



Sequestration of Am³⁺ and Eu³⁺ into ionic liquid containing Aza-macrocycle based multiple-diglycolamide ligands: Extraction, complexation, luminescence and DFT studies



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ABSTRACT

Extraction of Am³⁺ and Eu³⁺ was carried out into a room temperature ionic liquid, C₈mim-Tf₂N, using two multiple-diglycolamide extractants with three or four diglycolamide arms tethered to either a triaza- or tetraazamacrocyclic ligand termed as TAM-3-DGA and TAM-4-DGA, respectively. The metal ion extraction was highly efficient as only 5 × 10⁻⁴ M solutions of TAM-3-DGA resulted in *D* values of 680 and 845 for Am³⁺ and Eu³⁺, respectively, at pH 2.0, while the respective values with a five times lower concentration of TAM-4-DGA were 142 and 296, which is probably the best reported thus far. Though Eu³⁺ ion was preferentially extracted over Am³⁺, the selectivity was not as good as reported in molecular diluent-based extraction systems. The extracted species contained two units of the extractant and did not contain any nitrate ion suggesting a cation-exchange mechanism. Studies on the temperature effect on metal ion extraction were carried out to determine the thermodynamic parameters. Luminescence studies of the extracts were also performed which suggested strong complex formation with no inner-sphere water molecules. To understand the ligand coordination to Eu³⁺ and Am³⁺ and other bonding parameters, DFT studies were carried out.

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1. Introduction

One of the major steps in the safe management of radioactive wastes in the 'closed nuclear fuel cycle' is the recovery of actinides and their subsequent transmutation [1] by a strategy termed as 'Partitioning & Transmutation'. [2] Though actinide ions such as UO₂²⁺ and Pu⁴⁺ are separated from the spent nuclear fuel using the PUREX (Plutonium Uranium Redox Extraction) process, minor actinides such as Np, Am and Cm end up in the raffinate stream and contribute to the overall radiotoxicity of the high-level liquid waste (HLLW), which is a concentrated form of the PUREX raffinate. This has been overcome by the selective separation of the minor actinide ions by tailor made extractants such as CMPO (carbamoyl methyl phosphine oxide), [3–5] DIDPA (diisodecylphosphoric acid), [6–8] TRPO (trialkylphosphine oxide), [9,10] and other phosphorous bearing extractants and subsequently using 'green'

extractants such as malonamides [11–13] and diglycolamides [14] using the 'actinide partitioning' strategy. [15–17] Out of these extractants, the diglycolamide (DGA) extractants such as TODGA (N,N,N',N'-tetra-*n*-alkyl diglycolamide) have been found to be the most efficient and hence, are the extractants of choice of most of the research in this area in the past two decades. [18–21] The separation efficiency of TODGA is quite spectacular in the sense that the trivalent lanthanides (such as Eu³⁺) are extracted to a much larger extent than the trivalent actinides (such as Am³⁺) with a reported separation factor (SF = *D*_{Eu}/*D*_{Am}) value being as high as 9 at 1 M HNO₃. [21] However, the SF values are reported to be much lower with increasing HNO₃ concentration.

The extraction mechanism involving TODGA has been extensively studied and has been proposed to be through a reverse micellar mechanism where 3–4 units of TODGA form an aggregate, which imparts the extraordinary selectivity towards the tetra- or trivalent actinide ions. [34,35] In a separate study, Zhu *et al.* reported extraordinary selectivity of ions, of any valency, having ionic radii close to 100 pm suggesting a size selective complexation similar to macrocyclic ligands. [36] However, common to both

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these observations is the use of a non-polar diluent medium such as *n*-dodecane which facilitates the aggregate formation. Therefore, to maintain the selectivity one needs to append the ligand scaffold with three to four diglycolamide moieties to obtain highly efficient extractants. Recently, we have synthesized many such multiple-diglycolamide extractants with a calix[4]arene[24–26] or pillar[5]arene[37] scaffold or tripodals with carbon,[38–40] nitrogen[27] or a benzene[28,30] center or even dendrimers [22,29] (Fig. 1), which yielded very high extraction efficiencies for the trivalent actinide / lanthanide ions. In all these extractants, the separation efficiency of the trivalent lanthanide and actinides showed a decreasing trend as compared to TODGA (Table 1).

Recently, we introduced polyazamacrocyclic rings as the scaffold in two such multiple-diglycolamide extractants with a triaza-macrocycle with three DGA pendent arms, termed as TAM-3-DGA and a tetraazamacrocyclic with four DGA arms, termed as TAM-4-DGA (Fig. 1).[32,33] It resulted in the most robust solvent systems to both efficient extraction and separation of trivalent lanthanides

and actinides in a molecular diluent mixture of *n*-dodecane and isodecanol. Very high extraction of trivalent *f*-cations (distribution coefficient or *D* values of > 50) was obtained using a 0.1 millimolar concentration of the ligand with a SF value of close to 10, which was unprecedented.

Room temperature ionic liquids (RTILs) are a class of neoteric diluents with practically no vapor pressure leading to their non-flammability and hence, they can be used safely in industrial applications including those in the nuclear industry.[41–45] It has been reported that solutions of ligands in ionic liquids result in very high extraction efficiency,[46,47] which may be attributed to their unusual extraction mechanisms such as a cation-exchange mechanism (*vide infra*).[46,47] Ionic liquids, due to their reasonably high polarity, lead to favorable extraction of the metal ions via an ‘ion-pair’ extraction mechanism as well [47].

We have reported the unusually high separation efficiency of an ionic liquid-based solvent system containing C4DGA (Fig. 1).[48] Therefore, it was thought of interest to investigate the extraction

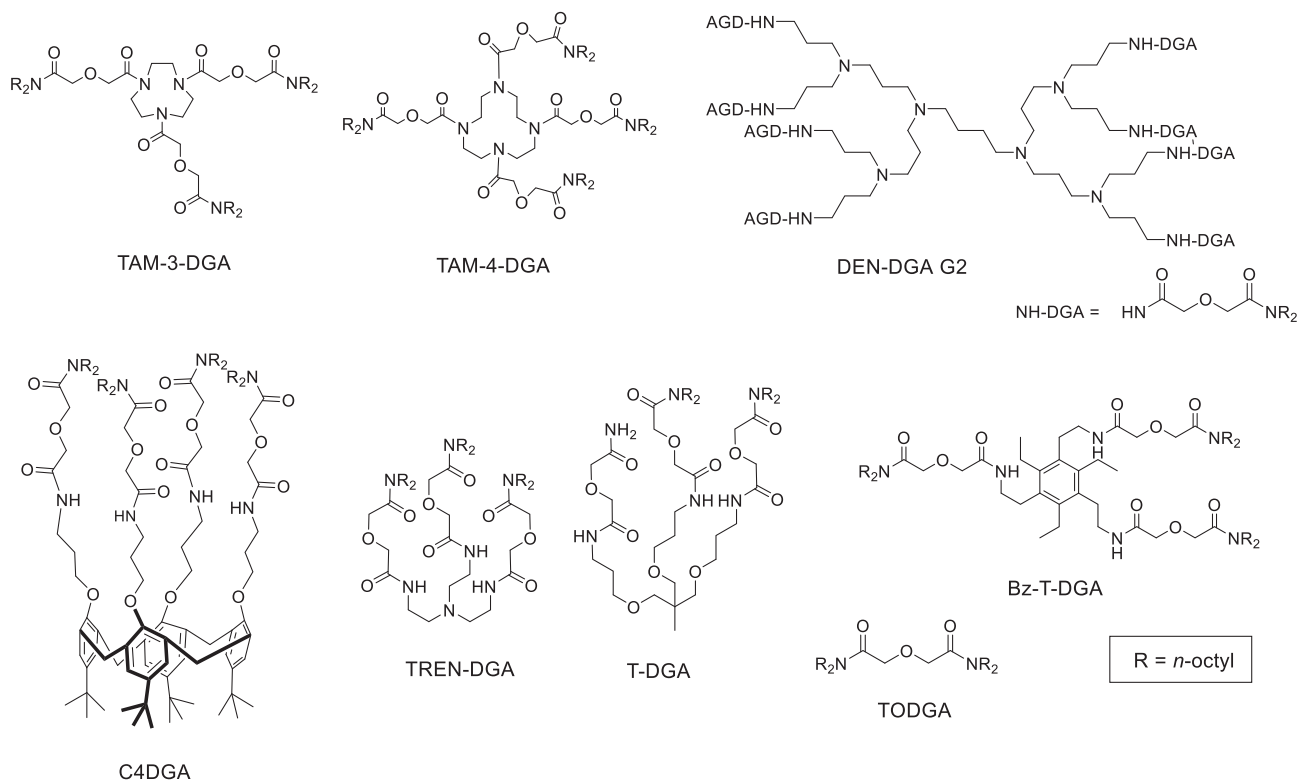


Fig. 1. Structures of different diglycolamide-based ligands.

Table 1

Extraction and separation efficiencies of 1.0×10^{-3} M solutions of TODGA and its multiple-DGA homologs in *n*-dodecane + 5% isodecanol from 3 M HNO₃. Values in parentheses refer to those in the ionic liquid (C₄mim.Tf₂N).

Solvent system	D_{Am}	D_{Eu}	SF(D_{Eu}/D_{Am})	Ref.
TODGA ^{a,b}	1.40	2.71	1.94	[22]
TODGA	235 (0.04) ^c	230 (0.44) ^c	0.98 (11) ^c	[23]
C4DGA	79.5 (9.34) ^{c,d,e}	225 (143) ^{c,d,e}	2.83 (15.3)	[24–26]
T-DGA	11.1 (0.08)	98.5 (0.09)	8.87 (1.13)	[27]
TREN-DGA	0.36 (161)	1.16 (126)	3.22 (0.78)	[27]
Bz-T-DGA	235 (8.29) ^d	390 (10.02) ^d	1.66 (1.21)	[28]
Den-DGA (Gen 2)	104 (52.0) ^d	300 (98.7) ^d	2.88 (1.90)	[29–31]
TAM-3-DGA	71.1	300	4.22	[32]
TAM-4-DGA	3.0	21	7	[33]

^a In 100% *n*-dodecane. ^b [ligand] = 1×10^{-2} M. ^c C₈mim.Tf₂N. ^d [ligand] = 5×10^{-4} M. ^e Aqueous phase 0.5 M HNO₃.

of lanthanides and actinides using solutions of the above mentioned extractants, TAM-3-DGA and TAM-4-DGA, in a room temperature ionic liquid. Apart from an extraction and separation efficiency evaluation, the complex formation constants were determined, and the complex structure was investigated by luminescence spectroscopy. To our knowledge, this is the first report on the complexation studies (where complex formation constants were determined and structural possibilities were assessed by DFT) of trivalent *f*-cations with the macrocyclic ligands with DGA pendent arms in a room temperature ionic liquid and the excellent results presented here, both in the complexation as well as extraction studies, add to the novelty and uniqueness of this study.

2. Experimental

2.1. Materials

The multiple DGA-containing ligands TAM-3-DGA and TAM-4-DGA (Fig. 1) were prepared as reported earlier.[32,33] The ionic liquid, 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide ($C_8mim \cdot Tf_2N$), was purchased from Iolitec, Germany, having a purity of > 95%. Trifluoromethane sulfonimide (HTf_2N) was purchased from Sigma Aldrich. Radiotracers, ^{241}Am , Pu (mainly ^{239}Pu), and ^{233}U were used from the laboratory stock solutions after confirming their radionuclidic purities. $^{152,154}Eu$, ^{137}Cs and $^{85,89}Sr$ were procured from BRIT (Board of Radiation and Isotope Technology, Mumbai). ^{239}Np was prepared as per a procedure reported before.[31] An $Eu(NO_3)_3$ standard solution was prepared by dissolving a known quantity of $Eu(NO_3)_3 \cdot 5H_2O$ (Aldrich; 99.9%) in water (pH ~ 2) followed by its volumetric titration with standard EDTA (BDH; AR grade). $Eu(Tf_2N)_3$ salt was prepared by reaction of Eu_2O_3 with HTf_2N in water as described earlier.[49] A stock solution of $Eu(Tf_2N)_3$ was prepared by dissolving an appropriated amount of its salt in $C_8mim \cdot Tf_2N$. The concentration of Eu^{3+} in the stock solution was confirmed by volumetric titration with a standard EDTA solution using bromothymol blue as the indicator in ethanol–water medium. All the other chemicals were of analytical reagent grade.

2.2. Distribution ratio measurements

The solvent extraction experiments were carried out by equilibrating equal volumes (usually 1 mL) of the ionic liquid phase containing 0.5 mM ligand in $C_8mim \cdot Tf_2N$ and the aqueous phase containing the required radiotracer. The equilibrations were done in leak tight Pyrex glass tubes (10 mL capacity) in a thermostated water bath at 25 ± 0.1 °C. The time of equilibration was maintained at about 24 h or less after confirming the extraction kinetics (*vide supra*). Subsequently, the tubes were rested, centrifuged and 100 μ L aliquots were taken out from both phases for subsequent radiometric assay. The radiometric assay of ^{241}Am , ^{239}Np , $^{152,154}Eu$, ^{137}Cs and $^{85,89}Sr$ was done using a well type NaI(Tl) scintillation counter (Para Electronics) coupled with a multi-channel analyzer (ECIL, India) while that of Pu and ^{233}U was done using a liquid scintillation counting system (Hidex, Finland). The distribution ratio of the metal ions (D_M) was calculated as the ratio of counts per unit time per unit volume in the organic phase to that in the aqueous phase. Each distribution experiment was carried out in triplicate and the accepted data were within the relative standard deviation of 5%. The distribution ratio values of the Eu (III) and Am(III) with TAM-3-DGA/ TAM-4-DGA were also measured as a function of temperature to evaluate the thermodynamic parameters of their extraction.

2.3. Luminescence studies

The emission spectra and lifetime of the Eu/ligand complex extracted in $C_8mim \cdot Tf_2N$ were recorded on a PTI QuantaMaster fluorometer (PTI QuantaMaster 400) adapted for time resolved measurements. The luminescence emission spectra were obtained in the wavelength region of 560–720 nm (0.5 nm/step, 2.0 nm bandwidth, 0.5 s integration time) by excitation at 394 nm (5 nm bandwidth). Signals were acquired and analyzed using PTI FelixGX Software from PTI QuantaMaster. The emission lifetime data were recorded in time-resolved mode after giving a delay time of 200 μ s to avoid a background contribution from the decay of the signal due to the ionic liquid. The emission lifetime data were fitted by the PTI FelixGX Software to get the decay constant.

For the luminescence titration of Eu^{3+} with ligands, its $Eu(Tf_2N)_3$ salt was used after dissolving it in $C_8mim \cdot Tf_2N$. The emission spectra of Eu^{3+} in $C_8mim \cdot Tf_2N$ medium were collected in the wavelength region of 675–710 nm (0.1 nm interval) at an excitation wavelength of 394 nm ($^7L_6 \leftarrow ^5D_0$ of Eu^{3+}). Eu^{3+} , once excited at 394 nm from 5D_0 to 7L_6 level, has a well-defined emission band between 675 and 710 nm, originating from the hypersensitive $^5D_0 \rightarrow ^7F^4$ transition.[31] For the titration experiments, the initial concentration of Eu^{3+} in the spectrophotometer cell was ca. 0.35 mmol/L to which a calculated aliquot of the titrant (ligand solution in $C_8mim \cdot Tf_2N$) was added. After addition of every increment of the titrant to the cell, the mixture was thoroughly stirred using a magnetic stirrer before the spectrum was recorded. Usually, a set of 15–20 spectra were recorded in each titration. Based on eqs (1) and (2), the stability constants of the Eu^{3+}/L complexes were calculated by nonlinear least-square regression analysis using the HypSpec[®] program.[50,51]

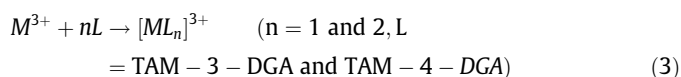


$$\beta_i = \frac{[EuL_i^{3+}]}{[Eu^{3+}][L]^i} \quad (2)$$

where L represents either the TAM-3-DGA or the TAM-4-DGA ligand.

2.4. Computational methodology

The structures of free TAM-3-DGA and TAM-4-DGA and their complexes with Eu^{3+} and Am^{3+} ions were optimized using the Becke-Lee-Young-Parr (B3LYP) density functional[52,53] employing the split-valence plus polarization (SVP) basis set[54,55] as implemented in the TURBOMOLE suite of program.[56] The scalar relativistic effective core potentials (ECP) were used for Eu^{3+} and Am^{3+} ions, where 28 electrons were kept in the core for Eu and 60 electrons in the core of Am.[57–60] The septet spin state was used during the computation of the structures and the energies. Optimization was performed without any symmetry restrictions. The free energy was computed at 298.15 K using the B3LYP functional.[52] The hybrid B3LYP functional has been shown to be quite successful in predicting the thermodynamic properties of actinides.[61–63] The solvent phase was accounted for using the popular conductor like screening model (COSMO).[64] The dielectric constant of water and the ionic liquid was taken to be 80 and 6.5, respectively.[65] The model complexation reaction was used as follows:



The free energy of complexation, ΔG_{com} , for the above complexation reaction was calculated using our earlier reported thermodynamic procedure.[66,67]

Scalar relativistic effects for heavier lanthanide and actinide elements were included in the present computation using the earlier reported procedure.[68–70] Since, there is a very small effect on the solvation energy between the gas phase and the solvent phase geometry,[62,63,71,72] the aqueous solvent effect was integrated by performing single point energy calculations using the optimized geometry obtained from the B3LYP level of theory employing the COSMO solvation model.

3. Results and discussion

3.1. Solvent extraction studies

The distribution behavior of Am^{3+} and Eu^{3+} was investigated with solutions of TAM-3-DGA and TAM-4-DGA ligands in $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$. The choice of $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$ as a RTIL solvent was based on the solubility of these rather bulky ligands, which were insoluble in the lower alkyl chain RTIL, $\text{C}_4\text{mim}\cdot\text{Tf}_2\text{N}$. The overall hydrophobicity of the RTIL increased with the increasing alkyl chain of the imidazolium cation, making $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$ RTIL more hydrophobic compared to the lower chain RTILs such as $\text{C}_n\text{mim}\cdot\text{Tf}_2\text{N}$ ($n: 4,6$). The higher hydrophobicity of $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$ led to better solubility of the bulky hydrophobic ligands. An initial test for the distribution measurement of $\text{Am}(\text{III})$ with 0.5 mM ligand at 0.1 M HNO_3 gave D_{Am} (distribution ratio of Am) values of 115 and > 300 for TAM-3-DGA and TAM-4-DGA, respectively. To get the D_{Am} values in the significant analytical range, it was considered judicious to use 0.5 mM TAM-3-DGA and 0.1 mM TAM-4-DGA for all the subsequent studies.

In view of the slow extraction kinetics reported for DGA ligands in a RTIL, at first the extraction kinetics of Am^{3+} and Eu^{3+} was investigated with these two ligands. As shown in Fig. 2, the extraction kinetics was slow for both the ligands and about 3 h was required to reach the equilibrium conditions. The extraction kinetics, on the other hand, was found to be fast (within 10 min of equilibration) with both the ligands when a molecular solvent such as

n-dodecane (modified with 5% isodecanol) was employed as the diluent medium.[32,33] Slow extraction kinetics in the case of viscous ionic liquids such as $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$ is expected due to slow diffusion of the extracted complex from the surface of the liquid to the bulk.[23] The experiment was repeated with larger glass tubes for an increased surface area and better mixing of the phase, but no improvement in the extraction kinetics was noted. The results confirmed that the extraction kinetics was slow indeed, which could be due to the higher viscosity of the $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$ phase (viscosity = 60 mPa.s).[23] Nonetheless, the kinetic data gave a guideline to maintain a sufficient time of equilibration for distribution measurements. Accordingly, a minimum equilibration time of 5 h was used for the subsequent distribution measurements. It is important to mention here that the kinetics can be improved when the studies are carried out at higher temperature where viscosity effects can be less pronounced.

The D values of Am^{3+} and Eu^{3+} from varying nitric acid solutions with these two ligands are shown in Fig. 3. The metal ion extraction was found to be highly efficient as only 5×10^{-4} M solutions of TAM-3-DGA resulted in D_{Am} and D_{Eu} values of 680 and 845, respectively, with a SF value of 1.24 at pH 2.0. On the other hand, D_{Am} and D_{Eu} values with 1×10^{-4} M solutions of TAM-4-DGA were 142 and 296, respectively, with an SF value of 2.09. While the D values obtained were higher than the highest reported values thus far, the SF values are not very impressive. The D values of both, Am^{3+} and Eu^{3+} , decreased sharply up to 3 M HNO_3 with TAM-3-DGA and remained almost unchanged or less steeply thereafter till 6 M HNO_3 . This behavior contrasts with the results of TAM-4-DGA where the curve is steeper, and the D values continue to decrease till 6 M HNO_3 . From the extraction of metal ions point of view, an ionic liquid gives better results than molecular diluents at 0.5 M HNO_3 , while there is an opposite trend at 3 M HNO_3 .

The extraction data for $\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ and the respective SF values are listed in Table 2. As seen from the table, the SF values for TAM-3-DGA are in the range of 3 to 4 in *n*-dodecane at both 0.5 and 3.0 M HNO_3 , which increase to values of ca. 7 for TAM-4-DGA in the same diluent medium. Interestingly, though the D_{M} ($\text{M} = \text{Am}$ or Eu) values increase for both the ligands in the ionic liquid medium *vis-a-vis* those obtained in the molecular diluent based solvent

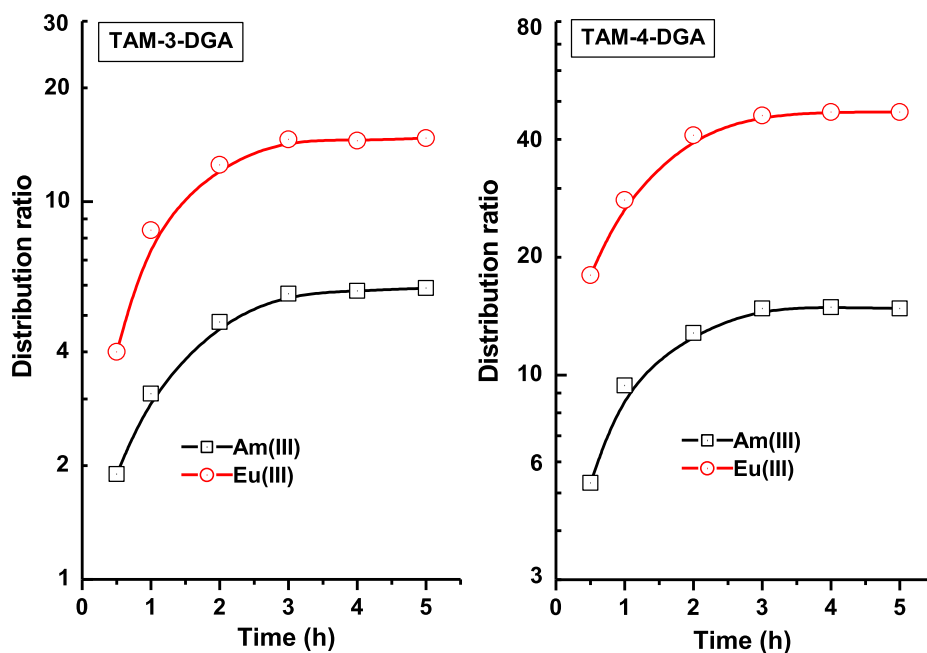


Fig. 2. Extraction kinetics for Am^{3+} and Eu^{3+} with TAM-DGA ligands. Ligand: 0.5 mM TAM-3-DGA and 0.1 mM TAM-4-DGA in $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$; aqueous phase: 0.5 M HNO_3 .

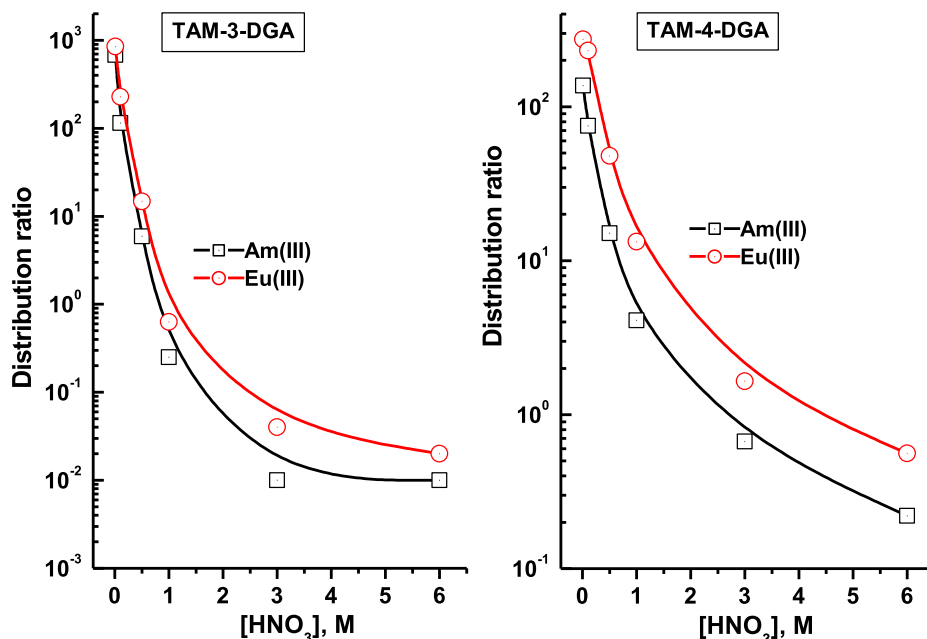


Fig. 3. Distribution ratio of Am^{3+} and Eu^{3+} as a function of nitric acid concentration. Ligand: 0.5 mM TAM-3-DGA and 0.1 mM TAM-4-DGA in $\text{C}_8\text{mim-Tf}_2\text{N}$; Aqueous phase: 0.01 – 6 M HNO_3 ; Temperature: 25 °C.

Table 2

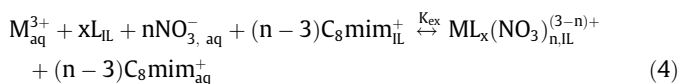
Comparison of the extraction and SF data for Am(III) and Eu(III) in molecular diluent as well as in ionic liquid using 1×10^{-4} M ligand solutions.

Ligand	HNO_3	D_{Am}	D_{Eu}	$\text{SF}_{(\text{Eu}/\text{Am})}$
TAM-3-DGA- <i>n</i> -dodecane ^{a,b}	0.5 M	1.3 ± 0.1	4.3 ± 0.1	3.3
	3.0 M	71 ± 6	301 ± 32	4.2
TAM-3-DGA- $\text{C}_8\text{mim.Tf}_2\text{N}^d$	0.5 M	5.9 ± 0.3	14.8 ± 0.6	2.5
	3.0 M	0.01 ± 0.001	0.04 ± 0.01	4.0
TAM-4-DGA- <i>n</i> -dodecane ^{a,c}	0.5 M	0.30 ± 0.05	2.0 ± 0.1	6.7
	3.0 M	3.0 ± 0.3	20.8 ± 2.1	6.9
TAM-4-DGA- $\text{C}_8\text{mim.Tf}_2\text{N}^d$	0.5 M	15.1 ± 0.7	47.9 ± 2.4	3.2
	3.0 M	0.67 ± 0.04	1.6 ± 0.2	2.4

^a Containing 5% isodecanol. ^b Ref. 32. ^c Ref. 33. ^d This work: 5×10^{-4} M.

system at 0.5 M HNO_3 , there is a sharp decrease in the extraction of both the metal ions for both ligands in ionic liquid medium at 3 M HNO_3 as compared to that in the solvent containing *n*-dodecane (and 5% isodecanol). The SF values increased with increasing acid concentration (from pH 2 to 3 M) for TAM-3-DGA with a maximum value of 4.2 obtained at 3 M HNO_3 , while no regular trend was seen for TAM-4-DGA in the same acid concentration range. Mincher *et al.* reported loss in selectivity (SF values close to 1) in an ionic liquid *vis-a-vis* that with a molecular diluent using TODGA as the extractant.[73] However, the present extraction systems are considered significantly superior in terms of extraction efficiency as well as selectivity.

The decrease in the D values with increasing feed acidity is an indication of a cation-exchange extraction mechanism, which is very common in RTIL-based solvents.[23] The extraction equilibrium defining a cation-exchange mechanism for extraction of trivalent metal ions from nitric acid medium is given as:



where the subscripts 'aq' and 'IL' represent the species present in the aqueous and the ionic liquid phases, respectively. The term K_{ex} represents the two-phase extraction equilibrium constant of the reaction, M^{3+} is either Am^{3+} or Eu^{3+} , L is the ligand (TAM-3-

DGA or TAM-4-DGA) and 'x' is the number of ligands present in the extracted complex. Here, it was shown that the extracted species may contain 1–2 nitrate ions, which one needs to confirm experimentally (*vide infra*). On solving the equilibrium reaction (4) and after simplification, gives the following linear equation:

$$\log D = \log K_{\text{ex}} + x \log [\text{L}]_{\text{IL}} + n \log [\text{NO}_3^-]_{\text{aq}} - (n-3) \log [\text{C}_8\text{mim}^+]_{\text{IL}} \quad (5)$$

In order to confirm the composition of the extracted complex, slope analysis was performed on the extraction data. A plot of $\log D$ vs. \log ligand concentration yielded a slope of approximately 2 for both Am(III) and Eu(III) with both TAM-3-DGA and TAM-4-DGA (Fig. 4a,b). These results confirm that the value of the coefficient 'x' in the equilibrium reaction is 2. Similarly, to confirm the participation of nitrate ions in the extracted complex, the D values were measured at varying NaNO_3 concentrations at a fixed aqueous phase acidity of 1 M HNO_3 (used to prevent hydrolysis). As shown in Fig. 4c, the D values of Am^{3+} and Eu^{3+} were unaffected in the presence of nitrate ions in the aqueous phase, suggesting the absence of nitrate ions in the extracted complex. Though one would expect an 'inclusion' complex with one ligand, i.e., TAM-3-DGA or TAM-4-DGA where all the DGA arms would 'wrap around' the metal ion (Scheme 1) thereby imparting good stability to the complex, there is also a possibility of a 1:2 complex as follows from the slope analysis in the solvent extraction studies (*vide supra*). As

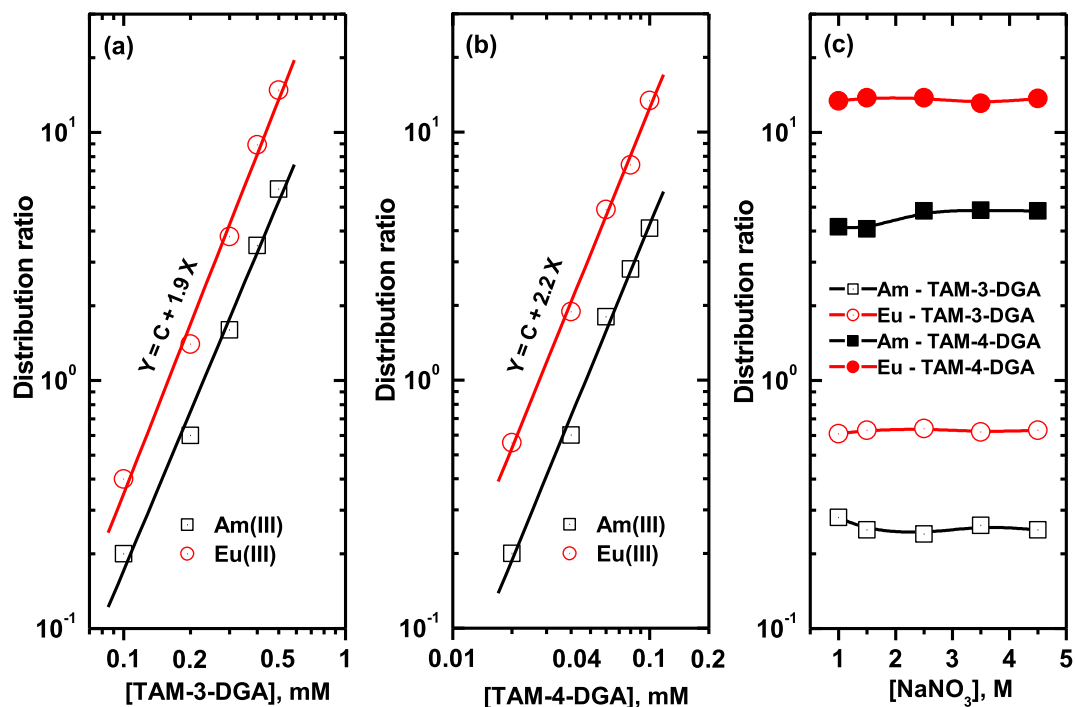
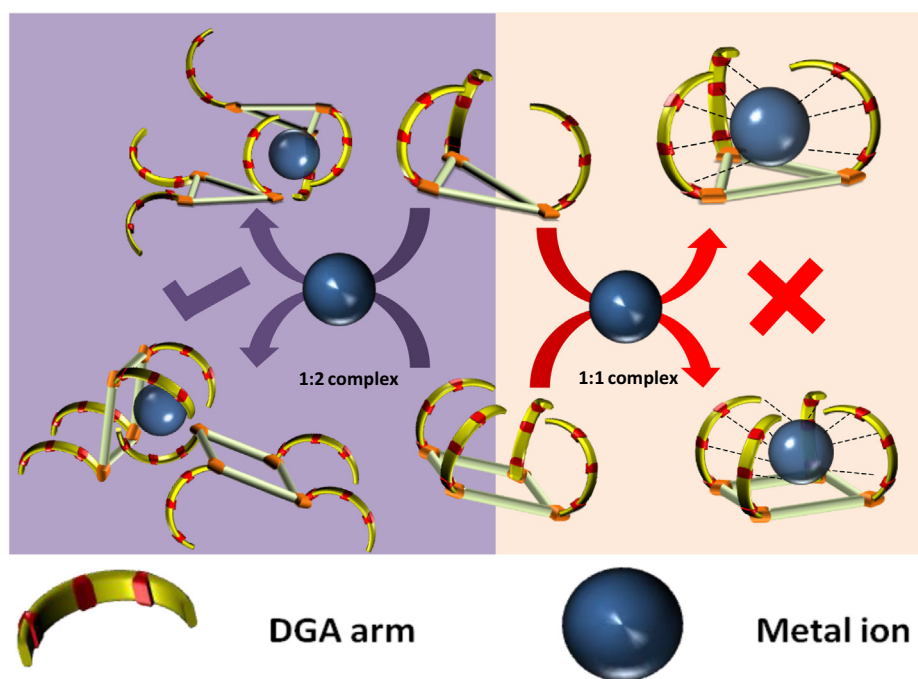


Fig. 4. Distribution ratio of behavior of Am³⁺ and Eu³⁺ under varying experimental conditions. (a) Varying TAM-3-DGA concentrations at 1.0 M HNO₃; (b) varying TAM-4-DGA concentrations at 0.5 M HNO₃; (c) varying NaNO₃ concentrations at fixed 1.0 M HNO₃. Solvent: C₈mim·Tf₂N; Temperature: 25 °C.

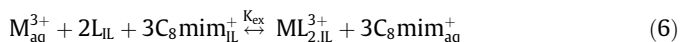


Scheme 1. Schematic representation of the various possible complex structures of Eu³⁺ - TAM-3/4-DGA. The red bands in the DGA arm indicate the 'O' atoms.

it is not possible for all the DGA moieties in the ligands (TAM-3/4-DGA) to participate in the bonding with the metal ion in a ML₂ type complex, only a few of the six (TAM-3-DGA) or eight (TAM-4-DGA) DGA arms will be used. A schematic representation of this metal ion binding is presented in Scheme 1. Subsequently, DFT calculations were performed to get the lowest energy structures (*vide infra*).

With these results, one may confidently conclude that the composition of the extracted complex of both cations is a (ML₂)³⁺ cationic species for both ligands. Since a complex with 3+ unit charge is transferred into the C₈mim·Tf₂N phase, consequently three C₈mim⁺ cations from the ionic liquid phase are simultaneously transferred into the aqueous phase for maintaining phase neutrality. This feature is very common for an ionic liquid system where a cation-

exchange mechanism is predominant.[24,26] In the light of the above observations, the equilibrium reaction involved during the extraction of either Am(III) or Eu(III) in the present work can be written as:



The performance of the present TAM-n-DGA ligands (n = 3 or 4) for the extraction of Am³⁺ and Eu³⁺ both from molecular solvent and from RTIL is compared in Table 2. The distribution data from the molecular solvent are given at 3 M HNO₃ as these ligands show a solvation type mechanism where the *D* values increased with increasing aqueous feed acidity with very low *D* values at 0.01 M HNO₃. On the other hand, these ligands extract Am³⁺ and Eu³⁺ in ionic liquid medium by a cation-exchange mechanism, where the *D* values decreased with increasing aqueous feed acidity with very high *D* values at 0.01 M HNO₃. It is appropriate to mention here that a cation-exchange mechanism has been suggested to be operating in ionic liquids with shorter alkyl chains viz., C₂mim-Tf₂N and C₄mim-Tf₂N,[74,75] while in the case of a longer chain ionic liquid such as C₈mim-Tf₂N or C₁₀mim-Tf₂N, the extraction mechanism has been reported to be similar to that in molecular diluents.[76] Therefore, it is rather surprising that in the present case with the TAM-n-DGA ligands a cation-exchange mechanism is operating using C₈mim-Tf₂N as the ionic liquid diluent. The extraction of other actinide and fission ions such as Sr(II) and Cs(I) was carried out and the results are listed in Table 3. As seen from the table, the extraction of the tetravalent ions such as Np(IV) and Pu(IV) are significantly high with TAM-4-DGA even at 1 × 10⁻⁴ M ligand concentration.

The separation factor values are, however, more favorable when TAM-3-DGA was used as the extractant. Though U(VI) extraction was very low, the extraction of Cs(I) and Sr(II) was very poor suggesting excellent decontamination from these notorious fission products.

3.2. Thermodynamics of extraction

As mentioned above, a cation-exchange mechanism (eq (6)) is operating for the extraction of the metal ions. The extraction equilibrium constant, *K*_{ex} can be given as:

$$K_{ex} = \frac{[ML_2]_{il}^{2+}}{[M^{3+}]_{aq}[L]_{il}^2\gamma_{M^{3+}}\gamma_L^2} \quad (7)$$

where the square brackets represent the concentration of each species and γ is the activity coefficient of the given species. The activity coefficients for various species are assumed to be close to unity as very small concentrations of the metal ions ([Am] or [Eu] < 10⁻⁶ M) and the ligands ([L]_{total} ≥ 1 × 10⁻⁴ M) were used in the present studies. Eq (4) can be approximated by eq (5) under the above assumptions:

$$K_{ex} = \frac{[ML_2]_{il}^{3+}}{[M^{3+}]_{aq}[L]_{il}^2} \quad (8)$$

Table 3

Extraction data of actinide and fission product ions in C₈mim-Tf₂N at 3 M HNO₃.

Metal ion	TAM-3-DGA ^a	SF(<i>D</i> _M / <i>D</i> _{Am})	TAM-4-DGA ^a	SF(<i>D</i> _M / <i>D</i> _{Am})
U(VI)	0.16 ± 0.01	16	0.25 ± 0.02	0.37
Np(IV)	0.95 ± 0.01	95	11.5 ± 0.01	17.2
Pu(IV)	1.16 ± 0.01	116	15.5 ± 0.05	23.1
Am(III)	0.01 ± 0.01	–	0.67 ± 0.04	–
Sr(II)	<0.001	0.1	<0.001	0.001
Cs(I)	0.023 ± 0.001	2.3	0.020 ± 0.001	0.03

^a 5 × 10⁻⁴ M.

Although the extraction of M(III) was independent of the nitrate concentration (*vide supra*), it was done from nitric acid medium. Hence, one has to take into account the nitrate complexation of M(III) with NO₃⁻ ions in the aqueous solution. The possible species involving the metal ions (M³⁺), viz., M(NO₃)₂⁺, M(NO₃)₂⁺, M(NO₃)₃, etc. are formed in the aqueous phase and hence, nitrate ion complexation should be taken into consideration (See [supporting information](#)).

The conditional extraction constants (log *K*'_{ex}) for M(III) with TAM-3-DGA and TAM-4-DGA can be calculated if the value of *K*_{Nit} is known ([Supporting Information](#)). In the present work, the value of *K*_{Nit} for M(III) was obtained from the literature.[77] The Gibbs free energy change (Δ*G*) associated with the extraction process was calculated from the value of the extraction constant (*K*'_{ex}) using eq (9):

$$\Delta G = -RT \ln K'_{ex} \quad (9)$$

The correlation between the Gibbs free energy change (Δ*G*), enthalpy change (Δ*H*) and entropy change (*T*Δ*S*) of the system is given by the Gibbs-Helmholtz equation (eq (10)) as follows:

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

Combining eqs (9) and (10) and taking the log on both sides results in the following equation:

$$\text{Log} K'_{ex} = -(\Delta H_0/2.303R)(1/T) + (\Delta S/2.303R) \quad (11)$$

Eqs (9) to (11) can be used to calculate the thermodynamic parameters for the extraction of trivalent Ln/An by TAM-3-DGA/TAM-4-DGA at 1 M HNO₃ assuming that the activity of NO₃⁻, free ligands and *K*_{Nit} (*vide infra*) remains unchanged or does not change significantly in the studied temperature range. The log *K*'_{ex} vs 1/*T* plots gave straight lines ([Supporting Information](#)), and the slope values were used to calculate the Δ*H* values (in kJ.mol⁻¹) using eq (12):

$$\Delta H = -2.303R \times \text{slope} \quad (12)$$

where *R* is the universal gas constant. The slope values were used for the calculation of Δ*H*. The values of *K*'_{ex} for the extraction of Am(III) and Eu(III) by TAM-3-DGA / TAM-4-DGA were calculated at 1 M HNO₃. The values of the thermodynamic parameters Δ*G*, Δ*H* and *T*Δ*S* were calculated as mentioned above. These values, together with the log *K*'_{ex} values are summarized in Table 4.

The total enthalpy change (Δ*H*) during the solvent extraction of M(III) can be viewed as the sum of the enthalpies of the different processes such as dehydration of the actinides (Δ*H*_w), complexation with ligands (Δ*H*_c) and dissolution/stabilization of the cationic M.L³⁺ complex in the ionic liquid (Δ*H*_D). The overall magnitude and the sign of Δ*H* depends on the contributions of all three, i.e., the Δ*H*_w, Δ*H*_c and Δ*H*_D terms.

$$\Delta H = \Delta H_w + \Delta H_D + \Delta H_c \quad (13)$$

The Δ*H*_w term is energy intensive (endothermic process). As dehydration of M(III) ions requires energy, it may be more positive for Eu(III) because of its relatively higher ionic potential compared

Table 4

Conditional extraction constant ($\log K'_{\text{ex}}$) and thermodynamic parameters (ΔG , ΔH , $T\Delta S$) for the extraction of Am(III) and Eu(III) by TAM-3-DGA/TAM-4-DGA in $C_8\text{mim}.\text{NTf}_2$ at 1 M HNO_3 and 298 K.

Ligand	ΔG (kJ/mol)	ΔH (kJ/mol)	$T\Delta S$ (kJ/mol)	$\log K'_{\text{ex}}$
Am(III)				
TAM-3-DGA	-36.79 ± 1.60	-31.14 ± 1.17	5.65 ± 0.54	6.45 ± 0.18
TAM-4-DGA	-51.69 ± 1.56	-16.79 ± 1.29	34.9 ± 0.44	9.06 ± 0.15
Eu(III)				
TAM-3-DGA	-39.24 ± 2.08	-29.10 ± 1.55	10.14 ± 0.99	6.88 ± 0.12
TAM-4-DGA	-54.77 ± 2.10	-15.72 ± 1.92	39.07 ± 0.82	9.60 ± 0.14

to Am(III). The more positive value of ΔH_w for Eu(III) is compensated by its higher negative value of ΔH_c compared to Am(III), giving a more negative value for Eu(III) with both ligands compared to Am(III). The ΔH_D values for the dissolution of the ML_2^{3+} complexes must be very similar for both metal ions as the overall size of the complexes is predominantly decided by the associated ligands, which is the same for both the ions. The Gibbs free energy change (ΔG) for Eu(III) extraction with both ligands is higher than for Am(III) extraction due to its higher extraction equilibrium constant, which is also reflected in its higher distribution ratio. This higher ΔG value suggests a stronger interaction of Eu(III) with the ligands. The enthalpy contribution to the overall ΔG is more favored for the extraction of M(III) with TAM-3-DGA than with TAM-4-DGA where the $T\Delta S$ term contributes significantly. The higher contribution of $T\Delta S$ in the case of a M(III)-TAM-4-DGA complex may be attributed to more disruption in the IL phase upon dissolution / stabilization due to its larger ML size compared to that of a M(III)-TAM-3-DGA complex. The other contribution to higher entropy may come from the release of the coordinated water molecules from the primary and some disturbance in the secondary hydration spheres due to a stronger complexation ability of TAM-4-DGA compared to TAM-3-DGA. Both these factors may be adding to the overall entropy increase.

3.3. Luminescence studies

Luminescence studies were performed with the Eu^{3+} ion extracted by the ligands (0.5 mM) either in $C_8\text{mim}.\text{Tf}_2\text{N}$ or n -dodecane medium. The excitation and emission spectra of the samples are shown in Fig. 5. It has to be noticed that the excitation spectra of the Eu^{3+} complex for both the ligands dissolved in n -dodecane were different from those in $C_8\text{mim}.\text{Tf}_2\text{N}$ medium. Efficient energy transfer from the TAM- n -DGA ligands to the Eu^{3+} metal center (LMCT) can be observed in n -dodecane, but such LMCT is missing in the $C_8\text{mim}.\text{Tf}_2\text{N}$ system. The emission spectrum of the Eu^{3+} complex with both the ligands shows the splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ peak into a doublet with peak positions at 612 and 617 nm, which is typical for a $\text{Eu}^{3+}/\text{DGA}$ complex as shown in several studies.[32,33,78]

The emission spectra of the Eu^{3+} extract with both the ligands look similar with respect to their relative peak positions but differed in the relative peak intensities of the 612 and 617 nm bands in $C_8\text{mim}.\text{Tf}_2\text{N}$. A similar result has also been reported earlier.[32,33] Comparison of the emission spectra of the Eu^{3+} complex extracted in ionic liquid and in molecular solvent suggests that the nature of the extracted complex is different in these two cases as the intensity ratio of the peaks at 612 and 617 nm differs (Table 5). The peak ratio of $\text{Eu}^{3+}/\text{TAM-3-DGA}$ is higher than that of $\text{Eu}^{3+}/\text{TAM-4-DGA}$ in n -dodecane, but this order is reversed in the ionic liquid. This difference can be attributed to the difference in the local symmetry around the extracted Eu^{3+} ion, though the nature of the extracted complexes, is in both cases, of the ML_2 type (*vide supra*).

Although the nature of the extracted complexes appears the same with respect to the number of ligands, but it differs in the number of nitrate ions present. The extracted complexes in the molecular solvent have three nitrate ions associated with it, while the solvent extraction studies in the ionic liquid medium, as discussed above, confirm the absence of any nitrate ions.[32,33] This presence of extra coordinating NO_3^- ions in the molecular diluents may alter the overall symmetry of the extracted complex in n -dodecane, and explains the difference in the overall emission spectra in the ionic liquid and n -dodecane mediums.

The lifetimes of the Eu^{3+} complexes with the different DGA ligands were recorded and the results are summarized in Table 5. The decay lifetime data (profiles are given in Figure S1 in the Supporting Information) can be used to ascertain the number of associated inner-sphere water molecules in the given Eu^{3+}/L complex under different chemical conditions using eq (14).[79]

$$N_{\text{H}_2\text{O}}(\pm 0.5) = 1.05/\tau(\text{ms}) - 0.44 \quad (14)$$

where $N_{\text{H}_2\text{O}}$ is the number of inner-sphere water molecules, τ (ms) is the lifetime of the Eu^{3+}/L complex. The lifetime data for both the $\text{Eu}^{3+}/\text{TAM-3-DGA}$ and $\text{Eu}^{3+}/\text{TAM-4-DGA}$ complexes point to the formation of inclusion complexes in the $C_8\text{mim}.\text{Tf}_2\text{N}$ and n -dodecane + isodecanol (5%) phases (Table 5). Though the asymmetric ratio for the $\text{Eu}^{3+}/\text{TODGA}/C_8\text{mim}.\text{Tf}_2\text{N}$ system is comparatively low (1.25), the decay lifetime is in the same range.[28,49]

3.4. Complexation of Eu^{3+} with TAM-DGA ligands

To determine the complexation constant between Eu^{3+} and the TAM- n -DGA ligands in the $C_8\text{mim}.\text{Tf}_2\text{N}$ medium, luminescence titrations were performed. Preliminary studies with 1 mM Eu^{3+} ion in a cuvette showed precipitation of the Eu^{3+}/L complex when the metal/L ratio reached about 1. This complex, however, became soluble after the addition of additional $C_8\text{mim}.\text{Tf}_2\text{N}$ diluent. Therefore, it was chosen to carry out the titrations with a 0.35 mM solution of Eu^{3+} . Under this condition, no precipitation was noticed till the entire titration was complete.

In the luminescence titration, the Eu^{3+} emission peak in the wavelength range of 680–705 nm, which arose due to the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition, was chosen. This transition is known to be affected significantly in the presence of a ligand field and, therefore, was followed for the determination of the conditional stability constants with different ligands.[32] Fig. 6 gives a representative titration of Eu^{3+} with TAM-4-DGA in $C_8\text{mim}.\text{Tf}_2\text{N}$. The peak intensity in the range of 680–705 nm increased upon the addition of the TAM-4-DGA ligand. Titration was continued till no further change in the peak intensity was observed and the dilution of the peak was noticed. We tried to fit the data obtained from the titrations into ML_1 and ML_2 species (based on the solvent extraction results presented above) in the HypSpec® program, but the data could not be converged. The data fitting was also poor when only a ML_1 complex was assumed. However, a good fitting of the data was obtained assuming only ML_2 species for both the ligands, i.e.,

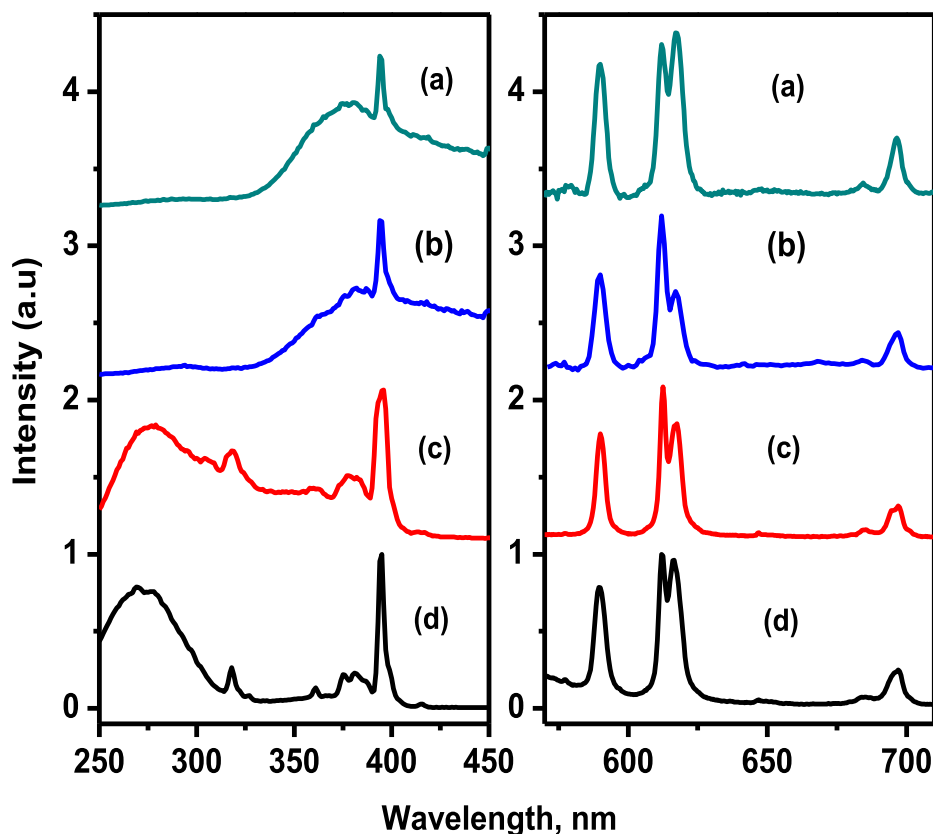


Fig. 5. Left: Excitation spectrum of Eu^{3+} complex with emission (λ_{em}) at 612 nm. Right: Emission spectrum of Eu^{3+} complex with excitation (λ_{ex}) at 394 nm. (a) TAM-3-DGA, (b) TAM-4-DGA in $\text{C}_8\text{mim-Tf}_2\text{N}$, (c) TAM-3-DGA, (d) TAM-4-DGA in n -dodecane.

Table 5

Asymmetric ratio (AR defined as the ratio of the 616 nm and 592 nm peaks), luminescence lifetime (τ) and number of inner-sphere water molecules ($N_{\text{H}_2\text{O}}$) in the Eu^{3+} complex with different DGA-based ligands in different solvents.

System	AR	$\tau(\mu\text{s})$	$N_{\text{H}_2\text{O}}$	$\tau(\mu\text{s})$	$N_{\text{H}_2\text{O}}$	ref
TAM-3-DGA / $\text{C}_8\text{mim-Tf}_2\text{N}$	2.67	–	–	2295 ± 5	0	p.w.
TAM-4-DGA / $\text{C}_8\text{mim-Tf}_2\text{N}$	2.11	–	–	2301 ± 3	0	p.w.
TODGA / $\text{C}_8\text{mim-Tf}_2\text{N}$	1.25	–	–	2280 ± 2	0	[49]
TAM-3-DGA / n -dodecane	2.26	–	–	1180 ± 1	0	[33]
TAM-4-DGA / n -dodecane	2.07	324 ± 3	3	1921 ± 2	0	[32]
TODGA / n -dodecane	2.03	–	–	2075 ± 1	0	[32]

TAM-3-DGA and TAM-4-DGA. The deconvoluted emission spectra of Eu^{3+} and the Eu/L complex are shown in Fig. 6. Analogous titration data were also generated for TAM-3-DGA with similar concentrations of $\text{Eu}(\text{Tf}_2\text{N})_3$ in the ionic liquid and the results are presented in Figure S2 (Supporting Information).

The stability constants for the Eu/TAM-3-DGA and Eu/TAM-4-DGA complexes ($\log \beta_2$) were calculated and are listed in Table 6 along with the constants previously reported in MeOH medium. For comparison purpose, the stability constant data for TODGA in both MeOH and ionic liquid (with Eu^{3+} and Nd^{3+} ions) are also listed in the table. The stability constant ($\log \beta_3$) value for Nd^{3+} ion with TODGA in the ionic liquid medium is significantly larger than that for Eu^{3+} in MeOH. Furthermore, the $\log \beta_2$ for TAM-3-DGA in the ionic liquid is comparable to that of TODGA, suggesting that maybe only two DGA arms are binding with the Eu^{3+} ion in MeOH where nitrate ions are forming inner-sphere complexes. However, the $\log \beta_2$ for TAM-3-DGA is also comparable to these values, suggesting again only two DGA arms of the ligand may be

binding in the ionic liquid medium. As the nitrate ions are not binding to this complex, one would expect the presence of inner-sphere water molecules (assuming six coordination sites occupied by four carbonyl 'O' atoms and two etheric 'O' atoms from the two DGA arms). However, the luminescence lifetime suggests on the opposite, i.e., no water molecule is bound to the Eu^{3+} ion. Such coordinatively unsaturated complexes without any inner-sphere water molecules are known to exist in ionic liquid medium.[81] The TAM-4-DGA complex has slightly higher complex formation constants as compared to that of TAM-3-DGA, which is probably responsible for the higher extraction of the complexes with the former.

In order to understand more about the nature of the species, we compared the emission spectra of the complexes obtained in titration and the complexes that were extracted in the IL phase. As shown in Fig. 7 the emission spectra are quite identical, which corroborates that the ligands formed ML_2 type of complexes in the ionic liquid medium.

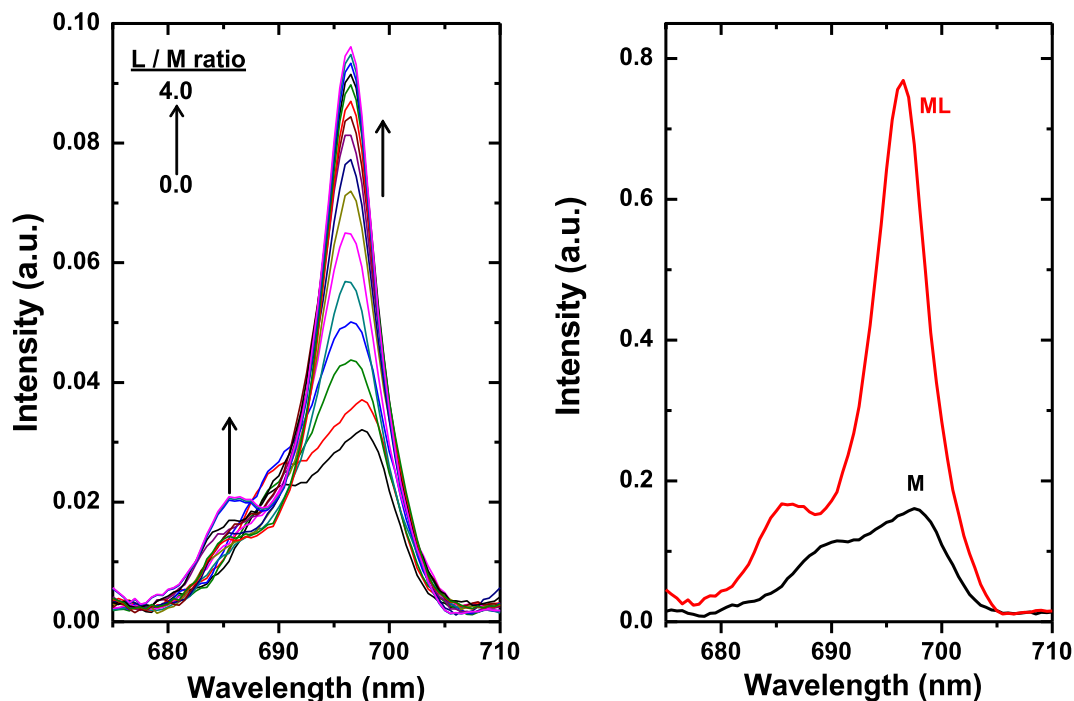


Fig. 6. Representative luminescence titration for the Eu^{3+} /TAM-4-DGA system (left) and deconvoluted spectra of Eu^{3+} and EuL_2 (right) in $\text{C}_8\text{mim-Tf}_2\text{N}$; $[\text{Eu}^{3+}]$: 0.70 μmoles , initial volume: 2 mL; [TAM-4-DGA]: 0.2 mM in $\text{C}_8\text{mim-Tf}_2\text{N}$; λ_{ex} : 394 nm.

Table 6
Stability constant data for DGA / Eu(III) complexes in MeOH or $\text{C}_8\text{mim.Tf}_2\text{N}$ at 25 °C.

DGA	Equilibrium reaction	$\log \beta$	[Ref]
TODGA	$\text{Eu}^{3+} + \text{L} \rightarrow \text{EuL}^{3+}$	6.11 ± 0.5^a	[80]
	$\text{Eu}^{3+} + 2\text{L} \rightarrow \text{EuL}_2^{3+}$	10.8 ± 0.7^a	[80]
	$\text{Eu}^{3+} + 3\text{L} \rightarrow \text{EuL}_3^{3+}$	14.3 ± 0.6^a	[80]
	$\text{Nd}^{3+} + 3\text{L} \rightarrow \text{NdL}_3^{3+}$	19.1 ± 0.2^a	[49]
TAM-3-DGA	$\text{Eu}^{3+} + \text{L} \rightarrow \text{EuL}^{3+}$	4.75 ± 0.11^a	[32]
	$\text{Eu}^{3+} + 2\text{L} \rightarrow \text{EuL}_2^{3+}$	9.12 ± 0.08^a	[32]
	$\text{Eu}^{3+} + 2\text{L} \rightarrow \text{EuL}_2^{3+}$	8.7 ± 0.4^b	This work
TAM-4-DGA	$\text{Eu}^{3+} + 2\text{L} \rightarrow \text{EuL}_2^{3+}$	9.0 ± 1.3^b	This work

^a Data refer to methanol. ^b $\text{C}_8\text{mim.Tf}_2\text{N}$.

3.5. DFT studies

3.5.1. Structural parameters

The minimum energy structures of the complexes of Eu^{3+} and Am^{3+} ions with TAM-3-DGA and TAM-4-DGA with 1:1 stoichiome-

try is displayed in Fig. 8. Three DGA groups of TAM-3-DGA and TAM-4-DGA are shown to be linked to the central metal ion leading to nona-coordination, whereas one DGA group of TAM-4-DGA does not participate in the coordination. The calculated structural parameters for both ions with TAM-3-DGA and TAM-4-DGA are presented in Table 7. The M–O bond length for amidic O atoms is longer than that involving the ethereal O atoms, indicating that the amidic O will lead to stronger interactions. The average Eu–O bond length is shorter than the average Am–O bond length in both the complexes of TAM-3-DGA and TAM-4-DGA, suggesting the preferred ‘hard’–‘hard’ interaction. Furthermore, the average M–O bond length in TAM-3-DGA is slightly shorter than in TAM-4-DGA. This may be due to lesser steric hindrance in the case of TAM-3-DGA *vis-à-vis* that with TAM-4-DGA having one additional pendent DGA arm. The minimum energy structures of the complexes of Eu^{3+} and Am^{3+} ions with TAM-3-DGA and TAM-4-DGA with 1:2 stoichiometry are presented in Fig. 9. Three DGA moieties of two TAM-3-DGA’s (one DGA moiety from one TAM-3-DGA and

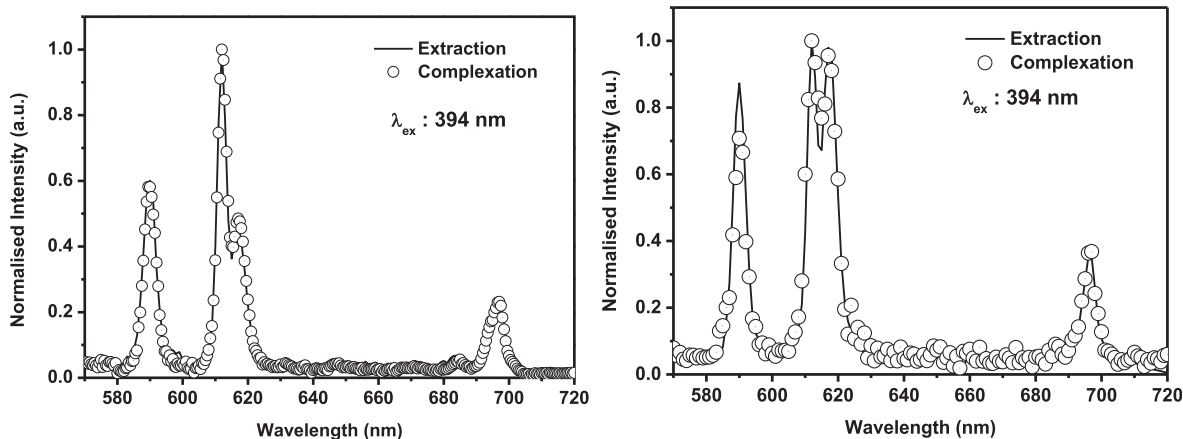


Fig. 7. Comparison of the emission spectra of Eu^{3+} with (a) TAM-3-DGA and (b) TAM-4-DGA in solvent extraction and complexation titration.

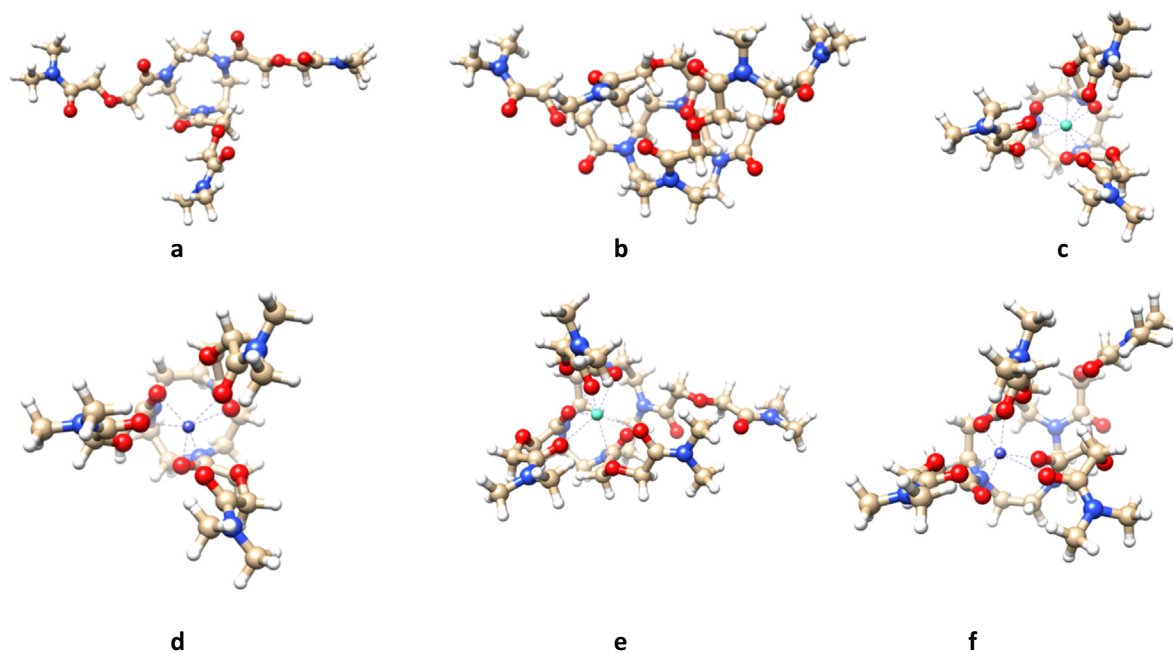


Fig. 8. Optimized structure of (a) TAM-3-DGA (b) TAM-4-DGA (c) TAM-3-DGA-Eu³⁺ and (d) TAM-3-DGA-Am³⁺ (e) TAM-4-DGA-Eu³⁺ and (f) TAM-4-DGA-Am³⁺ at the B3LYP/SVP level of theory. Keys: red: O; blue: N; buff: C; white: H; torquise blue: Eu; purple: Am.

Table 7
Calculated structural parameters in Å at the B3LYP level of theory using SVP basis set.

System	Eu-O (Å)	Eu-O (Å)	Am-O (Å)	Am-O (Å)
	O of > C = O	Ether > O	O of > C = O	Ether > O
TAM-3-DGA (1:1)	2.300, 2.298, 2.302, 2.489, 2.501, 2.513	2.799, 2.841, 2.895	2.346, 2.347, 2.38, 2.541, 2.550, 2.563	2.781, 2.857, 2.918
TAM-4-DGA (1:1)	2.282, 2.341, 2.474, 2.337, 2.508, 3.085	2.603, 2.736, 3.869	2.325, 2.360, 2.374, 2.400, 2.473, 2.566	2.699, 2.814, 4.586
TAM-3-DGA (1:2)	2.306, 2.365, 2.365, 2.369, 2.418, 2.429	2.640, 2.716, 3.650	2.335, 2.386, 2.407, 2.414, 2.445, 2.492	2.674, 2.746, 3.587
TAM-4-DGA (1:2)	2.365, 2.383, 2.387, 2.410, 2.458, 2.567	2.571, 2.616, 2.669	2.330, 2.357, 2.407, 2.420, 2.438, 3.973	2.625, 2.625, 2.665

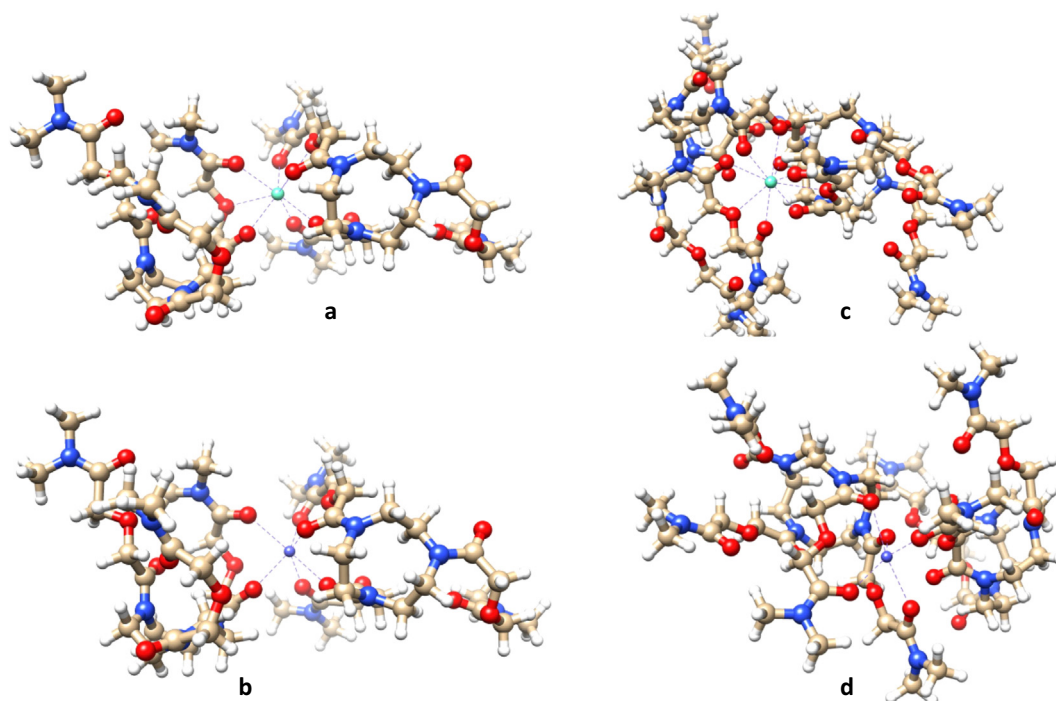


Fig. 9. Structures of the ML₂ type complexes at the B3LYP/SVP level of theory. (a) [(TAM-3-DGA)₂ -Eu]³⁺; (b) [(TAM-3-DGA)₂ -Am]³⁺; (c) [(TAM-4-DGA)₂ -Eu]³⁺ and (d) [(TAM-4-DGA)₂ -Am]³⁺.

two from the other) and two TAM-4-DGA's (one DGA moiety from one TAM-4-DGA and two from the other) are linked to the central metal ion leading to a nona-coordination geometry. The calculated structural parameters for both the ions with TAM-3-DGA and TAM-4-DGA with 1:2 stoichiometry are presented in Table 7. Here, also, the M–O bond length for amidic 'O' atoms is longer than for the ethereal 'O' atoms, indicating that the amidic 'O' atoms lead to stronger interactions. Furthermore, the average M–O bond length in TAM-3-DGA and TAM-4-DGA is slightly shorter in the 1:1 than in the 1:2 complexes.

3.5.2. Thermodynamical free energy of complexation

The free energies for the complex formation of Eu^{3+} and Am^{3+} ions towards TAM-3-DGA and TAM-4-DGA with 1:1 and 1:2 stoichiometries in the gas phase and the ionic liquid phase are presented in Table 8. The gas phase free energy change ($-\Delta G$) is higher for Eu^{3+} ion than for Am^{3+} ion for both TAM-3-DGA and TAM-4-DGA. This suggests that the bonding of Am^{3+} to the 'N' atoms of the macrocyclic ring is not taking place, in all probability, which may be explained based on steric factors (close interaction with the DGA arm restricts the interaction with the 'N' atoms). Furthermore, the free energy change is higher with TAM-4-DGA than with TAM-3-DGA and that of 1:2 species is higher than that of 1:1 complex formation. The gas phase free energy analysis suggests the preferential complexation of Eu^{3+} over Am^{3+} for both TAM-3-DGA and TAM-4-DGA with 1:1 and 1:2 stoichiometries. In addition, the free energy also indicates that the complex with 1:2 the stoichiometry is more probable than 1:1.

The well-known COSMO solvation approach was used to simulate the solvent phase as it can predict its properties quite accurately. The ionic liquid phase was modeled using a dielectric constant value of 6.5.[65] The gas phase free energy change was found to be reduced considerably due to the dielectric screening of the ionic liquid phase. It is interesting to note that the preferential complexation of Eu^{3+} over Am^{3+} is reversed in the ionic liquid phase for both TAM-3-DGA and TAM-4-DGA with 1:1 and 1:2 sto-

Table 8

Calculated values of complexation free energy, ΔG (kcal/mol), in the gas as well as the ionic liquid phase at the B3LYP level of theory using the TZVP basis set.

System	Complexation free energy	
	Gas phase	IL phase
TAM-3-DGA + Eu^{3+} = [TAM-3-DGA -Eu] ³⁺	-614.3	-159.7
TAM-3-DGA + Am^{3+} = [TAM-3-DGA -Am] ³⁺	-598.1	-170.8
TAM-4-DGA + Eu^{3+} = [TAM-4-DGA -Eu] ³⁺	-641.5	-183.5
TAM-4-DGA + Am^{3+} = [TAM-4-DGA -Am] ³⁺	-623.3	-192.9
2TAM-3-DGA + Eu^{3+} = [(TAM-3-DGA) ₂ -Eu] ³⁺	-689.4	-172.2
2TAM-3-DGA + Am^{3+} = [(TAM-3-DGA) ₂ -Am] ³⁺	-674.5	-188.4
2TAM-4-DGA + Eu^{3+} = [(TAM-4-DGA) ₂ -Eu] ³⁺	-715.1	-196.9
2TAM-4-DGA + Am^{3+} = [(TAM-4-DGA) ₂ -Am] ³⁺	-696.3	-204.3

Table 9

Calculated charge and orbital population using NBO analysis in the ionic liquid phase at B3LYP/TZVP level of theory.

System	charge	S	p	d	f
[TAM-3-DGA -Eu] ³⁺	1.996	4.13	11.98	10.81	6.05
[TAM-3-DGA -Am] ³⁺	2.033	4.14	11.98	10.70	6.13
[TAM-4-DGA -Eu] ³⁺	1.949	4.13	11.99	10.83	6.08
[TAM-4-DGA -Am] ³⁺	2.047	4.14	11.98	10.68	6.14
[(TAM-3-DGA) ₂ -Eu] ³⁺	1.993	4.13	11.98	10.80	6.08
[(TAM-3-DGA) ₂ -Am] ³⁺	2.026	4.14	11.98	10.70	6.13
[(TAM-4-DGA) ₂ -Eu] ³⁺	1.962	4.14	11.99	10.83	6.06
[(TAM-4-DGA) ₂ -Am] ³⁺	2.049	4.14	11.98	10.67	6.14

ichiometries when the complexation is considered in the ionic liquid medium alone. However, the liquid – liquid extraction step includes dehydration of the metal ions followed by their complexation and extraction into the ionic liquid phase. When the stronger hydration energy of the Eu^{3+} ion as compared to that of the Am^{3+} ion is considered[82] one can definitely get a good match between the theoretical prediction and the experimentally observed results.

3.5.3. Bonding analysis

In order to get an insight into the nature of bonding in the complexes of the metal ions with the TAM-3/4-DGA ligands, the charge on the metal ions and the atomic orbital population in the complexes was determined using the method of natural population analysis (NPA).[83–86] The calculated values are presented in Table 9. The substantial positive charge on the metal ion indicates an ion-dipole type of interaction. The ECP core in the present work represents a ground-state valence configuration for Eu^{3+} and Am^{3+} ions as $4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^7$ and $5s^2 5p^6 5d^{10} 5f^6 6s^2 6p^6$, respectively. The metal complexes show significant s, d and f occupations compared to the free metal ions. The increase of the electronic population in the s, d and f orbitals of the metal ions after complexation may be because of the covalent bonding nature. The charges on the metal ion with the ligands show that a considerable amount of charge was transferred to the ligands.

4. Conclusions

The extraction of Am(III) and Eu(III) was studied from nitric acid medium into $\text{C}_8\text{mim}\cdot\text{Tf}_2\text{N}$ ionic liquid solutions of TAM-3-DGA and TAM-4-DGA, indicating preferential extraction of the latter metal ion with SF values of 4 and 2.4, respectively, at 3 M HNO_3 . However, the extent of metal ion extraction is rather modest, and one would like to use 0.5 M as the feed for more meaningful extraction of the metal ions. Though the SF values were nearly comparable for TAM-3-DGA in both *n*-dodecane (with 5% isodecanol) and ionic liquid mediums, the lowering of the SF values in case of TAM-4-DGA with respect to those reported before with molecular diluents, is not in line with earlier observations with TODGA and C4DGA ligands (Fig. 1). In these cases, the ionic liquid medium improves the separation efficiency and the TAM-3-DGA based ionic liquid solvent resulted in reasonably good SF value at 3 M HNO_3 (Table 1).

The extraction conformed to a cation-exchange mechanism where the extracted species were found not to contain any nitrate anion. However, the coordinatively unsaturated complexes did not contain any inner-sphere water molecules as was clear from luminescence spectroscopy studies. It was also used to determine the stability constants which suggested 1:2 (M:L) complex formation with probable binding of the metal ion to two arms of the TAM-DGA ligands.

Its application to the radioactive waste processing needs to be tested by multi-stage counters current extraction studies. Of course, this work was carried out using very low concentrations of the ligands. The main reason for this was that unusually high *D* values ($>10^5$) were obtained when we used 0.01 M or higher concentrations of the ligands. While making actual applications, which contains large amounts of the minor actinides such as Am, Cm and Np, 100 times higher ligand concentrations can be used for an effective extraction of the metal ion. The preferential complexation of Eu^{3+} ion over Am^{3+} ion in the ionic liquid phase for both TAM-3-DGA and TAM-4-DGA with 1:1 and 1:2 stoichiometries is predicted by the DFT calculations, however, when the dehydration step is discounted. Different bonding analysis indicates the electrostatic and small covalent nature of the interactions between the metal ions and the chelating ligands.

CRediT authorship contribution statement

Parveen K. Verma: . **Rajesh B. Gujar**: . **Seraj A. Ansari**: . **Sk. Musharaf Ali**: . **Richard J. M. Egberink**: . **Jurriaan Huskens**: Supervision. **Willem Verboom**: . **Prasanta K. Mohapatra**: Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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