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Sequestration of tetravalent neptunium from acidic feeds using diglycolamide-functionalized dendrimers in a room temperature ionic liquid: extraction, spectroscopic and electrochemical studies†

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Quantitative extraction of Np(IV) was achieved using a room temperature ionic liquid containing sub-millimolar concentrations of two poly(propyleneimine) based dendrimer ligands with four (**L_I**) and eight (**L_{II}**) diglycolamide (DGA) moieties from nitric acid solutions. The extraction of the metal ion followed a cation exchange mechanism with decreasing extraction with increasing HNO₃ concentration up to 4 M, the major exchanging species being Np(NO₃)₃L⁺. Beyond this acidity an increased metal ion extraction was seen, which was attributed to an anion exchange mechanism. UV-visible spectrophotometric studies showed a different nature of the extracted Np-L (**L_I** or **L_{II}**) complexes in the ionic liquid and molecular diluent. Quantitative back extraction of Np(IV) was achieved by using aqueous complexing agents. Cyclic voltametric studies of the extracted complexes exhibited differences in the electron-donating ability of the two ligands towards Np(IV). Both ligands showed a non-reversibility or a quasi-reversible nature of the Np reduction couple. The radiation stability of the present extraction system was not so high.

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Introduction

Nuclear power production involves the controlled fission of a fissile nuclide such as ²³⁵U in a nuclear reactor. It results in the formation of a myriad fission products, while trans-uranium elements such as neptunium, plutonium, americium, *etc.* are formed as byproducts. For sustainable production of nuclear power, an effective way to manage the nuclides with very high radiotoxicities is required so as to minimize and mitigate their hazardous effects on the general population.¹ This is being achieved to a large extent using a 'closed' fuel cycle strategy wherein the fissile materials (U and Pu containing the unused ²³⁵U in the case of the former and the generated ²³⁹Pu in the case of the latter) are separated from the fission products such as rare earth ions, platinum group metals, and alkali and alkaline earth metals such as Cs, Sr, and Ba, and activation

products such as Np and Am (termed as the minor actinides) by the well known PUREX (Plutonium Uranium Redox EXtraction) process using 30% TBP (tri-*n*-butyl phosphate) in a paraffinic hydrocarbon diluent.² The raffinate stream from the PUREX process contains highly hazardous fission products and minor actinides which are proposed to be vitrified in a glass matrix and buried underground in deep geological repositories.^{3,4} This, however, requires long surveillance of the vitrified blocks to monitor their integrity under natural calamity conditions such as earthquakes and volcanic eruptions causing a huge economic burden. However, a recent strategy, termed as 'actinide partitioning'⁴⁻⁶ proposes to separate the minor actinides, with their half-lives ranging from thousands of years to several millions of years, and subsequently transmute the long-lived radionuclides to short-lived products thereby reducing the surveillance period drastically.

²³⁷Np, with a half-life of 2.14 × 10⁶ years, is considered one of the most long-lived radionuclides in high level liquid waste (HLLW) and there have been several attempts to separate Np from acidic feeds akin to HLLW.⁷ Diglycolamide (DGA) ligands have been employed for the separation of Np from acidic feeds and appeared to be quite effective for this purpose.⁸⁻¹⁰ DGA-based ligands such as TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide)

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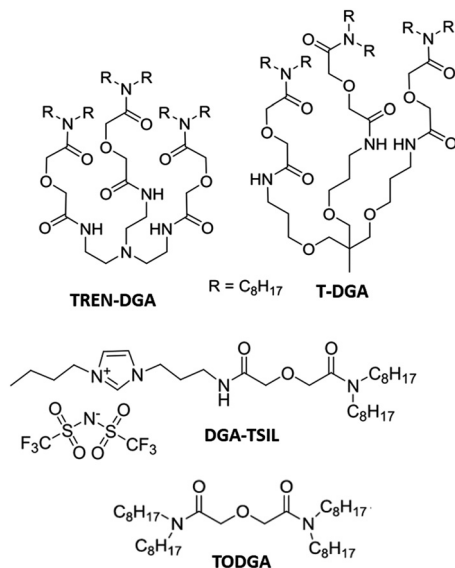


Fig. 1 Structure of TODGA and some other multiple DGAs.

(Fig. 1) have been found to be quite promising for minor actinide partitioning.^{11–13} Their extraction mechanism is based on a reverse micellar aggregation of 3–4 TODGA molecules in a non-polar diluent such as *n*-dodecane.^{14,15} Subsequent attempts to synthesize several multiple DGA-containing ligands such as calix[4]arenes,¹⁶ tripodals,¹⁷ pillar[5]arenes¹⁸ and DGA-based dendrimer¹⁹ ligands have shown extremely promising results for the extraction of trivalent f-cations. However, these ligands have not been evaluated for the separation of Np from acidic feeds as encountered in the HLLW. Our recent study to separate Np(IV) from acidic feeds using two DGA-based PPI (polypropylene imine) dendrimers, a Gen 1 dendrimer with four DGA moieties (**L_I**) and a Gen 2 dendrimer with eight DGA moieties (**L_{II}**) was highly promising (Fig. 2).²⁰

All these above studies used molecular diluents such as *n*-dodecane and its mixtures, which are considered hazardous due to their VOC contents. Room temperature ionic liquids (RTIL) are neoteric diluents extensively studied for metal ion extraction in view of their low volatility and non-flammability.^{21–26} Also, wide electrochemical windows are encountered in the case of RTIL-based solvents making them promising for direct electrowinning of the extracted metal ions.²⁷ In view of the promising results reported with the DGA-based dendrimer ligands in molecular diluents, it was of great relevance to evaluate these ligands in the RTIL, *C*₄mim-NTf₂ (1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide). In this solvent, a better extraction efficiency is expected in view of the prevailing cation exchange mechanism.^{21,24,26}

The present work involves the extraction of Np(IV) from nitric acid feeds using **L_I** and **L_{II}** in *C*₄mim-NTf₂. Solvent extraction studies were carried out to get an idea about the nature of the extracted species. UV-visible spectrophotometric studies were carried out to understand the redox speciation of Np based on the absorbance of various species. Finally, cyclic voltammetric

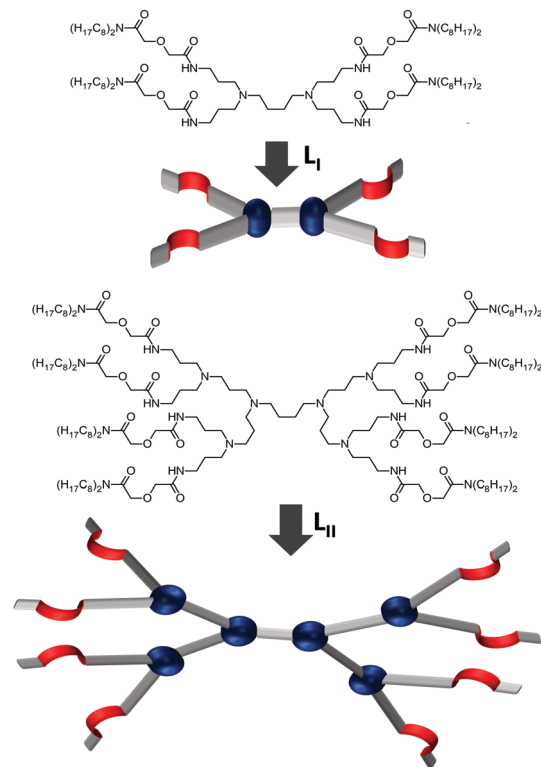


Fig. 2 Structure of poly(propylene imine) diaminobutane dendrimers (**L_I** and **L_{II}**) and its cartoon representation.

studies were performed. To our knowledge, this is the first report on the extraction of Np(IV) using DGA-based dendrimers in a RTIL, which may find application in radioactive waste management, based on the promising results.

Results and discussion

Solvent extraction studies

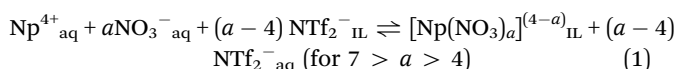
The DGA-functionalized poly(propylene imine) diaminobutane dendrimers **L_I** (Gen I) and **L_{II}** (Gen II) (Fig. 2) dissolved in *C*₄mim-NTf₂ were evaluated for the extraction of Np(IV) from nitric acid solutions. The uptake of water and nitric acid was also studied in the absence as well as in the presence of the ligands. The acid and water uptake were found to be in the similar (within error limits) range due to the very small concentration of ligands (**L_I**: 1×10^{-4} M and **L_{II}**: 1×10^{-5} M) used in the present studies. Most of the acid or water uptake is decided by the *C*₄mim-NTf₂ medium (Table 1). The extraction kinetics of Np(IV) for **L_I** and **L_{II}** dissolved in *C*₄mim-NTf₂ was found to be relatively slow as compared to the molecular diluent²⁰ and equilibrium was achieved in 30–40 minutes of equilibration (ESI). The preliminary studies showed a high D_{Np} for **L_{II}** compared to **L_I** even at 1×10^{-4} M ligand concentration. The high D value has the intrinsic problem of lower ²³⁹Np counts in the aqueous phase resulting in poor reproducibility of the data obtained in triplicate. Therefore, the concentration of **L_{II}** was

Table 1 Water, acid and distribution ratios of Np(IV) (D_{Np}) by neat $\text{C}_4\text{mim}\cdot\text{NTf}_2$ at different acidities at 298 K

| $[\text{HNO}_3]$, M | Water uptake (%) | Acid uptake (%) | D_{Np} |
|----------------------|------------------|-----------------|-----------------|
| 0.5 | — | — | < 0.01 |
| 1 | 1.57 | 3.4 | < 0.01 |
| 2 | 1.88 | 4.5 | 0.03 |
| 3 | 2.30 | 5.7 | 0.12 |
| 6 | 3.58 | 12.5 | 0.27 |

lowered by 10 times (1×10^{-5} M), while that of L_I was kept at 1×10^{-4} M in the subsequent studies.

Since these concentrations of the ligands are in the sub-millimolar region, it is important to determine the uptake of Np(IV) by the blank (without any ligand) $\text{C}_4\text{mim}\cdot\text{NTf}_2$ in the studied acidity range (Table 1). The extraction of Np(IV) was found to increase with the feed acidity in $\text{C}_4\text{mim}\cdot\text{NTf}_2$ due to anion exchange of the anionic Np-nitrate complex (specifically at high acidity)²⁸ with the NTf_2^- of $\text{C}_4\text{mim}\cdot\text{NTf}_2$ according to



where the subscripts 'IL' and 'aq' denote species present in the ionic liquid and aqueous phase, respectively. In the extraction

studies with L_I and L_II blank corrections for D_{Np} were made at the higher acidities.

A regular decrease in the D_{Np} was observed for both ligands with increasing HNO_3 concentration till 4 M HNO_3 , whereupon the Np(IV) extraction increased. Rout *et al.* observed a similar extraction profile for Pu(IV) using *N,N*-dioctyl-2-(3-methylimidazolium)acetamide bis(trifluoromethane sulfonyl) imide ($\text{DOAIm}\cdot\text{NTf}_2$) from $\text{C}_4\text{mim}\cdot\text{NTf}_2$ medium. The enhanced extraction of Pu(IV) at higher acidity is mainly governed by anion exchange of $[\text{Pu}(\text{NO}_3)_5(\text{H}_2\text{O})]^-$ or $[\text{Pu}(\text{NO}_3)_6]^{2-}$ species with the NTf_2^- of the $\text{C}_4\text{mim}\cdot\text{NTf}_2$ phase.²⁹ A similar anion exchange reaction is also possible for the present study on Np(IV) extraction at >4 M HNO_3 . An anion exchange mechanism for the extraction of tetravalent actinides with amines dissolved in ionic liquids was also observed by Ansari *et al.*³⁰ This Np(IV) extraction behaviour up to 4 M HNO_3 , is commonly observed for a cation exchange mechanism of metal ion uptake from RTIL media.^{21,24} A cation exchange mechanism for the extraction of Np(IV) was also observed by others using different neutral extractants dissolved in an ionic liquid.³¹⁻³³ Although the acid variation studies suggested a cation exchange mechanism of the metal ion extraction (Fig. 3), ligand, nitrate and C_4mim^+ variation studies were carried out to obtain information about the stoichiometry of the extracted species into the $\text{C}_4\text{mim}\cdot\text{NTf}_2$ medium by the two ligands. The nitrate ion

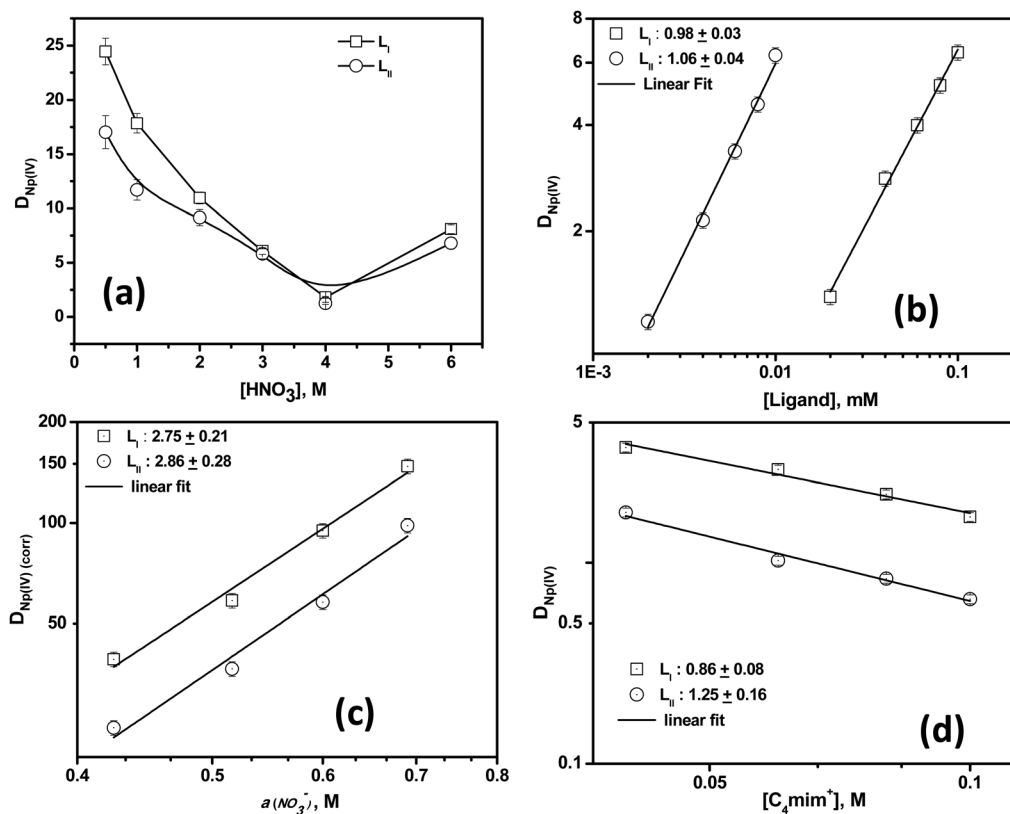


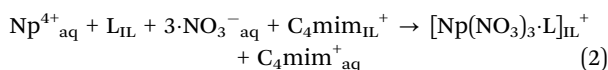
Fig. 3 Extraction of Np(IV) as a function of varying (a) acidity using $[\text{L}_\text{I}]$: 1×10^{-4} M and $[\text{L}_\text{II}]$: 1×10^{-5} M ligand solutions; (b) ligand concentration at 3 M HNO_3 and (c) nitrate ion concentration and (d) C_4mim^+ concentration using $[\text{L}_\text{I}]$: 1×10^{-4} M and $[\text{L}_\text{II}]$: 1×10^{-5} M ligand solutions, dissolved in $\text{C}_4\text{mim}\cdot\text{NTf}_2$; T: 298 K.

Table 2 Comparison of slope analysis results of the log–log plot of nitrate and ligand variation for Np extraction by L_I and L_{II} in $C_4mim\text{-NTf}_2$ and 5% isodecanol+ 95% *n*-dodecane²⁰

| Ligand | Nitrate variation ^a | | Ligand variation ^b | |
|----------|--------------------------------|-------------|-------------------------------|-------------|
| | Mol. dil. | RTIL | Mol. dil. | RTIL |
| L_I | 3.77 ± 0.47 | 2.75 ± 0.21 | 1.19 ± 0.01 | 1.06 ± 0.04 |
| L_{II} | 3.74 ± 0.36 | 2.86 ± 0.28 | 0.98 ± 0.02 | 0.98 ± 0.03 |

^a At 0.5 M HNO_3 . ^b At 3 M HNO_3 .

complexation corrected distribution ratio of Np^{4+} , $D_{Np(corr)}$, (for derivation and other details see the ESI†) with the activity of nitrate ions in the aqueous phase were used for the slope analysis in nitrate variation experiments.^{34,35} Slope analysis of the log D_{Np} versus log $[L(L_I/L_{II})]$, log $D_{Np(corr)}$ vs. log $a_{(NO_3^-)}$ and log D_{Np} vs. log $[C_4mim^+]$ plots for ligand and nitrate and C_4mim^+ variation (Table 2 and Fig. 3), respectively, indicated the extraction of $Np(NO_3)_3L^+$ species (Fig. 4) with the equilibrium reaction as given by eqn (2):



The decrease in the D_{Np} value with increasing C_4mim^+ in the aqueous phase also supports the proposed cation-exchange mechanism of Np^{4+} extraction based on the acid variation studies.

The present system offers high $D_{Np(IV)}$ values at 0.5 M HNO_3 in $C_4mim\text{-NTf}_2$ even at sub-millimolar ligand concentrations. The $D_{Np(IV)}$ values for different extraction systems are compared with those of the present system in Table 3. Normalizing the $D_{Np(IV)}$ values with respect to ligand concentration (assuming 1 : 1 M : L stoichiometry) shows high $D_{Np(IV)}$ values compared to the other systems. Previous studies suggested a solvation

Table 3 Distribution coefficients of tetravalent actinides ($D_{M(IV)}$) using different extractants (Fig. 1 and 2) dissolved in $C_4mim\text{-NTf}_2$ /molecular solvent^a; from HNO_3 media, T : 298 K

| Extractant | [Ligand], M | $D_{M(IV)}$ | Ref. |
|-----------------------|----------------------|---|--------------------|
| TODGA ^b | 1×10^{-2} | < 5 (250 ± 35) ^d | 28 and 37 |
| DGA-TSIL ^b | 3.6×10^{-2} | 7.6 | 33 |
| T-DGA ^c | 1×10^{-3} | 3227 ± 40 (145 ± 1) ^e | 38 and 39 |
| TREN-DGA ^c | 1×10^{-3} | 4.0 ± 0.1 (0.25 ± 0.1) ^e | 38 and 40 |
| L_I^c | 1×10^{-4} | 17.4 ± 0.87 (70.26 ± 4.27) | 20 and 41 |
| L_{II}^c | 1×10^{-4} | 97.2 ± 3.71 (77.48 ± 3.87) | 20 and 41 |
| L_I^b | 1×10^{-4} | 24.45 ± 1.22 (8.48 ± 0.21) | p.w. ²⁰ |
| L_{II}^b | 1×10^{-5} | 17.05 ± 0.1 (21.31 ± 0.64) ^f | p.w. ²⁰ |

^a Values in parenthesis: 5% isodecanol + 95% *n*-dodecane at 3 M HNO_3 . ^b $Np(IV)$ at 0.5 M HNO_3 . ^c $Pu(IV)$ at 3 M HNO_3 . ^d [TODGA]: 0.05 M. ^e [T-DGA]: 2.9×10^{-3} M. ^f [L_{II}]: 1×10^{-4} M; p.w.: present work.

mechanism for the extraction of $Np(IV)$ by L_I and L_{II} in a molecular diluent.²⁰ For both ligands the formation of 1 : 1 species was observed both in ionic liquid and molecular diluents, though the nature of the species is distinctly different. It is worthy to compare the UV-Vis spectra of the $Np(IV)$ -L extracts from the two media to gain some more insight into the nature of the extracted species. Cocalia *et al.*³⁶ suggested the formation of similar extracted species in the case of trivalent and hexavalent actinides, but not of tetravalent ions, from either a RTIL or a molecular diluent.

Absorption studies

The visible-near infrared (vis-NIR) spectra of the $Np(IV)$ extract with L_I/L_{II} dissolved in $C_4mim\text{-NTf}_2$ were recorded in the wavelength range of 600–1000 nm and compared with the $Np\text{-}L_I/L_{II}$ extract spectra in 5% isodecanol + *n*-dodecane. The vis-NIR spectrum of $Np(IV)_{aq}$ shows several absorption lines due to the f–f transitions at 0.5 M HNO_3 .⁴² The $Np(IV)$ system is isoelectronic with that of Nd^{3+} with the f^3 outer electronic configuration.^{43–46} The optical transitions for $Np(IV)$ (f^3 system) are mainly arising from the $^4I_{9/2}$ state to the higher $^4I_{11/2}$, $^4I_{13/2}$, $^2G_{7/2}$, $^2H_{9/2}$, etc., states.^{43,47–50}

The vis-NIR spectra of the extracted $Np\text{-}L_I$ and $Np\text{-}L_{II}$ complexes look similar in 5% isodecanol + 95% *n*-dodecane medium (Fig. 5(a) and (b)), suggesting a similar ligand environment around $Np(IV)$ in both species in line with the speciation studies performed previously.²⁰ Although formation of 1 : 1 complexes was observed for $Np(IV)$ extraction by L_I and L_{II} into the RTIL, their vis-NIR spectra were very different (Fig. 5(c) and (d)).

The exact symmetry analysis of $Np\text{-}L$ (L_I and L_{II}) extracted complexes in $C_4mim\text{-NTf}_2$ is difficult from the very limited information gathered in this work and further investigation is required. The only information that can be obtained from these limited studies is that the local symmetry around the extracted $Np(IV)$ in the L_{II} case is very different from that of the L_I extract in $C_4mim\text{-NTf}_2$.

The vis-NIR spectrum of $Np\text{-}L_{II}$ shows a prominent absorption band between 950–990 nm, which is quite different from the $Np(IV)$ -ligand spectra under different conditions.^{43,44,47,49–52} The only close resemblances to the present $Np\text{-}L_{II}$ spectrum can

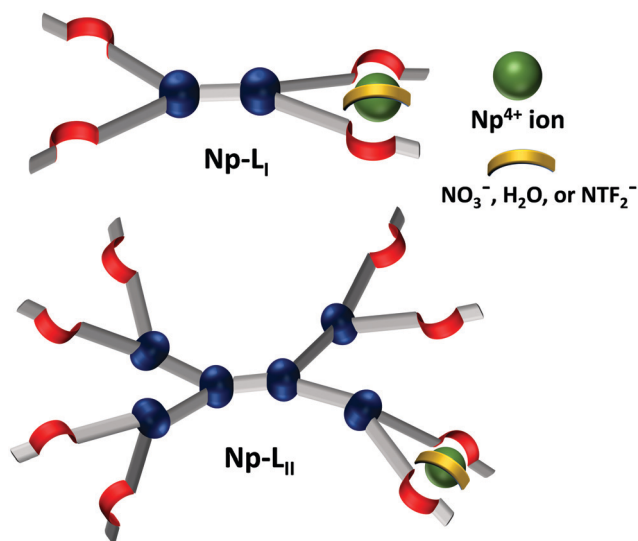


Fig. 4 Structure of the extracted $Np(IV)$ -L (L: L_I or L_{II}) complex in $C_4mim\text{-NTf}_2$.

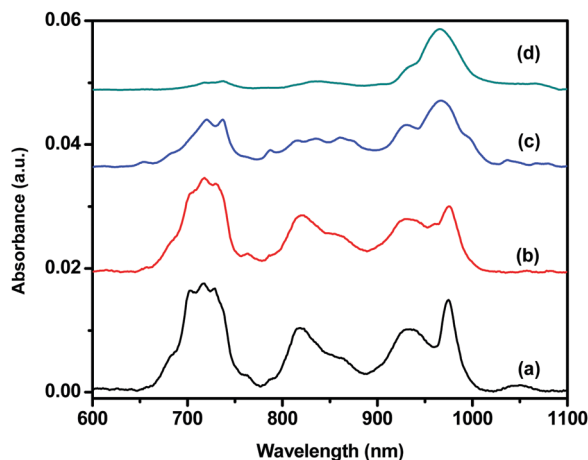


Fig. 5 Vis-NIR absorption spectra of Np(IV) extract with (a) L_I and (b) L_{II} in 5% isodecanol + *n*-dodecane and (c) L_I and (d) L_{II} in $C_4mim-NTf_2$; [Np]: 0.55 mM; T: 298 K.

be found with Np(IV)-triamidoamine complexation,⁴⁵ pointing to a possibly similar coordination geometry around Np(IV).

The vis-NIR spectra of the extracted Np-L (L_I or L_{II}) complexes from RTIL and molecular diluent media differ considerably in the present study (Fig. 5), suggesting a difference in the symmetry around Np(IV) in the extracted species. This difference may arise from the involvement of a lower number of nitrate ions present in the Np(IV)-L ($L = L_I$ or L_{II}) extracted complexes from $C_4mim-NTf_2$ as compared to those extracted from molecular diluent medium and also may be due to the presence of higher amounts of water/acid in the $C_4mim-NTf_2$ phase compared to that in a molecular diluent.²⁰

The relative position of various f-f transitions for the Np- L_I and Np- L_{II} complexes can be used to get information about the relative complexing strength of the ligands.^{32,46,53-55} The peak positions of the most intense transition of the Np- L_I and Np- L_{II} complexes are 966 ± 2 nm and 738 ± 2 nm, respectively. Hence, it becomes difficult to comment on the relative stability of the two complexes on the basis of Vis-NIR studies. Some insight into the difference in the complexation ability of L_I and L_{II} with Np^{4+} can be gained by cyclic voltammetry studies of the Np- L_I/L_{II} extracted complexes in the $C_4mim-NTf_2$ medium (*vide infra*).

Back extraction and radiation stability studies

For a sustainable extraction system, it is required to check the back extraction and reusability of the solvent by studying its radiation stability. As seen from Fig. 3a, the back extraction of the extracted Np(IV)-L ($L = L_I$ or L_{II}) complexes from $C_4mim-NTf_2$ merely by acid concentration adjustment was difficult. Hence, different aqueous complexing agents such as oxalic acid and HEDTA (hydroxyethyl ethylenediamine triacetic acid) were used. The ionic liquid phase with Np(IV)-L ($L = L_I$ or L_{II}) complex was equilibrated with an aqueous phase containing either 0.1 M HEDTA or 0.5 M oxalic acid in 0.5 M HNO_3 . Quantitative back extraction of Np(IV) was observed by both complexing agents (Table 4).

Table 4 Effect of irradiation dose on $D_{Np(IV)}$ from 0.5 M HNO_3 and % back extraction of Np(IV) using different aqueous complexing agents; 0.1 M HEDTA or 0.5 M oxalic acid (OA) in 0.5 M HNO_3 ; Organic phase: $1 \times 10^{-4} L_I/1 \times 10^{-5} M L_{II}$ in $C_4mim-NTf_2$; T: 298 K

| Ligand | $D_{Np(IV)}$ at varying dose | | % Stripping with complexing agent | |
|----------|------------------------------|-----------------|-----------------------------------|------|
| | 0 | 300 kGy | HEDTA | OA |
| L_I | 6.07 ± 0.32 | 0.07 ± 0.01 | >99% | >98% |
| L_{II} | 5.42 ± 0.41 | 0.06 ± 0.01 | >98% | >97% |

The radiolytic stability is an important parameter to decide the applicability of a given extraction system in the nuclear industry. Therefore, the present solvent system was irradiated with ^{60}Co to a cumulative dose of 300 kGy, whereupon the extraction of Np(IV) was done with the irradiated solvents from a 0.5 M HNO_3 solution. The $D_{Np(IV)}$ decreased drastically upon irradiation, suggesting a poor radiation stability of the present systems at higher irradiation doses (Table 4). In general, the radiolytic stability of RTILs is known to be reasonably good.^{56,57} However, the poor extraction data indicate that the extractant is degrading significantly even in a relatively viscous medium like this RTIL. The degradation products are generally formed from the rupture of the ether linkages and the N-C_{carbonyl} bond. The commonly observed degradation products for DGA based ligands in RTIL are carboxylic acid, hydroxyl acetamides, and octyl as well as fragmented dioctyl diglycolamide radicals.⁵⁸

Cyclic voltammetry studies

The extraction of Np(IV) by L_I and L_{II} was done at 0.5 M HNO_3 to minimize or avoid the uptake of HNO_3 , which can interfere with the cyclic voltammetry (CV) studies and can also reduce the working potential window. The cyclic voltammogram of the blank $C_4mim-NTf_2$ does not have any prominent peaks in the potential range of -2 to +2 volt (Fig. 6 (inset)). The CV study was carried out after extracting 0.5 mM Np(IV) in the $C_4mim-NTf_2$

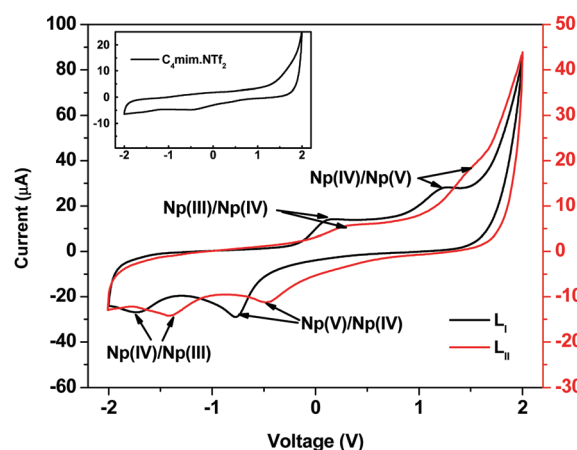


Fig. 6 Cyclic voltammetry studies of the Np-L (L_I and L_{II}) complex extracted in $C_4mim-NTf_2$; [Np]: 0.55 mM for L_I and 0.25 mM for L_{II} ; T: 298 K. The inset shows the CV of pristine $C_4mim-NTf_2$ under similar conditions.

phase containing 2 mM and 1 mM of L_I and L_{II} , respectively. For the CV study, a three-electrode system consisting of glassy carbon as the working electrode (2 mm diameter disk electrode) and two platinum disk electrodes (2 mm diameter) were used as the counter and the reference electrode. The selection of these electrodes was done based on our previous study where CV of Np was done in a TBP- $C_4mim\cdot NTf_2$ system.⁵⁹ The cyclic voltammogram of the Np(IV)-L (L: L_I/L_{II}) complex in the RTIL was recorded at a scan rate of 0.1 V s⁻¹ and is shown in Fig. 6. The cyclic voltammograms of both the L_I and L_{II} containing ionic liquid phases show two prominent peaks in the cathodic scan suggesting two successive reductions and two oxidation peaks in the anodic scan indicating two successive oxidations. The first peak with Np- $L_I\cdot C_4mim\cdot NTf_2$ at -0.77 V in the cathodic scan may be due to the reduction of Np(v) \rightarrow Np(IV), whereas the cathodic peak at -1.73 V corresponds to the Np(IV)/Np(III) reduction couple. Similarly, the peaks at +0.10 and +1.22 V correspond to the oxidation of the Np(III)/Np(IV) and Np(IV)/Np(V) couples, respectively, with Np- $L_I\cdot C_4mim\cdot NTf_2$ (Table 5). The corresponding reduction peaks with Np- $L_{II}\cdot C_4mim\cdot NTf_2$ are observed at -0.46 V and -1.41 V, respectively, for the Np(v)/Np(IV) and Np(IV)/Np(III) couples and the corresponding oxidation peaks are at +0.28 V and +1.50 V for Np(III)/Np(IV) and Np(IV)/Np(V) couples, respectively. The nature of the CV of Np with the L_I/L_{II} ligands in $C_4mim\cdot NTf_2$ is distinctly different from that obtained with the Np-TBP- $C_4mim\cdot NTf_2$ system.⁵⁰ In the present study, we observed a reduction in the peak corresponding to the Np(v)/Np(IV) couple, which is absent in the Np-TBP- $C_4mim\cdot NTf_2$ system.⁵⁹ The presence of Np(v) in the present system may be due to the *in situ* aerial oxidation of the Np(IV) extract or another possible reason may be the co-extraction of Np(v) (present in traces) with Np(IV) due to the cation-cation interaction, as also observed by Sarsfield *et al.*, in the extraction of Np(IV) by TBP.⁶⁰ However, the characteristic peak of Np(v) (at 980 nm) is not clearly observed in the corresponding vis-NIR spectrum of the Np(IV) extract with $L_I/L_{II}\cdot C_4mim\cdot NTf_2$, but a broad peak in the region of 950–990 nm may indicate the presence of Np(v) along with Np(IV) in the respective extract (Fig. 5).

The overall nature of the cyclic voltammograms of the Np- L_I and Np- L_{II} complexes is very similar, except for the shift in both the cathodic and anodic peak potentials. The peak potentials of the Np- L_{II} complex are at lower values in the cathodic scan (more positive), suggesting easy reduction. The more negative shift in the cathodic scan points to better complexation.^{55,61,62} Sengupta *et al.* have also observed that the reduction potentials (Np(IV)/(III)) are more negative for Np-TODGA compared to the

Table 5 Peak potentials (V) observed for different couples in the CV study of Np- L_I and Np- L_{II} complexes extracted in $C_4mim\cdot NTf_2$ at 298 K

| Redox couple | Np- L_I | Np- L_{II} |
|------------------------------|-----------|--------------|
| Np(v) \rightarrow Np(IV) | -0.77 | -0.46 |
| Np(IV) \rightarrow Np(III) | -1.73 | -1.41 |
| Np(III) \rightarrow Np(IV) | +0.10 | +0.28 |
| Np(IV) \rightarrow Np(V) | +1.22 | +1.50 |

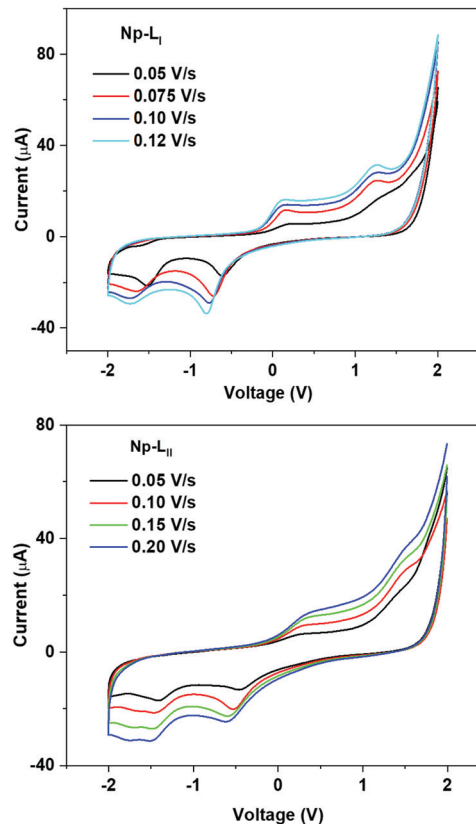


Fig. 7 Cyclic voltammetry studies of the extracted Np(IV) complex with (a) L_I and (b) L_{II} dissolved in $C_4mim\cdot NTf_2$ at different scan rates; T : 298 K.

Np-DGA-TSIL extracted complex in ionic liquid, suggesting the better stability of the former complex.⁶² In the present study, the Np(IV)- L_I system is at a more negative potential than that of the Np(IV)- L_{II} system, suggesting stronger complexation with the former ligand. On the other hand, the D -value of Np(IV) was found to be higher with L_{II} (*vide supra*), indicating that the hydrophobicity of the ML complex, the phase transfer energetics, the solvation of the ML solvates, *etc.*, may be significant factors in the extraction of metal ions along with the ML complexation strength.

Scan rate variation experiments (Fig. 7a and b) were carried out to get information about the reversibility of the Np couple. They can be used to deduce the diffusion coefficient of the electroactive species under suitable conditions.

The Randles-Sevcik expression (eqn (3)) can be used for the calculation of the diffusion coefficient (D) of the Np-L (L: L_I or L_{II}) species in the present system.

$$i_p^c = 0.496 \cdot nFCAD^{1/2} \left(\frac{\alpha n_2 Fv}{RT} \right)^{1/2} \quad (3)$$

where n is the number of electrons involved, F is the Faraday constant, A is the area of the electrode (cm²), C_o is the bulk concentration of the oxidized species (mol cm⁻³), D is the diffusion coefficient (cm² s⁻¹), v is the scan rate (V s⁻¹), R is the gas constant, and T is the temperature in K. The value

of αn_z can be obtained from the CV data at a given scan rate by using eqn (4).

$$\left| E_p^c - E_{p/2}^c \right| = \frac{1.857RT}{\alpha n_z F} \quad (4)$$

Eqn (3) shows that the intercept of I_c vs. $v^{1/2}$ should pass through the origin.⁶³ Although the linear fit to the plot gives $R^2 > 0.95$ (ESI) it does not pass through the origin, so the diffusion coefficient calculated in the present system may have significant errors and hence, not listed here. The scan rate variation studies show a change in the cathodic peak potential towards the left (more negative value) with the scan rate for both extracts, *i.e.* Np-L_I and Np-L_{II}, suggesting non-reversibility or a quasi-reversible nature of the reduction process.^{63–65}

Conclusions

Solutions of L_I and L_{II} in the RTIL C₄mim·NTf₂ were evaluated for the extraction of Np(IV) ions to investigate its applicability in back-end processes. The extraction of Np(IV) was higher in the RTIL medium as compared to that in a molecular diluent at lower acid concentrations, while the situation changed at higher acid concentrations. This arises due to difference in the extraction mechanisms at higher acidity. Interestingly, 1 : 1 ligand-Np(IV) extracted complexes were formed both in RTIL and in molecular diluents. Np(IV) was extracted to a larger extent by L_{II} than L_I in C₄mim·NTf₂. The nature of the extracted complexes was ascertained by slope analysis and was also studied by vis-NIR spectrophotometry and cyclic voltammetry. The vis-NIR studies indicate a difference in the nature of the extracted Np-L complex in RTIL compared to that in a 5% isodecanol + 95% *n*-dodecane mixture. The peak positions of the f–f transition for the Np-L_I and Np-L_{II} extracted complexes in C₄mim·NTf₂ were found to be very close (within ±2 nm) making it difficult to comment on the relative stability of the two complexes in C₄mim·NTf₂ solely based on vis-NIR studies. The CV studies were done to understand the relative stability of the Np-L_I and Np-L_{II} extracted complex in C₄mim·NTf₂ medium. The CV studies showed relatively strong complexation of Np-L_I compared to Np-L_{II}, where the extraction of Np was higher for the latter. Though the back extraction of the extracted metal ion was quite efficient using either oxalic acid/HEDTA, the radiolytic stability of the ligand solutions in RTIL was rather poor suggesting that long term use in a high radiation field was not recommended.

Experimental

Materials

The DGA-functionalized poly(propylene imine) diaminobutane dendrimers L_I and L_{II} were prepared as per the procedure described previously.⁶⁶ NMR spectroscopy and HR-MS were used to check the purity of the ligands. C₄mim·NTf₂, *n*-dodecane and isodecanol (>99% purity) were obtained from Iolitec, Germany, Lancaster, UK, and SRL, Mumbai,

respectively, and were used as received. Nitric acid solutions of different molarity were prepared from Suprapur nitric acid (Merck, Germany) and MilliQ water (Millipore) and standardized using a conventional acid–base titrimetric method using AR grade NaOH (BDH) with phenolphthalein (Fluka, Switzerland) as the indicator. Oxalic acid dihydrate (Thomas Baker, > 99%) and HEDTA (Sigma-Aldrich, > 99%) for the back extraction studies were used as received without any purification.

Radiotracer

The ²³⁹Np tracer was purified from a neutron irradiated UO₂(NO₃)₂·6H₂O target by extracting it, after Np oxidation state adjustment to Np(IV) (*vide infra*), with 0.5 M TTA (2-thenoyl trifluoroacetone; Sigma-Aldrich) in xylene at 1 M HNO₃, followed by its subsequent back extraction in 8 M HNO₃. The resulting Np(IV) aqueous solution was washed several times with xylene to remove any traces of organic impurities. The purity of the stock ²³⁹Np was checked by gamma as well as alpha spectrometry.

Oxidation state adjustment

A freshly prepared solution of ferrous sulfamate (0.3 M) was used along with a few drops of hydroxylamine nitrate (1 M) as the reductant for the conversion of Np to the Np(IV) state. The oxidation state of Np in the stock solution was confirmed intermittently by TTA extraction for tracer ²³⁹Np (ESI⁺), whereas vis-NIR spectroscopy was applied for the ²³⁷Np solution by monitoring the reduction of the peak at 980 nm (Np(V) signature) with the formation of the peak at 964 nm (Np(IV) signature).^{59,67}

Distribution studies

Stock solutions of L_I and L_{II} were prepared by dissolving known amounts of the ligands in C₄mim·NTf₂. The ligand solution was diluted as per the experimental requirements. The distribution ratios (*D*) of Np(IV) were measured by equilibrating equal volumes (usually 1 mL) of ligand solution in C₄mim·NTf₂ with an aqueous solution containing ²³⁹Np (10^{−12} M) in 5 mL stoppered glass centrifuge tubes for the required time in a constant temperature (25 ± 0.1 °C) water bath. The glass centrifuge tubes were taken out, rested, and centrifuged at 5000 rpm for 5 min to get good phase separation. Fixed volumes of both phases (100 μL) were removed and assayed using a well type NaI(Tl) detector coupled with a multichannel analyzer. The *D* values were determined from the ratio of the activity per minute per unit volume of the organic phase to that in the aqueous phase. All the extraction experiments were carried out in duplicate and the reported values are average values with an error < 5%. The radiolytic stability of the present solvent system *i.e.* L_I (10^{−4} M) and L_{II} (10^{−5} M) dissolved in C₄mim·NTf₂ was investigated by irradiating the solvent system in air with a ⁶⁰Co gamma irradiator at a dose rate of 5.2 kGy h^{−1}. The *D*_{Np(IV)} for both the back-extraction of the extracted Np(IV) with L_I or L_{II} and for the radiation stability studies was evaluated as discussed above.

Absorption studies

The samples (~2 mL) for the visible-near infrared (vis-NIR) spectroscopic studies were prepared by liquid-liquid extraction of Np(IV) using ligand (L_I or L_{II}) dissolved in C₄mim-NTf₂ or 5% isodecanol + *n*-dodecane from 0.5 M HNO₃. The vis-NIR spectra were recorded using a Jasco-530(V) (Japan) double beam spectrophotometer in the wavelength range of 600–1100 nm. All the spectra were recorded in quartz cuvettes with 10 mm path length against a suitable blank.

Titration

The water content in the organic phase was determined with Karl-Fisher (KF) titration using a Titrano 905 from Metrohm. Single solution KF reagent from Merck was used as received. The initial strength (in volume of KF required/mg of water) of the KF reagent was determined by titrating a known weight of the water sample with the KF reagent in triplicate. The KF strength of the solution was found to be 5.17 mL mg⁻¹. The acidity of the organic phase was determined by conventional acid-base titration in a neutralized 50% ethanol-water mixture using standard NaOH with a phenolphthalein (Merck) indicator.

Electrochemical studies

Np(IV)-L (L: L_I or L_{II}) extracts were prepared by equilibration of 2.5 mL of 1 mM of ligand dissolved in C₄mim-NTf₂ with an equal volume of 0.5 M HNO₃ containing ~0.5 mM Np(IV). A three-electrode system with a platinum disc (2 mm diameter) both as the counter and reference electrode and glassy carbon (2 mm diameter) as the working electrode were used for the cyclic voltammetry (CV) studies using an AUTOLAB electrochemical setup of Metrohm. Cyclic voltammograms of acid equilibrated ligand solutions in C₄mim-NTf₂ were recorded as the blank to access the working potential window in this medium. All the solutions were purged with high purity N₂, at least for 15 min prior to the CV studies, whereupon a constant N₂ atmosphere was maintained.

Conflicts of interest

There are no conflicts of interest to declare.

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