from the log *D* *vs.* log[L] plots.

3.6 Determination of thermodynamic parameters

The effect of temperature on the extraction of americium from 3 M HNO_3 by 0.01 M TODGA or 5×10^{-4} M C4DGA into $C_8\text{mim}^+\cdot\text{PF}_6^-$ was studied as this RTIL gave reasonably high distribution coefficient values with faster extraction kinetics. The distribution ratio of americium either with TODGA (Fig. 6(a)) or with C4DGA (Fig. 6(b)) was found to decrease with increasing temperature, indicating the extraction process to be exothermic. The change in enthalpy (ΔH) during the complexation can be calculated by using the Van't Hoff equation:

$$\Delta H = -2.303\ R\ \Delta\log D/\Delta(1/T) \quad (15)$$

A plot of log *D* *vs.* 1/*T* gives a straight line with a slope of $-\Delta H/2.303\ R$, while the change in Gibb's free energy (ΔG) can be calculated from the following equation

$$\Delta G = -2.303\ RT\ \log K'_{\text{Am}} \quad (16)$$

The change in entropy (ΔS) at a particular temperature can be calculated using the equation

$$\Delta G = \Delta H - T\Delta S \quad (17)$$

The thermodynamic parameters calculated for the two extraction systems are summarized in Table 4. The ΔH values, calculated from the slope of the log *D* *vs.* 1/*T* plot (*vide supra*), are −71.61 kJ mol^{-1} and −86.93 kJ mol^{-1}, respectively, for TODGA and C4DGA. The overall enthalpy change during extraction (ΔH) is a sum of the contribution due to dehydration of the metal ion (ΔH_1), formation of the complex (ΔH_2), and dissolution of the metal complex into the organic phase (ΔH_3). The favourable ΔH in C4DGA over TODGA can be mainly attributed to the contributions from ΔH_2 and ΔH_3. Due to the pre-organized structure of C4DGA, ΔH_2 (C4DGA) > ΔH_2(TODGA) and on account of the higher lipophilicity of C4DGA, ΔH_3(C4DGA) > ΔH_3(TODGA). The ΔG calculated from eqn (17) shows that the extraction of americium by C4DGA ($\Delta G = -46.53$ kJ mol^{-1}) is energetically more favoured than that by TODGA ($\Delta G = -34.63$ kJ mol^{-1}), which is also reflected in their D_{Am}-values (*vide supra*). On the other hand, the negative entropy change in case of TODGA ($\Delta S = -123.24$ J mol^{-1}) as well as C4DGA ($\Delta S = -134.67$ J mol^{-1}) can be attributed to the loss of rotational entropy of the ligands during complexation.

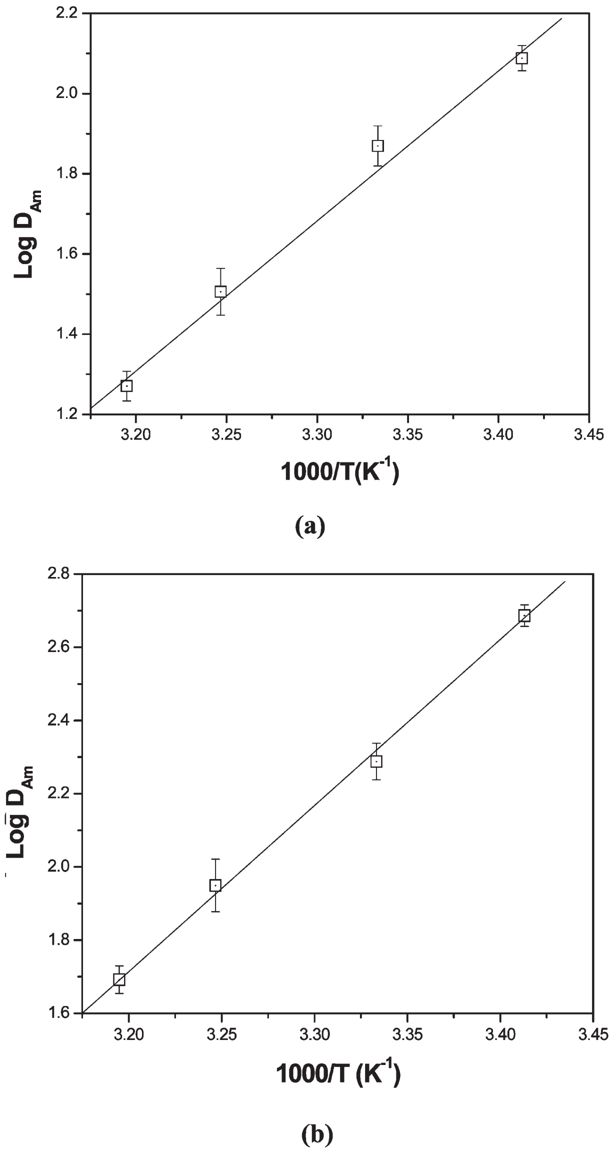


Fig. 6 Variation in distribution ratio of americium at (a) different temperatures from 3 M HNO_3 feed using 1.0 × 10^{-2} M TODGA in $C_8mim^+{\cdot}PF_6^-$ and (b) different temperatures from 3 M HNO_3 feed using 5 × 10^{-4} M C4DGA in $C_8mim^+{\cdot}PF_6^-$.

3.7 Extraction of actinides and selective Am extraction from wastes

Solvent extraction studies of several other actinide ions such as UO_2^{2+}, Np^{4+}, Pu^{4+}, and PuO_2^{2+} were carried out and the results are listed in Table 5. As most radioactive wastes consist of long lived fission product nuclides such as ^{90}Sr ($t_{1/2}$: 28.5 y) and ^{137}Cs ($t_{1/2}$: 30.1 y), distribution data of Sr(II) and Cs(I) are also included using both TODGA as well as C4DGA in $C_8mim^+{\cdot}PF_6^-$ at concentrations of 1 × 10^{-2} and 5 × 10^{-5} M, respectively, from 3 M HNO_3 feed solutions (Table 5). It is interesting to note that the *D*-values for Am(III), Np(IV), and Pu(IV) are significantly higher compared to those obtained with other metal ions, *viz.* PuO_2^{2+}, UO_2^{2+}, Cs^+ and Sr^{2+}, indicating the effectiveness of TODGA in RTIL for minor actinide partitioning.

Table 4 Thermodynamic parameters (ΔG, ΔH and ΔS) of americium extraction from 3 M HNO_3 using TODGA/C4DGA in $C_8mim^+{\cdot}PF_6^-$ at 300 K

Ligand	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
1.0 × 10^{-2} M TODGA	−34.64	−71.61	−123.24
5.0 × 10^{-4} M C4DGA	−46.53	−86.93	−134.67

Table 5 Distribution data of actinides and fission products from 3 M HNO_3 feed solutions using TODGA and C4DGA as the extractant in $C_8mim^+{\cdot}PF_6^-$ as the diluent

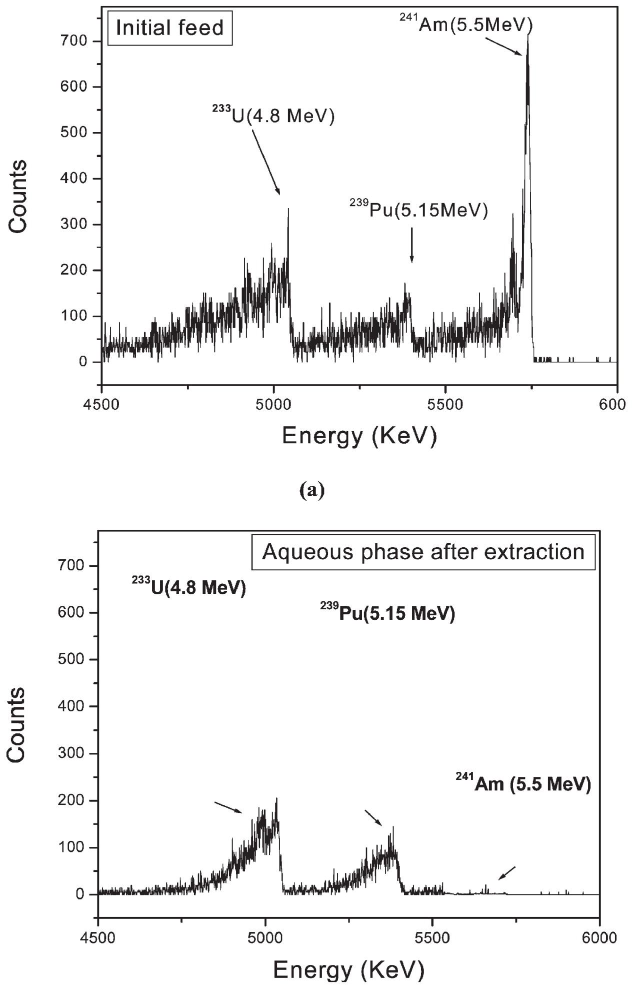
	Distribution coefficient values using DGA extractants	
Metal ion	TODGA	C4DGA
Am(III)	75	194
Pu(IV)	30.7	20.6
PuO_2^{2+}	1.19	0.64
UO_2^{2+}	0.52	0.19
Np(IV)	3.92	7.46
Sr^{2+}	0.024	0.017
Cs^+	0.12	0.15

Table 6 Comparative separation behaviour in ionic liquid and conventional diluent with TODGA and C4DGA

Solvent system	SF_{AmU} (D_{Am}/D_U)	SF_{AmPu} (D_{Am}/D_{Pu})
TODGA–*n*-dodecane[a]	132	25
TODGA–$C_8mim^+{\cdot}PF_6^-$[a]	144	63
C4DGA–*n*-dodecane[b]	45	173
C4DGA–$C_8mim^+{\cdot}PF_6^-$[b]	1021	303

[a] 1.0 × 10^{-2} M TODGA was used. [b] 5.0 × 10^{-4} M C4DGA was used.

Interestingly, the D_{Am}-values with C4DGA are much higher than those obtained with TODGA, while the *D*-values for U(VI) and Pu(VI) are significantly lower with C4DGA than with TODGA. The low extraction of U and Pu in the hexavalent oxidation state is rather surprising and may be based on the unusual coordination geometry of the actinyl ion and the strain associated with complex formation using the ligand. The separation factor values (defined as the ratio of the distribution ratio values of the concerned metal ions) were determined for the metal ions Am–U and Am–Pu in both extractants, *viz.* TODGA and C4DGA, in $C_8mim^+{\cdot}PF_6^-$ as well as *n*-dodecane (the conventional diluent used for metal ion separations, especially actinide separations) and the results are listed in Table 6. It is interesting to note that the ionic liquid medium shows an unusually high enhancement in the separation factor values of the metal ions as compared to *n*-dodecane. Moreover, C4DGA was found to be a superior extractant from the actinide separation point of view as well. And finally, the combination C4DGA in $C_8mim^+{\cdot}PF_6^-$ results in a highly efficient separation system involving Am extraction (Table 6).



(a)

(b)

Fig. 7 Alpha spectra of the aqueous feed solution (3 M HNO_3): (a) before and (b) after extraction using 5 × 10^{-4} M C4DGA in $C_8mim^+ \cdot PF_6^-$.

These results are encouraging and can be applied for the selective extraction of Am from radioactive wastes containing actinide elements such as U and Pu (usually present in high level radioactive wastes or PUREX process raffinates). A synthetic sample containing U (^{233}U tracer was used as a surrogate due to the very long half life of natural U), Pu and Am in 3 M HNO_3 was subjected to treatment with AgO, followed by extraction with 5 × 10^{-4} M C4DGA in $C_8mim^+ \cdot PF_6^-$. The alpha spectra of the aqueous phase before and after the extraction are presented in Fig. 7. Complete extraction of Am with almost no uptake of U and Pu is clearly demonstrated by this study suggesting that selective Am recovery from high level waste can be performed using C4DGA in RTIL. This is of interest due to its use as a neutron source (Am–Be source) or in smoke detectors.

4. Conclusions

From the above studies it can be concluded that extraction of Am(III) can be considerably enhanced when diglycolamide (DGA) extractants such as TODGA or a specially designed calix[4]arene containing four DGA moieties (C4DGA) are used in room temperature ionic liquids instead of the conventional *n*-dodecane as the diluent showing improved separation factors. The unusually high extraction of Am(III) can be attributed to the unique ion-exchange extraction mechanism in the RTIL medium, while the high viscosity of the RTILs is responsible for the slower extraction kinetics. Am(III) can be selectively extracted from a mixture containing U(VI), Pu(IV) and Pu(VI), and Am(III) by adjusting the oxidation state of Pu to +6. The large negative entropy changes observed during the thermodynamic studies, point to the formation of ordered extracted complexes with both TODGA as well as C4DGA, possibly without the liberation of the inner-sphere water molecules, indicating outer-sphere interactions.

The analytical significance of this work lies in the exceptionally high separation factors obtained and this can be applied for the selective extraction of Am(III) from acidic waste samples. Moreover, Am(III) can be selectively recovered from high level waste, which is of utmost importance for possible applications in industry.

Acknowledgements

The authors (A.S., P.K.M.) thank Dr A. Goswami, Head Radiochemistry Division, BARC for his keen interest in this work.

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