

Cite this: *RSC Advances*, 2012, 2, 7492–7500

www.rsc.org/advances

PAPER

Extraction of Am(III) using novel solvent systems containing a tripodal diglycolamide ligand in room temperature ionic liquids: a ‘green’ approach for radioactive waste processing†

A. Sengupta,^a P. K. Mohapatra,^{*a} M. Iqbal,^b W. Verboom,^b J. Huskens^b and S. V. Godbole^a

Received 29th March 2012, Accepted 10th June 2012

DOI: 10.1039/c2ra20577g

Extraction of Am³⁺ from acidic feed solutions was investigated using novel solvent systems containing a tripodal diglycolamide (T-DGA) in three room temperature ionic liquids (RTIL), *viz.* [C₄mim][NTf₂], [C₆mim][NTf₂] and [C₈mim][NTf₂]. Compared to the results obtained with *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA), T-DGA gave significantly higher distribution coefficients in these RTILs. The D_{Am} values decreased with increasing carbon chain length in the RTILs, which was related to the solubility of the RTIL in the aqueous phase. The distribution studies included the effect of equilibration time, aqueous phase acid concentration variation and T-DGA concentration variation. In general, significantly higher equilibration times were observed for the extraction systems, which was partly due to the viscous RTIL phase and partly due to the slow conformational changes of the T-DGA ligand during complexation. Apart from Am³⁺, extraction of Pu⁴⁺, UO₂²⁺, Eu³⁺, Sr²⁺ and Cs⁺ was also investigated, since they have significant implications in radioactive waste processing. Stripping studies indicated >99% stripping in three stages using 0.5 M EDTA or DTPA in 1 M guanidine carbonate. Slope analysis indicated the extraction of 1 : 1 complexed species of Am(III) with T-DGA. Time resolved laser fluorescence spectroscopy (TRLFS) studies showed a strong complexation with no inner-sphere water molecules in the Eu(III)–T-DGA complexes for [C₄mim][NTf₂] as the diluent. Radiolytic degradation studies of the solvent systems containing T-DGA in the three RTILs were also carried out and while the D_{Am} values decreased marginally when the solvents were exposed to 500 kGy absorbed dose, a relatively sharp decrease (60%) was seen when the solvents were exposed further to 1000 kGy absorbed dose, suggesting the possibility of recycling. Extraction studies were also carried out at varying temperatures and the thermodynamic parameters were calculated.

1. Introduction

Extraction of actinides is one of the key issues in the remediation of high level radioactive wastes emanating from the back end of the nuclear fuel cycle. Effective actinide extraction makes the waste benign and ready for disposal as vitrified waste blocks in deep geological repositories. However, conventional solvent extraction methods, though being routinely used for actinide separations, have several disadvantages, which include a large VOC (volatile organic compounds) inventory and generation of huge volumes of secondary wastes. Growing concern for the environment has led to increasing interest in room temperature

ionic liquids (RTIL) as an alternative to molecular diluents in a myriad of applications including synthesis,¹ catalysis,² separation³ and electrochemistry.⁴ Out of these, the application of RTILs to separation science has increased enormously as can be seen from the rapid rise in the number of publications in this area in the last decade, due to their unique characteristics of high thermal stability and low volatility. Some of the thoroughly studied areas include the extraction of Cs⁺ and Sr²⁺ by crown ethers.⁵ Extraction of actinide ions, however, is hardly studied and only a handful of papers are available on this topic.

Some of the early work on actinide extraction using ionic liquids include extraction of UO₂²⁺ by tributyl phosphate (TBP) in [C₄mim][PF₆], [C₆mim][PF₆] or [C₈mim][NTf₂] (mim = 1-alkyl-3-methylimidazolium).⁶ Usually, the extraction mechanism with RTILs was found to be in variant to that reported with molecular diluents such as *n*-dodecane. However, the extraction mechanism and the mode of complexation have been surprisingly found to be identical for uranyl ion extraction using Cyanex 272 in *n*-dodecane or 1-decyl-3-methylimidazolium

^aRadiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India. E-mail: mpatra@barc.gov.in; Fax: +91-22-25505151

^bLaboratory of Molecular Nanofabrication, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500, AE Enschede, The Netherlands

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ra20577g

bis(trifluoromethanesulfonyl)imide as indicated by EXAFS studies when longer carbon chain RTILs were used.⁷ Task specific ionic liquids with a quaternary ammonium cation and bearing a phosphoryl group have been synthesized and used for the extraction of UO_2^{2+} .⁸ CMPO (carbamoyl methyl phosphine oxide) grafted task specific ionic liquids have also been prepared and the solid phase extraction of Pu(IV) was investigated using PAN fibers and carbon nano tubes as the support.⁹ In another study, CMPO dissolved in RTILs has been used for the extraction of Am(III) from slightly acidic feed solutions and its separation from Eu(III) using a variety of complexing agents.¹⁰

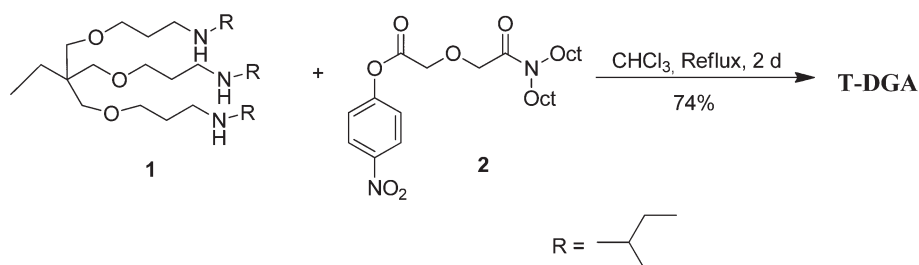
Diglycolamide extractants, such as *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA) have been found to be significantly more effective for minor actinide partitioning as compared to CMPO and several test counter-current runs have been carried out using 'hot' radioactive waste solutions.¹¹ On the other hand, functionalized diglycolamides were found to be more efficient than TODGA and a tripodal diglycolamide (T-DGA) has shown unique actinide extraction properties.^{12–14} Usually, the dielectric constant of the diluent decides the number of extractant molecules being associated in the extracted species.¹⁵ With TODGA as the extractant, the number of extractant molecules in the extracted species vary from 2 for nitrobenzene (dielectric constant of 35.6¹⁶) to 4 for *n*-dodecane (dielectric constant of 2.012¹⁶) for Am(III) bearing extracted species.¹⁵ The objective of using the tripodal diglycolamide extractant is to discount this diluent dependent metal ion extraction and to enable the formation of large organophilic complexes with high distribution ratio values in any diluent system. Further, in view of the improved extraction and separation behaviour of room temperature ionic liquids, it was of interest to carry out actinide extractions using T-DGA in ionic liquids.

The present work deals with the extraction of Am(III) from acidic feed solutions using a tripodal diglycolamide (T-DGA, Fig. 1(a)) in three commercially available room temperature ionic liquids, viz. $[\text{C}_4\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_8\text{mim}][\text{NTf}_2]$. The extraction data are compared with those obtained with TODGA (Fig. 1(b)) which has been used in several process test runs. In addition to the effects of equilibration time and feed acidity, the stoichiometry of the complexes, the thermodynamic parameters, and the radiolytic stability are studied.

2. Experimental

2.1 Materials

2.1.1 General. *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA) was obtained from Thermax Ltd, India and was



Scheme 1 Synthesis of T-DGA.

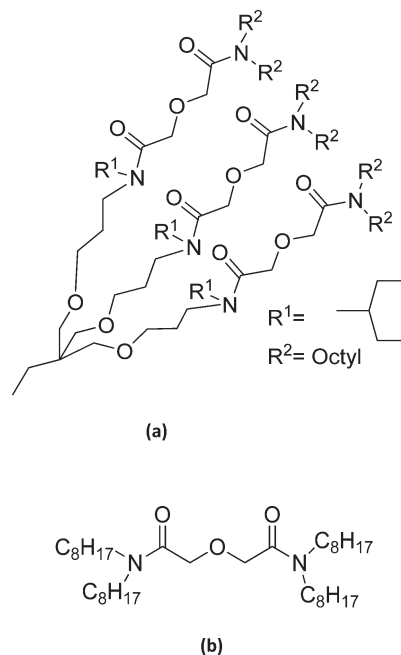


Fig. 1 Structural formulae of the extractants used.

characterized by NMR, HPLC, GC-MS as well as by distribution measurements (distribution data obtained at 3 M and 0.01 M HNO_3 were compared with those reported previously¹⁷). ^{241}Am , Pu (mainly ^{239}Pu), and ^{233}U tracers were purified prior to their use by ion-exchange methods, while $^{85,89}\text{Sr}$ and ^{137}Cs and $^{152,154}\text{Eu}$ tracers were purchased from BRIT, Mumbai. Assaying of ^{241}Am , ^{137}Cs , $^{85,89}\text{Sr}$ and $^{152,154}\text{Eu}$ was done by gamma counting using a NaI(Tl) scintillation counter, while nuclides such as ^{239}Pu and ^{233}U were assayed by liquid scintillation counting.

2.1.2 Synthesis of T-DGA. Recently, we reported the synthesis of the tripodal diglycolamide T-DGA¹² by reaction of the tripodal amine **1**¹³ with diglycolic anhydride and subsequent reaction with di-*n*-octylamine. Meanwhile, we developed an improved procedure for T-DGA in which the tripodal amine **1** is reacted with *p*-nitrophenol activated DGA (**2**) to give the target compound in 74% yield (Scheme 1).

A mixture of **1** (1.10 g, 2.1 mmol), *p*-nitrophenol activated DGA (**2**) (3.20 g, 6.6 mmol) and triethylamine (0.65 g, 6.5 mmol) in chloroform (70 mL) was refluxed for 2 d. 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 (SiO_2 , CH_2Cl_2 : MeOH = 95 : 5 \rightarrow 7 : 3) to afford T-DGA as an oil (2.42 g, 74%).

2.2 Methods

2.2.1 Distribution studies. The distribution studies were carried out by mixing 1 mL of the ligand solution in a suitable room temperature ionic liquid with an equal volume of the aqueous phase containing the required radiotracers in a given concentration of HNO_3 . Studies with Am involved the use of ^{241}Am tracer and the concentration of the metal ion in a typical distribution experiment was $\sim 10^{-7}$ M. The equilibration of the tubes was carried out in a thermostated water bath at 25 ± 0.1 °C for about 3 h, which was optimized after the studies with varying equilibration times. After centrifugation, the phases were separated and assayed radiometrically (usually 100 μL aliquots were taken for radiometric assay) as mentioned above. The valency of Pu to the +4 state was adjusted by using NaNO_2 as the redox agent and ammonium metavanadate as the holding oxidant and its conversion was checked by the TTA extraction method.¹⁸ Radiometric assay of ^{233}U and Pu was done using an alpha-liquid scintillation counting system (Hidex, Finland) using an Ultima Gold scintillator cocktail (Sisco Research Laboratory, Mumbai), while that of $^{85,89}\text{Sr}$, ^{137}Cs and ^{239}Np was done by gamma ray counting using a $\text{NaI}(\text{Tl})$ scintillation counter (Para Electronics, India) inter phased to a multi-channel analyzer (ECIL, India).

The distribution ratio, D_M , was defined as the ratio of the activity per unit volume in the ionic liquid phase to that in the aqueous phase. In view of the uncertainties involved in sampling due to the high viscosity of the ionic liquid phase, the D_M (distribution ratio of the metal ion) values were also calculated by obtaining the counts in the ionic liquid phase by the difference of the initial and final counts in the aqueous phase as follows:

$$D_M = (C_i - C_f)/(C_f) \quad (1)$$

where, C_i and C_f are the initial and final concentrations of the metal ion, respectively. The experiments were carried out in duplicate and the precision was within $\pm 5\%$.

The radiolytic degradation studies were carried out using a ^{60}Co irradiation source at a dose rate of 1.6 kGy h^{-1} . Usually, about 5 mL of the solution containing T-DGA in RTIL were irradiated for the required period so as to correspond to absorbed doses of 500 and 1000 kGy . A thermostated water bath was used for carrying out the temperature variation studies

wherein the two phases were equilibrated at varying temperatures in the range of 20–40 °C. Aliquots from both phases (usually ~ 100 μL) were taken while keeping the equilibration tubes in the thermostat and the temperature changes were kept within ± 0.2 °C of the set temperature.

Stripping studies were carried out by equilibrating the equal volumes of the loaded organic phase with aqueous phases containing either 0.05 M DTPA or EDTA in 1 M guanidine carbonate or a buffer mixture containing 0.1 M citric acid + 0.4 M formic acid + 0.4 M hydrazine hydrate which have been used for the stripping of Am(III) from CMPO loaded organic phases.¹⁹

2.2.2 Fluorescence studies. Time resolved laser fluorescence spectroscopy (TRLFS) measurements were carried out using a luminescence spectrometer equipment supplied by Edinburgh Analytical Instruments, UK controlled by CD 920 controller and pumped by OPO lasers as excitation sources. The excitation wavelength was fixed at 230 nm, while emission spectrum was recorded in the range of 575–750 nm. The luminescence decay curves were fitted into the exponential function to obtain the lifetimes/decay rates of the excited states using inbuilt software GEM/3 (Edinburgh). The reproducibility of lifetimes of the excited states was within ± 3 μs .

3. Results and discussion

Though no extraction of Am(III) was noticed with RTIL alone ($D_{\text{Am}} < 0.01$), in the absence of the extractants TODGA or T-DGA, a sharp increase in the D_M values was observed when a small amount (about 1.0×10^{-3} M) of the extractant was added to the ionic liquid phase. With comparable concentrations of the extractants, the D_M values obtained with RTILs were significantly higher than those obtained with molecular diluents in the organic phase.¹⁴ This is in line with the observations made by Nakashima *et al.*,²⁰ during their studies on lanthanide extraction using CMPO dissolved in RTILs. They have also reported that ionic liquids with NTf_2^- counter anions extracted the metal ions more efficiently as compared to those with PF_6^- counter anions. Similar observations were also made by us during our studies on Sr(II) extraction using di-*tert*-butylcyclohexano-18-crown-6 in both types of RTILs.²¹ The extraction data for Am(III) are listed in Table 1 with the three ionic liquids, *viz.* $[\text{C}_4\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_8\text{mim}][\text{NTf}_2]$ and a 1.0×10^{-3} M concentration of both the extractants. For comparison purposes, D_{Am} values in molecular diluents, *viz.* *n*-dodecane and an *n*-dodecane/*iso*-decanol mixture (10 : 1) are also included in Table 1. As previously reported, T-DGA has limited solubility in

Table 1 Distribution data of Am(III) using 1.0×10^{-3} M TODGA and T-DGA in room temperature ionic liquids from aqueous nitric acid feed solutions

[HNO_3], M	D_{Am} in T-DGA in different RTILs ^a			D_{Am} in T-DGA in <i>n</i> -dodecane + <i>iso</i> -decanol	D_{Am} in TODGA in different RTILs ^a			D_{Am} in TODGA in <i>n</i> -dodecane
	$[\text{C}_4\text{mim}][\text{NTf}_2]$	$[\text{C}_6\text{mim}][\text{NTf}_2]$	$[\text{C}_8\text{mim}][\text{NTf}_2]$		$[\text{C}_4\text{mim}][\text{NTf}_2]$	$[\text{C}_6\text{mim}][\text{NTf}_2]$	$[\text{C}_8\text{mim}][\text{NTf}_2]$	
3	0.6	0.2	0.17	30.1	0.25	0.13	0.12	0.003
0.5	91.1	32.0	3	0.05	0.76	0.29	0.22	0.002
1.0×10^{-2}	1518	161	105	0.02	208	27.9	26.2	5.0×10^{-4}

^a Note: the D_{Am} values in the absence of the extractants were typically < 0.01 in all the three ionic liquids.

n-dodecane alone and is fairly soluble in the diluent mixture, *n*-dodecane and *iso*-decanol (10 : 1).¹⁴ The observed trend of Am(III) extraction is [C₄mim][NTf₂] > [C₆mim][NTf₂] > [C₈mim][NTf₂], which is similar to that reported in several systems such as the extraction of Am³⁺ and UO₂²⁺ using CMPO and TODGA as the extractants, respectively.²² Apparently, the relatively higher aqueous solubility of the butyl form of the ionic liquid was responsible for the higher metal ion extraction as will be discussed below.

3.1 Extraction kinetics

Though extraction kinetics is an important parameter in all liquid–liquid extraction studies, it requires great significance in studies involving ionic liquids as these diluents invariably display higher viscosities as compared to the molecular diluents. The extraction kinetics of Am(III) was studied from a feed solution containing 1.0×10^{-3} M T-DGA in [C_{*n*}mim][NTf₂]. Fig. 2 represents the extraction kinetics data up to a period of 4 h, within which time complete attainment of the equilibrium was seen for all three RTILs. The rate of attainment of the equilibrium follows the trend: [C₄mim][NTf₂] > [C₆mim][NTf₂] ~ [C₈mim][NTf₂], suggesting that while 1 h is sufficient for the butyl derivative, 2 h are required for both the *n*-hexyl and *n*-octyl derivatives of the ionic liquids. The observed slower kinetics in all cases as compared to the conventional diluents like *n*-dodecane can be attributed to the high viscosity of the ionic liquids.²³ It is well known that the viscosity increases with the increase in the number of carbon atoms in the side chain.²³ Therefore, the attainment of the equilibrium was the slowest with [C₈mim][NTf₂], while the extraction kinetics was much faster with [C₄mim][NTf₂]. Though the attainment of the equilibrium with [C₆mim][NTf₂] as the diluent should be in between those observed with [C₄mim][NTf₂] and [C₈mim][NTf₂], the results indicate an Am(III) extraction kinetics with [C₆mim][NTf₂] similar to that of [C₈mim][NTf₂].

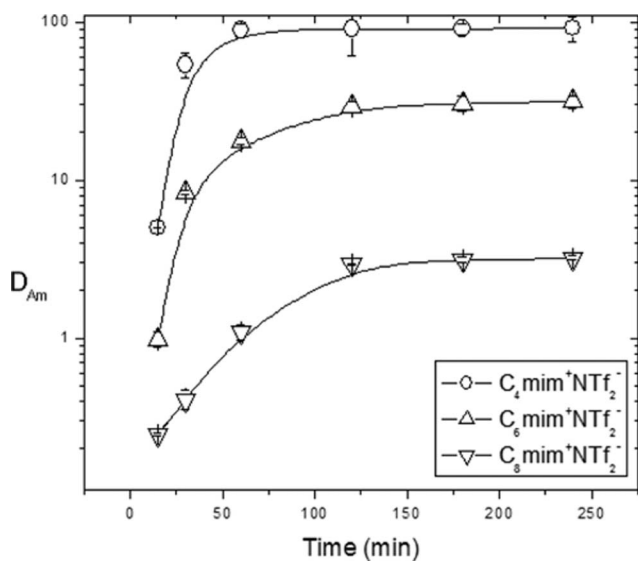


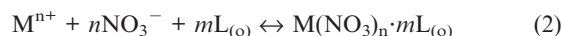
Fig. 2 Extraction kinetics of Am from 0.5 M HNO₃ feed into 1.0×10^{-3} M T-DGA in [C_{*n*}mim][NTf₂] (*n* = 4, 6, 8).

3.2 Relative extraction and separation behaviour

Apart from the Am³⁺ ion, the extraction of several actinide ions *viz.*, UO₂²⁺ and Pu⁴⁺ was also investigated using 0.5 M HNO₃ as the aqueous feed and 1.0×10^{-3} M T-DGA in the ionic liquids as the extractant; the results are listed in Table 2. Distribution ratio data for some important fission product elements were also determined under identical experimental conditions. The results are included in the table for comparison purposes, the extraction trend being Eu³⁺ > Am³⁺ > Pu⁴⁺ > UO₂²⁺ ~ Sr²⁺ > Cs⁺. The extractability trend for the elements is similar to that reported with the T-DGA–*n*-dodecane–*iso*-decanol system.¹⁴ The relative extraction behaviour of Am³⁺ *vis-à-vis* that of Sr²⁺ and UO₂²⁺ is interesting when compared to those observed with the analogous TODGA–*n*-dodecane system.²⁴ The separation factor values are listed in Table 3. Though the Sr²⁺ extraction with TODGA–*n*-dodecane system was about 50%, the S.F. (separation factor is defined as D_{Am}/D_{Sr}) value was as high as 302 (Table 3). On the other hand, the D_{Sr} (0.02) as well as the S.F. (1.08×10^4) values were reported to be favourable for Sr decontamination in T-DGA in *n*-dodecane–*iso*-decanol. It is clearly seen from Table 3 that U decontamination is significantly higher with T-DGA as the extractant, while ionic liquids are less effective than the molecular diluents (*n*-dodecane–*iso*-decanol mixture). On the other hand, a higher U decontamination was observed in T-DGA + ionic liquid solvent systems as compared to the TODGA–*n*-dodecane system. This indicates that the decontamination is due to T-DGA and not due to the ionic liquid, which is the opposite of the trend shown with a calix[4]arene-tetra-diglycolamide extractant.²³ For Pu and Eu decontamination, the results are not very favourable and hence are not discussed here (Table 3).

3.3 Effect of the feed acidity

Usually, for solvating type extractants, such as TBP, CMPO and TODGA, the extraction of the metal ion increases with increasing the feed acidity, which is based on an increase in the counter anion concentration which helps in the formation of neutral extractable species as per eqn (2):



where, species with the subscript '(o)' indicate those present in the organic phase, while those without any subscript indicate species in the aqueous phase. Though this trend has invariably been observed in molecular diluents such as *n*-dodecane,¹² an entirely different trend, *i.e.*, decrease in the metal ion extraction with increasing aqueous feed acidity has been reported in ionic

Table 2 Comparative extraction data of actinides and fission product elements using 1.0×10^{-3} M T-DGA in different room temperature ionic liquids. Feed: 0.5 M HNO₃

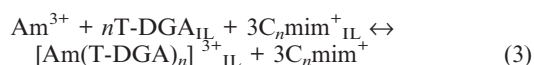
Metal ions	[C ₄ mim][NTf ₂]	[C ₆ mim][NTf ₂]	[C ₈ mim][NTf ₂]
Am(III)	91.1	32.6	3.1
Pu(IV)	30	16.9	1.4
U(VI)	0.24	0.23	0.06
Cs(I)	0.12	0.04	0.01
Sr(II)	0.27	0.12	0.02
Eu(III)	218.7	63.96	12.7

Table 3 Separation factors of Am(III) with respect to other actinides and fission products using T-DGA (1.0×10^{-3} M) in various room temperature ionic liquids. Feed: 0.5 M HNO_3

Extraction system	Separation factors				Reference
	Am(III)/U(VI)	Am(III)/Pu(IV)	Am(III)/Eu(III)	Am(III)/Sr(II)	
T-DGA in $[\text{C}_4\text{mim}][\text{NTf}_2]$	380	3.04	0.42	337	Present work
T-DGA in $[\text{C}_6\text{mim}][\text{NTf}_2]$	142	1.93	0.51	272	Present work
T-DGA in $[\text{C}_8\text{mim}][\text{NTf}_2]$	51.7	2.21	0.24	155	Present work
TODGA in <i>n</i> -dodecane ^{a,b}	28.9	—	1.04	302	Ref. 21
T-DGA in <i>n</i> -dodecane + <i>iso</i> -decanol ^{a,c}	895	1.48	—	1.08×10^4	Ref. 14

^a Note: data obtained with 3.0 M HNO_3 as the feed. ^b 0.1 M TODGA was used. ^c 2.9×10^{-3} M T-DGA was used.

liquids as the diluent due to a ion-exchange mechanism,^{6,23} as indicated in eqn (3) (subscript “IL” means species in ionic liquid phase):

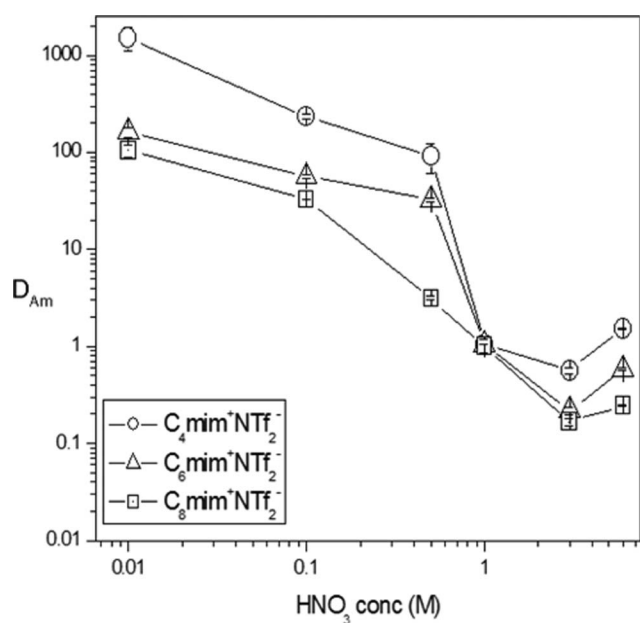
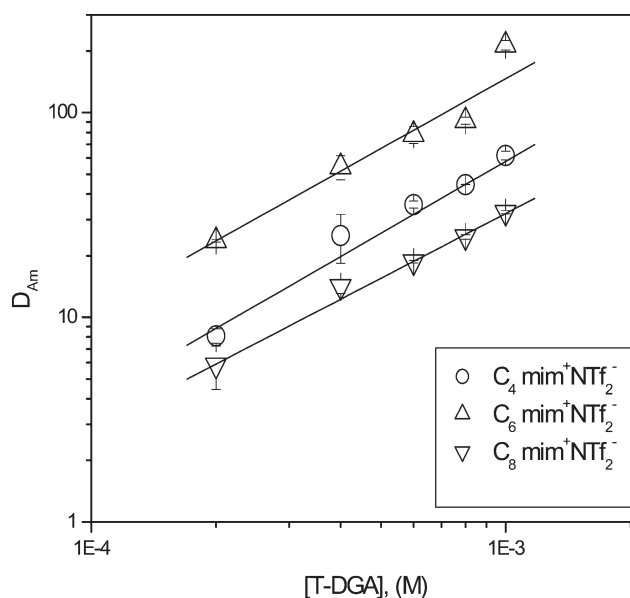


As discussed above, eqn (3) suggests that a higher solubility of the $[\text{C}_n\text{mim}]^+$ part of the ionic liquid will result in higher metal ion extraction. Fig. 3 shows the dependence of the distribution ratio of Am(III) with the change in the feed nitric acid concentration for the ionic liquid solvents containing 1.0×10^{-3} M T-DGA. It is clear that an increase in the feed nitric acid concentration led to a decrease in the D_{M} values in the acidity range of 0.01–3 M, beyond which a slight increase was noticed. The decrease was less significant for $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_8\text{mim}][\text{NTf}_2]$ where the D_{Am} values decreased by about 600–700 times as compared to about 2700 times when $[\text{C}_4\text{mim}][\text{PF}_6]$ was used as the ionic liquid (Fig. 3). The extraction profiles obtained in the present study indicate that the extraction mechanism is not the same as that in the case of conventional molecular diluents such as *n*-dodecane is used. Apparently, an ion-exchange mechanism is responsible for the extraction of

Am(III) to the ionic liquid phase. The ion-exchange mechanism also gets credence from the fact that the extraction of Am(III) increased with decreasing carbon chain length of the RTIL. As shown in Fig. 3, there is a marginal increase in the D_{Am} values for all the three ionic liquids beyond 3 M HNO_3 (about 3 times for the $[\text{C}_6\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{NTf}_2]$ and about 1.5 times for $[\text{C}_8\text{mim}][\text{NTf}_2]$). This can be attributed to a solvation mechanism with nitrate ion participation as described previously for a crown ether extraction system.²⁵

3.4 Effect of T-DGA concentration

In order to get an idea on the nature of the extracted species, the extraction of Am(III) with varying T-DGA concentrations was investigated using all the three RTILs from aqueous feed solutions of 0.1 M HNO_3 and the time of equilibration was kept as 3 h. The results, presented in Fig. 4, show an increase in Am(III) extraction with increasing T-DGA concentration for all the three ionic liquids. The slope values of the plots are close to 1 (1.17 ± 0.05 for $[\text{C}_4\text{mim}][\text{NTf}_2]$; 1.13 ± 0.02 for $[\text{C}_6\text{mim}][\text{NTf}_2]$; and 1.05 ± 0.04 for $[\text{C}_8\text{mim}][\text{NTf}_2]$) suggesting that one T-DGA unit is present in the extracted species, which is in sharp contrast to the extracted species in the molecular diluent containing 95% *n*-dodecane + 5% *iso*-decanol mixture.¹⁴ It is well

**Fig. 3** Extraction behavior of Am from different feed acidities into 1.0×10^{-3} M T-DGA in $[\text{C}_n\text{mim}][\text{NTf}_2]$ ($n = 4, 6, 8$) after 3 h**Fig. 4** Dependence of Am(III) extraction on varying T-DGA concentrations from 0.5 M HNO_3 feed into $[\text{C}_n\text{mim}][\text{NTf}_2]$ ($n = 4, 6, 8$).

known that a lower number of ligands may be present in the extracted species with the increasing dielectric constant of the diluent.¹⁵ On the other hand, higher metal ion extraction has been reported with diluents of high dielectric constant even though lesser number of ligand molecules are associated in the extracted complexed species as compared to those with low dielectric constant diluents. In view of this, it is expected that the relatively high dielectric constant of the ionic liquids²⁶ as compared to the molecular solvents used, would prevent the participation of a second T-DGA unit, which would otherwise lead to 'stereochemical crowding'. A similar increase in the extraction of actinide ions with TODGA and C4DGA (a calix[4]arene containing four DGA moieties) was reported recently where $[C_n\text{mim}][\text{PF}_6]$ was used as the RTIL.²³

3.5 Stripping studies

With room temperature ionic liquids, the stripping of the metal ion from the ionic liquid phase is one of the major challenges. Usually, with studies involving diglycolamide extractants such as TODGA, the extraction is carried out at higher acidity (3–6 M HNO_3), while the stripping is done at lower acidity (pH 2.0). However, with ionic liquids as the diluent the D values at pH 2.0 are very high (*vide supra*), which do not decrease significantly with increasing the aqueous phase acidity, so that effective stripping is not possible under these conditions (Fig. 3). Nakashima *et al.*,²⁰ have employed 0.05 M DTPA + 1 M guanidine carbonate, 0.05 M EDTA + 1 M guanidine carbonate and a buffer mixture comprising of 0.1 M citric acid + 0.4 M formic acid + 0.4 M hydrazine hydrate for the effective stripping of rare earth metal ions from ionic liquid extracts. These solutions were employed in the present study for the stripping of Am(III) from the T-DGA in $[C_4\text{mim}][\text{NTf}_2]$ extracts. The results are shown in Fig. 5 which suggest that EDTA and DTPA solutions in 1 M guanidine carbonate are effective as strippant where close to 80% stripping of Am was observed in a single stage. On the other hand, the buffer mixture was not very effective as a strippant as only <10% stripping was obtained in a

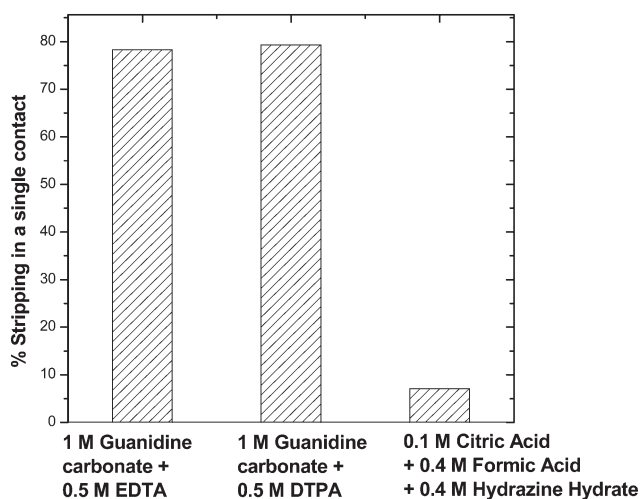


Fig. 5 Stripping behaviour of Am(III) from an extract made using 1.0×10^{-3} M T-DGA in $[C_4\text{mim}][\text{NTf}_2]$.

single step. The results are encouraging as >99% stripping of Am is possible using the complexing agents in three stages.†

3.6 Laser induced fluorescence studies

Though the nature of the extracted species was determined by slope analysis from T-DGA concentration variation studies, further evidence was obtained by time resolved laser fluorescence spectroscopy (TRLFS) using the Eu^{3+} -T-DGA complexes. In view of the similarities in the chemical properties of the trivalent actinides and lanthanides, Eu^{3+} was taken as the surrogate of Am^{3+} and the results of the Eu^{3+} fluorescence studies can be extended for the Am^{3+} system as well. Fluorescence spectroscopic investigations on the Eu^{3+} aqueous complex and Eu^{3+} -T-DGA complex (both containing 1.0×10^{-3} M Eu^{3+}) showed interesting behaviour as the intensity of the characteristics peaks at 617 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ hyper sensitive transition, electric dipole), 592 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, magnetic dipole), and at 690 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition, electric dipole, sensitive to Eu^{3+} environment) increased significantly (the former by more than 100 times) when T-DGA was added in an acetonitrile–water mixture as the solvating medium (Fig. 6). The acetonitrile–water mixture (5 : 1) contained dilute nitric acid to prevent hydrolysis of Eu^{3+} . Further, an extract containing the Eu^{3+} -T-DGA complex in $[C_4\text{mim}][\text{NTf}_2]$ also showed a similar increase in the emission spectra intensities suggesting similarity between the complexes in both the acetonitrile–water mixture and the ionic liquid medium. The mode of complexation was studied by time resolved laser fluorescence spectroscopy (TRLFS), where the presence of inner-sphere water molecules or the lack of them would be reflected in the lifetime of the $^5\text{D}_0$ emitting level of the Eu^{3+} -T-DGA complex. It is well known that the luminescence lifetime depends on several radiation (independent of the environment) and non-radiation decay processes and that the number of inner-sphere water molecules is determined by the lifetime of the $^5\text{D}_0$ emitting level of Eu^{3+} .²⁷ Uncomplexed Eu^{3+} has nine water molecules in its primary co-ordination sphere. In the presence of nitric acid in the aqueous phase, some nitrate complexation is expected, which can decrease the number of water molecules in the inner hydration sphere, which is also reflected by an increase of the emission lifetime. Further, with a decreasing number of water molecules in the primary hydration sphere, which results in the addition of the T-DGA ligand, the lifetime should show an increasing trend. The fluorescence decay profiles of Eu^{3+} and Eu^{3+} -T-DGA both in the acetonitrile–water mixture and the extract containing the Eu^{3+} -T-DGA complex in $[C_4\text{mim}][\text{NTf}_2]$ point to the presence of a single complexed species with 1 : 1 stoichiometry in all cases; the lifetime data† are presented in Table 4. The number of water molecules was calculated from the lifetime (τ) using eqn (4):²⁸

$$N_{\text{H}_2\text{O}} = (1.06/\tau) - 0.19 \quad (4)$$

The lifetime of Eu^{3+} in the absence of T-DGA was found to be 155 μs , which increased to about 2.5 ms in the presence of the complexing extractant. It has been reported that the Eu^{3+} aqueous ion has a fluorescence lifetime of 114 μs , which increases in the presence of nitric acid, apparently due to the replacement of some inner-sphere water molecules by nitrate ions.²⁹ The appearance of an additional peak at 617 nm indicates a strong

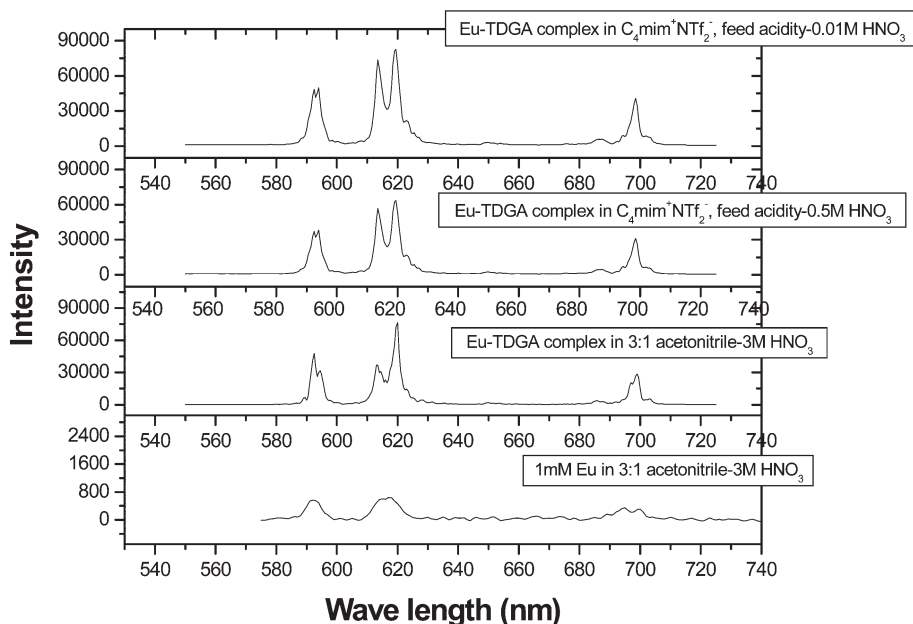


Fig. 6 Emission spectra of Eu^{3+} (1 mM) in the absence and presence of T-DGA in acetonitrile : water (5 : 1) and those of the Eu^{3+} -T-DGA extract in $[\text{C}_4\text{mim}][\text{NTf}_2]$ obtained from different feed acidities.

interaction with the DGA moieties of T-DGA similar to that observed with a calix[4]arene containing four DGA units.³⁰ In case of the extract containing the Eu^{3+} -T-DGA complex in $[\text{C}_4\text{mim}][\text{NTf}_2]$, a similar pattern was observed with a lifetime of 2.5 ms. However, the intensity of the split lines at 617 nm changed significantly. These results indicate very strong complex formation with the DGA moieties of T-DGA with practically no inner-sphere water molecules. Comparable lifetimes for extracts made from both 0.01 M and 0.5 M HNO_3 suggested extraction of similar 'inclusion' complex species, in which all the water molecules are replaced by the coordinating sites of the DGA groups.

3.7 Radiolytic degradation

A recycling option in process applications for radioactive waste treatment requires that the solvent system should have an adequate radiation stability. Fig. 7 shows the changes in the D_{Am} values as a function of absorbed radiation dose (gamma ray) up to a maximum of 1000 kGy. Interestingly, the decrease in the D_{Am} values was insignificant when the solvents were exposed to a 500 kGy dose for all the three ionic liquids. However, an appreciable decrease in the D_{Am} values was seen when the solvents were exposed to a 1000 kGy radiation dose. It is interesting to note that the D_{Am} value of 91.2 with 1.0×10^{-3} M T-DGA in $[\text{C}_4\text{mim}][\text{NTf}_2]$ decreased to 37 when the solvent was irradiated up to a 1000 kGy dose. This decrease is little over 60%,

which means that T-DGA is far more stable than a Cs-selective calix-crown extractant containing the same ionic liquid ($[\text{C}_4\text{mim}][\text{NTf}_2]$) where the decrease was >95% even for an absorbed dose of 550 kGy.³¹ Though the very poor irradiation stability of the Cs-selective solvent system was attributed to the degradation of the ionic liquid leading to acidic products, a similar effect might have affected the D_{Am} values in the present system as well, which is shown by the sharp dependence of the Am(III) extraction on the aqueous phase acidity. On the other hand, Allen *et al.*,³² have reported that the radiation stability of the ionic liquids is higher than that of diluents like *n*-dodecane, due to the presence of aromatic groups such as the imidazolium group. The radiation stability of solutions of T-DGA in ionic liquids is far higher compared to that of TODGA in a molecular solvent, where the degradation was >95% for an absorbed dose of 1000 kGy.³³ The amazingly high stability of the solvent system containing T-DGA $[\text{C}_4\text{mim}][\text{NTf}_2]$ may be attributed to the high viscosity of the ionic liquid system (leading to recombination of the free radicals) as compared to the TODGA in *n*-dodecane solvent system. Similar high radiolytic stability of T2EDGA (a branched diglycolamide extractant) was seen when undiluted extractant was irradiated, which can also be attributed to the recombination of the radicals in a viscous medium.³⁴ These results, together with the very high extraction and effective stripping, suggest that the solvent containing T-DGA in $[\text{C}_4\text{mim}][\text{NTf}_2]$ may be used as a possible 'green' alternative for

Table 4 Time resolved laser induced fluorescence spectroscopy data for Eu^{3+} (1.0×10^{-3} M) under varying experimental conditions in the absence and presence of T-DGA (as shown in Fig. 6)

Sample	Lifetime (ms)	Inference
Eu in ACN-3 M HNO_3	0.155	6 water; 3 nitrate
Eu-T-DGA complex in ACN-3 M HNO_3	2.285	No inner-sphere water
Eu-T-DGA complex in $[\text{C}_4\text{mim}][\text{NTf}_2]$, feed acidity 0.5 M HNO_3	2.251	No inner-sphere water
Eu-T-DGA complex in $[\text{C}_4\text{mim}][\text{NTf}_2]$, feed acidity 0.01 M HNO_3	2.249	No inner-sphere water

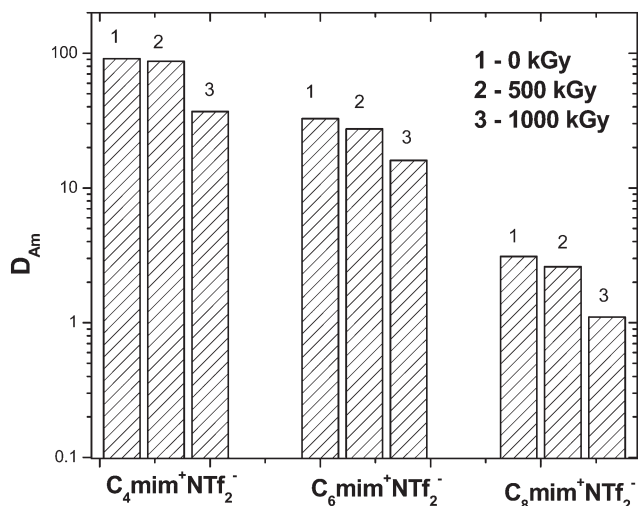


Fig. 7 Effect of absorbed dose on the extraction of Am(III) from 0.5 M HNO₃ using 1.0×10^{-3} M T-DGA solutions in [C_nmim][NTf₂] ($n = 4, 6, 8$).

actinide partitioning instead of TODGA-*n*-dodecane based solvents.

3.8 Determination of thermodynamic parameters

With T-DGA as the extractant, significant stereochemical ordering is required during the complexation reaction. The thermodynamic parameters were determined to throw light on the nature of the complexation. Temperature variation studies on Am(III) extraction were carried out from 0.5 M HNO₃ using

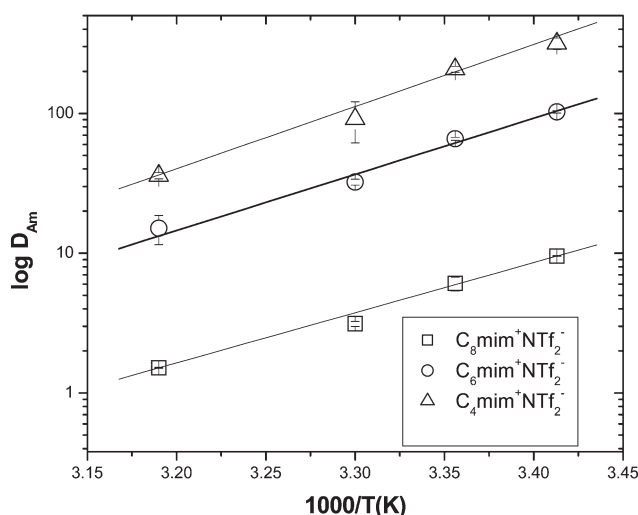


Fig. 8 Variation in distribution ratio of Am(III) at different temperatures from 0.5 M HNO₃ feed using 1.0×10^{-3} M T-DGA in [C_nmim][NTf₂] ($n = 4, 6, 8$) after 3 h equilibration.

Table 5 Extraction data and thermodynamic parameters (ΔG , ΔH and ΔS) of Am(III) extraction from 0.5 M HNO₃ using T-DGA in various room temperature ionic liquids at 300 K

Extractant	Ionic liquid	D _{Am}	Log K _{ex}	Slope	Intercept	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
T-DGA	[C ₄ mim][NTf ₂]	91	5.56	32.9	19.1	-31.937	-0.630	552.3
	[C ₆ mim][NTf ₂]	32	5.27	28.83	16.5	-30.271	-0.551	450
	[C ₈ mim][NTf ₂]	3	4.66	27.53	14.8	-26.767	-0.532	443

1.0×10^{-3} M T-DGA in the three RTILs being studied. The Van't Hoff plots for the distribution ratio data as a function of temperature† are presented in Fig. 8. The change in enthalpy (ΔH) during the complexation was calculated by using the Van't Hoff eqn (5):

$$\Delta H = -2.303 R \Delta \log D / \Delta(1/T) \quad (5)$$

The slope ($-\Delta H/2.303 R$) values of the log D vs. $1/T$ plots are listed in Table 5. The Gibbs free energy (ΔG) and the entropy change (ΔS) at a particular temperature were calculated from eqn (6) and (7):

$$\Delta G = -2.303RT \log K_{\text{ex}} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

The thermodynamic parameters are also listed in Table 5. The ΔH values are similar in all the three ionic liquids and are very small; the extraction reaction was exothermic. This is possibly due to the large amount of heat required to dehydrate the hydrated metal ion, which is nearly compensated by the strong complexation with the polydentate T-DGA ligand. The complete removal of the inner-sphere water molecules is understood from the very high positive entropy values. Overall, the reactions are spontaneous with large ΔG values. It is quite clear that larger distribution coefficient values in the RTIL system as compared to the molecular diluents resulted in higher extraction constants (log K_{ex}, Table 5) which are responsible for the large negative ΔG values.

4. Conclusions

The solvent extraction studies of Am(III) using T-DGA in various room temperature ionic liquids clearly demonstrate that the ionic liquid medium extracts the metal ions more efficiently as compared to molecular diluents such as *n*-dodecane. Furthermore, the tripodal diglycolamide T-DGA is a far superior extractant as compared to TODGA. It extracts Am(III) from acidic feed solutions with the butyl derivative being the most efficient ionic liquid. The extracted species follow an ion-exchange mechanism at lower acidity and possibly a solvation mechanism at higher acidities. Though the extraction of the trivalent actinide ion was much lower as compared to the trivalent lanthanide and actinide ions (both Eu(III) and Am(III) were highly extracted), the extraction of the hexavalent actinyl ion was insignificant. The extracted species was a 1 : 1 complex formed between Am(III) and T-DGA with no inner-sphere water molecules, which was confirmed by the TRIFS studies using the analogous Eu(III) complexes. The stripping results were very encouraging with the possibility of >99% stripping after three stages when a complexing agent such as

EDTA or DTPA was used in guanidine carbonate. The thermodynamics of the extraction indicated a highly entropy driven reaction, suggesting the removal of a large number of water molecules from the inner-coordination sphere. Radiolytic stability studies showed a significantly higher stability of the ionic liquid solvent systems as compared to those reported previously in the literature, which may lead to possible long term recycling options. This also makes the proposed solvent system a viable 'green' alternative to the TODGA based solvent systems with molecular diluents.

Acknowledgements

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

References

- (a) C. J. Adam, M. J. Earle and K. R. Sneddon, *Green Chem.*, 2000, **2**, 21–23; (b) G. Toma, B. Gotov and E. Solkaniova, *Green Chem.*, 2000, **2**, 149–151; (c) C. E. Song and E. J. Roh, *Chem. Commun.*, 2000, 837–838; (d) P. J. Dyson, D. J. Ellis, D. C. Parker and T. Welton, *Chem. Commun.*, 1999, 25–26.
- T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
- (a) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. N. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766; (b) L. A. Blanchard, D. Hancut, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28–29; (c) A. G. Fadeev and M. M. Meagher, *Chem. Commun.*, 2001, 295–296; (d) V. A. Cocalia, M. P. Jensen, J. D. Holbrey, S. K. Spear, D. C. Stepinski and R. D. Rogers, *Dalton Trans.*, 2005, 1966–1971; (e) A. E. Visser and R. D. Rogers, *J. Solid State Chem.*, 2003, **171**, 109–113.
- (a) I. W. Sun and C. L. Hussey, *Inorg. Chem.*, 1989, **28**, 2731–2737; (b) C. L. Hussey, in *Chemistry of nonaqueous solvents: current progress*, ed. G. Mamantov and A. I. Popov, VCH, New York, 1994.
- (a) A. N. Turanov, V. K. Karandashev and V. E. Baulin, *Solvent Extr. Ion Exch.*, 2010, **28**, 367–387; (b) S. Dai, Y. H. Yu and C. E. Barnes, *J. Chem. Soc., Dalton Trans.*, 1999, 1201–1202; (c) A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin and R. D. Rogers, *Ind. Eng. Chem. Res.*, 2000, **39**, 3596–3604; (d) H. Luo, S. Dai, P. V. Bonnesen, A. C. Buchanan III, J. D. Holbrey, N. J. Bridges and R. D. Rogers, *Anal. Chem.*, 2004, **76**, 3078–3083; (e) S. A. Ansari, P. K. Mohapatra, D. R. Raut and V. K. Manchanda, *Radiochim. Acta*, 2011, **99**, 713–717.
- P. Giridhar, K. A. Venkatesan, T. G. Srinivasan and P. R. V. Rao, *J. Nucl. Radiochem. Sci.*, 2004, **5**, 21–26.
- V. A. Cocalia, M. P. Jensen, J. D. Holbrey, S. K. Spear, D. C. Stepinski and R. D. Rogers, *Dalton Trans.*, 2005, 1966–1971.
- A. Ouadi, O. Klimchuk, C. Gaillarda and I. Billard, *Green Chem.*, 2007, **9**, 1160–1162.
- I. L. Odinet, E. V. Sharova, O. I. Artyshin, K. A. Lyssenko, Y. V. Nelyubina, G. V. Myasoedova, N. P. Molochnikova and E. A. Zakharchenko, *Dalton Trans.*, 2010, **39**, 4170–4178.
- A. Rout, S. Karmakar, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *Sep. Purif. Technol.*, 2011, **81**, 109–115.
- (a) R. B. Gujar, S. A. Ansari, D. R. Prabhu, P. K. Mohapatra, P. N. Pathak, A. Sengupta, S. K. Thulasidas and V. K. Manchanda, *Solv. Extr. Ion Exch.*, 2012, in press; (b) G. Modolo, A. Hanna, C. Schreinemachers and H. Vijgen, *Solvent Extr. Ion Exch.*, 2007, **25**, 703–729.
- D. Jańczewski, D. N. Reinhoudt, W. Verboom, C. Hill, C. Allignol and M. T. Duchesne, *New J. Chem.*, 2008, **32**, 490–495.
- D. Jańczewski, D. N. Reinhoudt, W. Verboom, E. Malinowska, M. Pietrzak, C. Hill and C. Allignole, *New J. Chem.*, 2007, **31**, 109–120.
- P. K. Mohapatra, M. Iqbal, D. R. Raut, W. Verboom, J. Huskens and V. K. Manchanda, *J. Membr. Sci.*, 2011, **375**, 141–149.
- (a) Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, *Solvent Extr. Ion Exch.*, 2001, **19**, 91–103; (b) S. Panja, P. K. Mohapatra, S. C. Tripathi, P. M. Gandhi and P. Janardan, *J. Membr. Sci.*, 2012, **403–404**, 71–77.
- W. M. Haynes, *Handbook of chemistry and physics*, CRC Press, Florida, 1992.
- R. B. Gujar, S. A. Ansari, M. S. Murali, P. K. Mohapatra and V. K. Manchanda, *J. Radioanal. Nucl. Chem.*, 2010, **284**, 377–385.
- M. S. Sajun, V. V. Ramakrishna and S. K. Patil, *J. Radioanal. Chem.*, 1981, **63**, 57–63.
- A. K. Dinkar, P. K. Mohapatra, A. Dakshinamoorthy and V. K. Manchanda, *Desalin. Water Treat.*, 2009, **12**, 73–78.
- K. Nakashima, F. Kubota, T. Maruyama and M. Goto, *Ind. Eng. Chem. Res.*, 2005, **44**, 4368–4372.
- A. Sengupta and P. K. Mohapatra, *Supramol. Chem.*, accepted for publication.
- (a) A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem.*, 2011, **290**, 215–219; (b) Y. Shen, X. Tan, L. Wang and W. Wu, *Sep. Purif. Technol.*, 2011, **78**, 298–302.
- A. Sengupta, P. K. Mohapatra, M. Iqbal, W. Verboom and J. Huskens, *Dalton Trans.*, 2012, **41**, 6970.
- S. A. Ansari, P. K. Mohapatra, D. R. Prabhu and V. K. Manchanda, *J. Membr. Sci.*, 2007, **298**, 169–174.
- M. L. Dietz and D. C. Stepinski, *Green Chem.*, 2005, **7**, 747–750.
- T. Singh and A. Kumar, *J. Phys. Chem. B*, 2008, **112**, 12968–72.
- (a) W. D. Horrocks and D. R. Sudnick, *J. Am. Chem. Soc.*, 1979, **101**, 334–340; (b) W. D. Horrocks and D. R. Sudnick, *Acc. Chem. Res.*, 1981, **14**, 384–392.
- S. Colette, B. Amekraz, C. Madic, L. Berthon, G. Cote and C. Moulin, *Inorg. Chem.*, 2004, **43**, 6745–6751.
- P. N. Pathak, S. A. Ansari, S. V. Godbole, A. R. Dhobale and V. K. Manchanda, *Spectrochim. Acta, Part A*, 2009, **73**, 348–352.
- P. K. Mohapatra, M. Iqbal, D. R. Raut, W. Verboom, J. Huskens and S. V. Godbole, *Dalton Trans.*, 2012, **41**, 360–363.
- C. Xu, L. Yuan, X. Shen and M. Zhai, *Dalton Trans.*, 2010, **39**, 3897–3902.
- D. Allen, G. Baston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healey, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims and R. C. Thied, *Green Chem.*, 2002, **4**, 152–158.
- R. B. Gujar, S. A. Ansari, A. Bhattacharyya, A. S. Kanekar, P. N. Pathak, P. K. Mohapatra and V. K. Manchanda, *Solv. Extr. Ion Exch.*, 2012, **30**, 278–290.
- P. Deepika, K. N. Sabharwal, T. G. Srinivasan and P. R. Vasudeva Rao, *Solvent Extr. Ion Exch.*, 2011, **29**, 230–246.