



Liquid-liquid extraction and facilitated transport of *f*-elements using an N-pivot tripodal ligand



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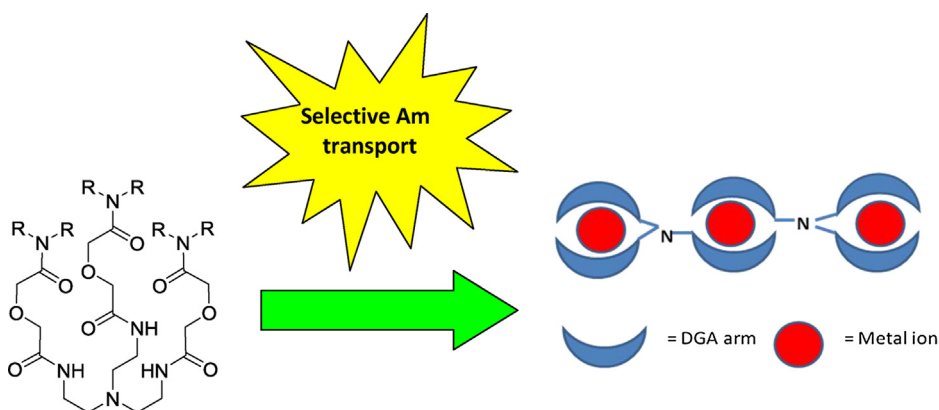
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HIGHLIGHTS

- Solvent extraction and supported liquid membrane of actinides were studied using TREN-DGA as the carrier.
- The trend of extraction of the lanthanide and actinides was: $\text{Eu}^{3+} > \text{Am}^{3+} \sim \text{Pu}^{4+} \gg \text{UO}_2^{2+}$.
- Am can be separated from a mixture of U and Pu by oxidizing the latter to its +6 oxidation state.
- Diffusion coefficient of the Am^{3+} and Eu^{3+} complexes was determined by the lag-time method.
- Stability of the SLM was studied and was found to be not stable due to leaching out of the ligand.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 August 2017

Received in revised form 7 December 2017

Accepted 28 December 2017

Available online 29 December 2017

Keywords:

Diglycolamide
Separation
Radioactive waste
Liquid membrane
Americium

ABSTRACT

Diglycolamide (DGA)-functionalized tripodal ligands offer the required nine-coordinated complex for effective binding to a trivalent lanthanide/actinide ion. A N-pivot tripodal ligand (TREN-DGA) containing three DGA pendant arms was evaluated for the extraction and supported liquid membrane transport studies using PTFE flat sheets. Solvent extraction studies indicated preferential extraction of 1:1 (M:L) species, while the metal ion extraction increased with increasing HNO_3 concentration conforming to a solvated species extraction. Flat sheet-supported liquid membrane studies, carried out using 4.0×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol indicated faster mass transport for Eu^{3+} ion as compared to Am^{3+} ion. The determined transport parameters indicated slow diffusion of the M-TREN-DGA (M = Am or Eu) complex being the rate-determining step. The transport of lanthanides and actinides followed the trend: $\text{Eu}^{3+} > \text{Am}^{3+} \sim \text{Pu}^{4+} \gg \text{UO}_2^{2+}$ and Am can be selectively separated from a mixture of U and Pu by oxidizing the latter to its +6 oxidation state. The liquid membrane stability was not encouraging and was deteriorating the transport efficiency with time, which was attributed to carrier loss into the aqueous phases.

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1. Introduction

One of the major challenges of the nuclear power program is the mitigation of the long lived radioactive wastes emanating from various processes; those from the front end processes such as milling,

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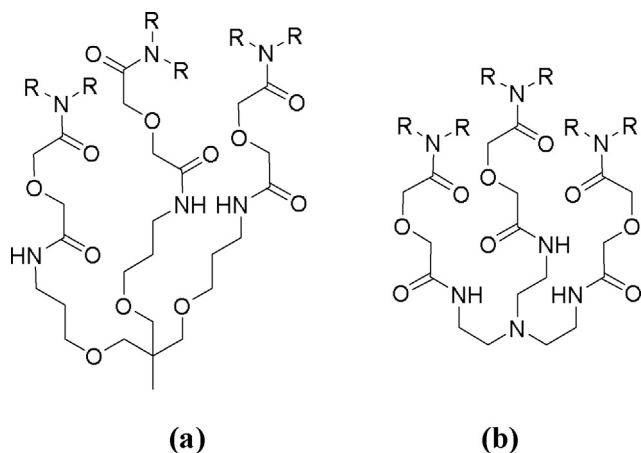


Fig. 1. Structural formulae of (a) T-DGA and (b) TREN-DGA.

mining, purification, fuel fabrication, etc. and also from the back end processes such as reprocessing and waste management [1,2]. The back end processes appear more challenging due to the possibility of handling long-lived actinide elements such as Np, Pu, Am, Cm, etc. and fission product nuclides such as ^{90}Sr and ^{137}Cs , which are associated with very high radiotoxicity values. Though Pu, an element with high strategic relevance, is mostly separated from the spent fuel along with U in the PUREX (Plutonium Uranium Reduction EXtraction) process, the raffinate stream contains the minor actinides (Np, Am, Cm) and almost the entire lot of the fission product nuclides. These highly radioactive nuclides make the radioactive waste management a costly affair and even the conventional vitrification by borosilicate glass is not termed effective in view of the long surveillance required for over a million years [3]. This requires separation of the long-lived minor actinides and even the fission product nuclides by dedicated separation methodologies. The former can be accomplished by a strategy called 'Actinide Partitioning', which can effectively separate the minor actinides from the high level liquid waste (HLLW) for subsequent transmutation in high flux reactors or accelerator driven sub-critical systems [4].

Over the past four decades, several extractants have been evaluated for 'Actinide Partitioning' at lab scale and in certain cases hot counter current runs have been taken up [5–8]. Out of the various extractants, thus evaluated, diglycolamides (DGA), with two amidic and one etheric 'O' atom, are considered to be the most promising [9–14]. A series of basic studies has been performed to understand the extraction mechanism in case of DGA ligands such as TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide). It was demonstrated a diluent mediated aggregation to be responsible for the unusual selectivity for trivalent actinide ions, i.e., Am^{3+} being better extracted than Pu^{4+} and UO_2^{2+} [15,16]. This has prompted to the synthesis and evaluation of a host of multiple DGA extractants where the DGA moiety was tethered to a calix[4]arene or a pillar[5]arene, resulting in highly encouraging results [17,18]. In view of the participation of three TODGA molecules in the extracted complex, several tripodal DGA ligands, with three DGA arms, have also been synthesized and used for actinide extraction [19–22]. While the C-pivot tripodal DGA (T-DGA; Fig. 1a) has given encouraging results, a recent study with an N-pivot tripodal DGA ligand (DGA-TREN; Fig. 1b) showed a very interesting extraction/separation behavior [23]. However, a detailed investigation on the liquid–liquid extraction of actinide ions using DGA-TREN is lacking and needs to be taken up.

In view of the very high efficiency of the multiple DGA ligands, and also due to their high cost, it has been proposed to evaluate liquid membrane-based separation methods where the

ligand inventory is very low [24]. Additionally, liquid membrane-based separation methods are known to be 'green' alternatives to solvent extraction-based separation methods which make use of large volumes of volatile organic carbon (VOC). Out of the liquid membrane-based separation methods, the supported liquid membrane (SLM) technique uses very small amounts of the extractant making it one of the most attractive separation methods [25]. Though DGA ligands such as TODGA and multiple DGA ligands such as calix [4] arenes and T-DGA have been evaluated for the transport of actinide ions with highly encouraging results, there is no report available on the use of DGA-TREN as the carrier extractant in SLM studies.

In the present study, liquid–liquid extraction of several actinide ions such as Am^{3+} , Pu^{4+} and UO_2^{2+} (representative tri-, tetra- and hexa-valent actinide ions) were investigated using solutions of DGA-TREN in 95% *n*-dodecane + 5% iso-decanol. The composition of the diluent mixture has been optimized in previous studies. The separation behaviour of trivalent actinides and lanthanides was studied by using Eu^{3+} as the representative lanthanide ion. Apart from the solvent extraction studies, flat sheet supported liquid membrane (FSSLM) studies were carried out for the above mentioned metal ions and the effect of the feed HNO_3 concentration was investigated. Transport parameters were determined and the membrane stability was evaluated over several days. Selectivity studies were carried out using a mixture of actinide ions. The possibility of leaching out of the protonated form of the carrier extractant was investigated by impedance measurements.

2. Experimental

2.1. Materials

TREN-DGA (Fig. 1b) was synthesized by a procedure reported recently [23]. The ligands were characterized by ^1H NMR and HR-MS to ascertain their purities. *n*-Dodecane (99%) and iso-decanol (99%) were procured from Lancaster, UK and SD Fine Chem, Mumbai, respectively. Poly tetra fluoro ethylene (PTFE) membranes (pore size: 0.45 μm ; porosity: 72%; diameter: 47 mm; thickness: 85 μm) were purchased from Sartorius, Germany. All the other reagents were of AR grade and were used without further purification. All aqueous feed solutions were prepared using Suprapur HNO_3 (Merck) and Milli Q deionized water (18.2 $\text{M}\Omega\text{ cm}$).

2.2. Radiotracers

The actinide tracers were taken from laboratory stock solutions after purification and checking their radiochemical purities. ^{241}Am and Pu (mainly ^{239}Pu) stocks were purified (from their decay products, ^{237}Np and ^{241}Am , respectively) by their selective extraction using a xylene solution of HTTA (2-thenoyltrifluoroacetone) and subsequently checking their radiochemical purities by alpha spectrometry [26]. ^{233}U was purified from its daughter products using a reported method [27]. The Pu was converted to the +4 state by the addition of a few drops of $1 \times 10^{-3}\text{ M}$ NaNO_2 followed by selective extraction of the converted Pu^{4+} ions by 0.5 M HTTA in xylene. The extracted Pu^{4+} was subsequently stripped by 8 M HNO_3 and was used in the presence of ammonium metavanadate as the holding oxidant. On the other hand, conversion to PuO_2^{2+} was accomplished by the addition of AgO [28]. The oxidation states of Pu^{4+} and PuO_2^{2+} were confirmed by slope analysis by HTTA concentration variation experiments at a fixed aqueous phase acid concentration (1 M HNO_3 for Pu^{4+} and pH 3 for PuO_2^{2+}) which yielded slopes of +4 and +2, respectively. $^{152,154}\text{Eu}$ radiotracer was procured from BRIT (Board of Radiation and Isotope Technology), Mumbai, and was used after checking its radiochemical purity. The

concentrations of Am and Pu, were 10^{-7} M and 10^{-6} M, respectively while the concentrations of both Eu and U were 10^{-5} M. ^{241}Am and $^{152,154}\text{Eu}$ were assayed by gamma ray counting employing a well type NaI(Tl) scintillation counter (Para Electronics) coupled with a multi-channel analyzer (ECIL, India). On the other hand, the alpha emitting radionuclides (^{239}Pu and ^{233}U) were assayed using a liquid scintillation counting system (Hidex, Finland) and Ultima Gold (Perkin Elmer) scintillator cocktail.

2.3. Distribution measurements

The liquid-liquid extraction studies were carried out by equilibrating ca. 1 mL of the aqueous phase (containing the required radiotracer) with an equal volume of organic phase containing 4.0×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol in leak tight Pyrex glass stoppered tubes in a thermostated water bath maintained at $25 \pm 0.1^\circ\text{C}$ for about 60 min. The time required to attain equilibrium was obtained by a separate set of experiments (vide infra). After settling for 10 min, the equilibration tubes were centrifuged (2000 rpm) and ca. 100 μL aliquots were removed from both the constituent phases for their subsequent radiometric assay (vide supra). The distribution ratio of the metal ions (D_M) was calculated as follows:

$$D_M = \frac{\text{counts per unit time per unit volume in the organic phase}}{\text{counts per unit time per unit volume in the aqueous phase}} \quad (1)$$

All solvent experiments were carried out in duplicate and the data presented here were within the accepted error limits of $\pm 5\%$.

2.4. Supported liquid membrane studies

PTFE flat sheet membranes of 0.45 μm pore size were used for the supported liquid membrane (SLM) studies. The pores of the PTFE flat sheets were filled with a 4.0×10^{-3} M TREN-DGA solution in 95% n-dodecane + 5% iso-decanol by overnight soaking the membrane filters in the carrier solution. The pore filled flat sheet membranes were wiped carefully with a tissue paper to remove the sticking carrier solution. Subsequently, the membrane filter was carefully mounted in between the two compartments (20 mL capacity each) of the glass transport cell. The feed solution was dilute HNO_3 spiked with the required radiotracer, while the receiver solution contained 0.01 M HNO_3 . The transport cell was kept erect over a heavy duty magnetic stirrer equipped with precise speed control. Each compartment was continuously stirred using Teflon coated magnetic stirring bars (4 mm diameter and 10 mm length), which ensured a minimal thickness of the aqueous boundary layers [29]. The radiotracer content in the feed and the receiver compartments was monitored by removal of 100 μL samples at regular intervals followed by their subsequent radiometric assay. The cumulative percent transport (%T) of the metal ions at any given time t was calculated as:

$$\%T = \left(\frac{C_{f,0} - C_{f,t}}{C_{f,0}} \right) \cdot 100 \quad (2)$$

Where $C_{f,0}$ and $C_{f,t}$ are the concentrations of metal ion in the feed at $t=0$ and at time t . The permeability coefficient was calculated by the following equation [29]:

$$-\ln \left(\frac{C_t}{C_0} \right) = P \cdot \left(\frac{A}{V} \right) \cdot t \quad (3)$$

All transport experiments were carried out at ambient temperatures ($24 \pm 1^\circ\text{C}$) and the results obtained from duplicate runs were reproducible within $\pm 5\%$.

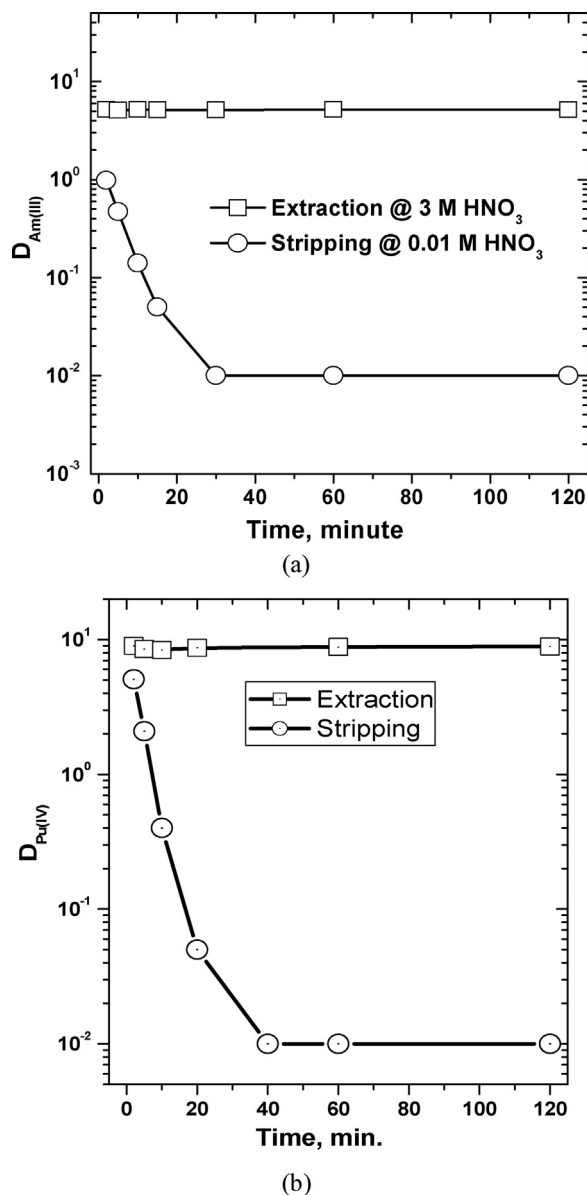


Fig. 2. Extraction and stripping kinetics of (a) Am^{3+} ; Feed: 3 M HNO_3 ; Strip: 0.01 M HNO_3 ; [TREN-DGA]: 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol; (b) Pu^{4+} ; Feed: 3 M HNO_3 ; Strip: 0.5 M oxalic acid + 0.5 M HNO_3 ; [TREN-DGA]: 2×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol.

3. Results and discussion

3.1. Solvent extraction studies

Solvent extraction studies were carried out for optimization of the best extraction and stripping conditions to be used for the subsequent flat sheet-supported liquid membrane studies. Furthermore, solvent extraction studies also give an idea on the nature of the extracted species. The following sections discuss the results of the solvent extraction studies carried out in a systematic manner.

3.1.1. Extraction and stripping kinetics

The extraction kinetics was investigated by carrying out Am(III) as well as Pu(IV) extraction from 3 M HNO_3 as the feed solution using 4.0×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol (in view of higher D_{Pu} values, lower ligand concentration was used for Pu(IV) extraction). U extraction was not investigated as the D values were very low. The corresponding D_{Am} and D_{Pu} data are plot-

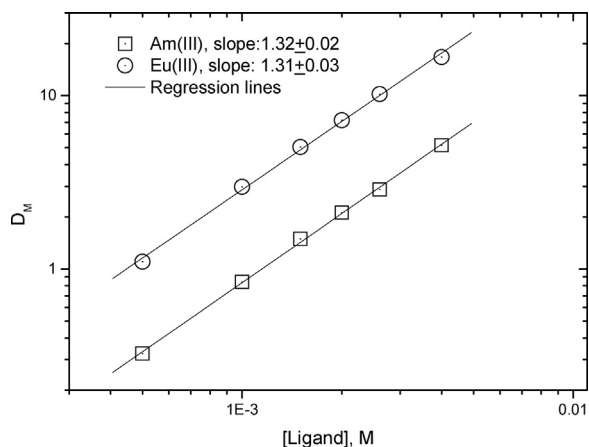


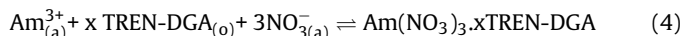
Fig. 3. Variation of D_{Am} or D_{Eu} with the ligand (TREN-DGA) concentration. Feed acidity: 3 M HNO_3 .

ted against time and are presented in Fig. 2, which indicated that the forward extraction is rather fast and only 2 min time is sufficient to reach the equilibrium distribution ratio values for both the metal ions. A similar fast attainment of equilibrium for Am(III) extraction from 3 M HNO_3 as the feed solution was reported in our previous studies when either 2.90×10^{-3} M T-DGA [30] or 1.0×10^{-3} M TREN-DGA were used in a mixture of 90% *n*-dodecane + 10% iso-decanol as the diluent [23].

The back extraction of Am(III) from the loaded organic phase was subsequently carried out using 0.01 M HNO_3 and the kinetics of stripping was significantly slower as it took ca. 30 min to reach the equilibrium D_{Am} value of 0.01 (Fig. 2). On the other hand, the back extraction of Pu(IV) carried out using a mixture of 0.5 M oxalic acid and 0.5 M nitric acid (nitric acid was used to prevent hydrolysis of the metal ion) took nearly 40 min (Fig. 2(b)). While the fast extraction kinetics may be attributed to rapid complexation by the pre-organized tripodal ligand ((TREN-DGA)), the slow back extraction may be due to the difficult breaking of multiple metal-ligand bonds in the complexes to set free the Am^{3+} (or Pu^{4+}) ion into the aqueous phase. An equilibration time of 60 min was given for all subsequent solvent extraction studies.

3.1.2. Effect of ligand concentration

The effect of the ligand concentration on the extraction of Eu^{3+} and Am^{3+} ions was studied from 3 M HNO_3 feed solutions by varying the TREN-DGA concentration from 0.5×10^{-3} M to 4.0×10^{-3} M in 95% *n*-dodecane + 5% iso-decanol and the data are presented in Fig. 3. The extraction of Am^{3+}/Eu^{3+} by TREN-DGA can be given by the following equation,



where the subscripts '(a)' and '(o)' refer to the species present in the aqueous and the organic phases, respectively. As can be seen from Fig. 3, the plots of $\log D$ vs $\log [\text{TREN-DGA}]$ at 3 M HNO_3 are linear and the slope values of the fitted lines are 1.32 ± 0.02 and 1.31 ± 0.03 for Am^{3+} and Eu^{3+} , respectively, when the ligand concentration was varied in the concentration range of 0.5×10^{-3} M to 4.0×10^{-3} M. This indicates that the extracted species is $M(NO_3)_3 \cdot \text{TREN-DGA}$ ($M = Am$ or Eu). This is in sharp contrast to our earlier report of extraction of species of the type $M(NO_3)_3 \cdot 2\text{TREN-DGA}$ for Am^{3+} ion extraction in the solvent system containing 90% *n*-dodecane + 10% iso-decanol. Though it is tempting to conclude that the diluent composition may be playing a significant role in deciding the number of ligand molecules that bind to the metal ion, a thorough investigation is required with a

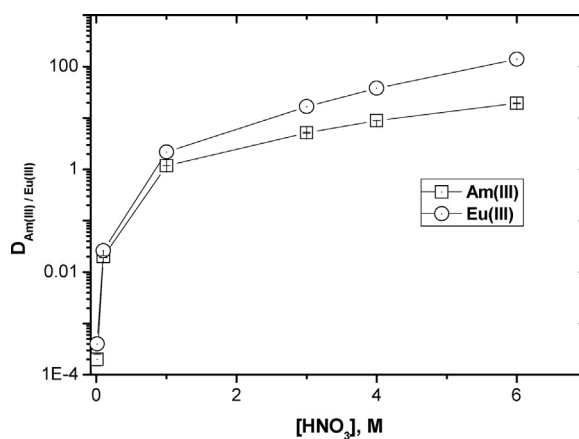


Fig. 4. Effect of HNO_3 concentration on the extraction of Am(III) and Eu(III). Extractant: 4×10^{-3} M TREN-DGA in 95% *n*-dodecane + 5% iso-decanol.

Table 1

Solvent extraction data of Eu^{3+} and actinides from feed solution at 3 M HNO_3 using 4×10^{-3} M TREN-DGA as the extractant.

Metal ion	Distribution ratio
Eu^{3+}	16.67 ± 0.15
Am^{3+}	5.17 ± 0.04
Pu^{4+}	18.54 ± 0.16
UO_2^{2+}	0.07 ± 0.01

variety of diluents of varying polarity and compositions to draw hard conclusions.

3.1.3. Effect of the feed acid concentration

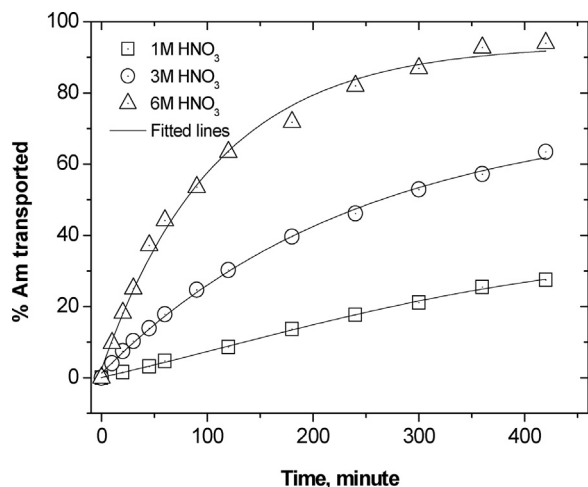
As indicated by Eq. (4), the forward extraction is facilitated by increasing the NO_3^- ion concentration. Therefore, the extraction of Am^{3+} and Eu^{3+} was studied by varying the nitric acid concentration from 1.0 to 6.0 M at a fixed concentration of the ligand (4×10^{-3} M TREN-DGA in 95% *n*-dodecane + 5% iso-decanol). Fig. 4 shows that there is a gradual increase in the D values of both metal ions with increasing HNO_3 concentration. This trend is in line with the results expected with most of the neutral extractants where a typical solvation mechanism (as given in Eq. (4)) is followed. The separation factor (SF) of Eu^{3+} over Am^{3+} is defined as the ratio of D_{Eu} to D_{Am} at a given experimental condition. As can be seen from Fig. 4, the SF values increased with increasing feed acid concentration indicating preferential Eu^{3+} extraction over Am^{3+} in the HNO_3 concentration range of 1–6 M. The extraction of nitric acid by the TREN-DGA ligand was found to be negligible (<1%), which is a direct consequence of the very low concentration of the ligand used in the extraction studies.

3.1.4. Extraction of other actinides and separation behaviour

Solvent extraction studies with other metal ions, viz. Pu^{4+} and UO_2^{2+} , were also carried out using 4.0×10^{-3} M TREN-DGA in 95% *n*-dodecane + 5% iso-decanol at 3 M HNO_3 and the corresponding results are summarized in Table 1 showing that the D values of the metal ions follow the trend: $D_{Pu} > D_{Eu} > D_{Am} \gg D_U$. The higher extraction of Pu^{4+} ion as compared to Eu^{3+} can be explained by the higher ionic potential of the former, whereas the poor extraction of the uranyl ion is attributed to the steric factors arising due to the presence of the axial oxygen atom, which forces the ligand to bind along the equatorial plane. Although the SF value of Eu^{3+} with respect to Am^{3+} at 3 M HNO_3 is not very encouraging ($D_{Eu}/D_{Am} = 3.2$), those of the different ions with respect to the uranyl ion are quite high. For example, the D_{Eu}/D_U , D_{Am}/D_U and D_{Pu}/D_U values obtained are 246.3, 76.4 and 273.8, respectively. Thus, the lower D_U value (<0.1)

Table 2Transport data of Am(III) with 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol as the carrier solvent. Feed: 3 M HNO₃; Receiver: 0.01 M HNO₃.

Feed acidity, M	% Am(III) in feed at 5 h (24 h)	% Am(III) in receiver at 5 h (24 h)	$P_{\text{Am(III)}} \times 10^3$ (cm/s)
1	78.3 (44.8) ^a	21.1 (53.3) ^a	4.82 ± 0.12
3	45.9(11.7) ^a	52.9(85.2) ^a	16.0 ± 0.29
6	15.4(3.0) ^a	86.9(98.2) ^a	37.2 ± 1.7

^a Values inside parentheses refer to the 24 h data.**Fig. 5.** Transport profile of Am(III) with 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol as the carrier solvent. Feed: 3 M HNO₃, Receiver: 0.01 M HNO₃.

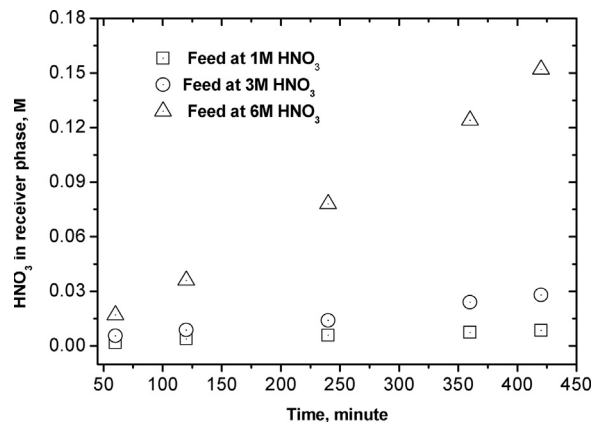
and the higher separation factors indicate that selective recovery of the other ions with respect to the uranyl ion is quite possible from a 3 M HNO₃ containing metal ion mixture feed.

3.2. Supported liquid membrane studies

In view of the encouraging results obtained with the solvent extraction studies and the exotic nature of the extractant (which may be quite expensive), supported liquid membrane studies were carried out for Am³⁺, Pu⁴⁺, UO₂²⁺ and Eu³⁺ ions from 3 M HNO₃ feed solutions using pore-filled (with 4.0×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol) PTFE flat sheets. Different transport parameters, such as the permeability coefficient (P) and the effective diffusion coefficient (D_{eff}), were experimentally determined for these metal ions.

3.2.1. Effect of feed acidity on permeation of Am³⁺

The permeation of Am³⁺ through the PTFE flat sheet membrane was studied by varying the nitric acid concentration in the feed from 1.0 to 6.0 M, while keeping the receiver phase at 0.01 M HNO₃. The cumulative transport percentage of the metal ion was found to increase with the feed HNO₃ concentration (Fig. 5). For example, 21.1% transport of Am(III) was observed after 5 h with 1 M HNO₃ as the feed, which significantly increased to 52.9% and 86.9% with 3 and 6 M HNO₃, respectively, after the same time interval (Table 2). The transport rates were significantly lower than those reported previously with a T-DGA-containing SLM [30]. This can be attributed to the much higher extraction efficiency of T-DGA as compared to TREN-DGA. The permeability coefficient (P) values were determined from the slope of the linear fitted plot of $\ln(C_t/C_0)$ vs. time by using Eq. (3). The P values increased as the feed phase HNO₃ concentration increased from 1 to 6 M (Table 2), indicating a more facile extraction of the metal-ligand complex via the solvation mechanism discussed above (Eq. (4)), which is the driving force for a favourable mass transport.

**Fig. 6.** Transport of HNO₃ across the SLM at different feed acidity. Carrier: 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol; Support: 0.45 μm PTFE; Solution volume: 20 mL; Receiver: 0.01 M HNO₃.

It is well known that HNO₃ extraction and subsequent transport across a SLM can result in retardation in the transport behaviour [30] on two counts: firstly, formation of a HNO₃·L complex:



(where L = TREN-DGA) can significantly lower the D value of the metal ion and secondly, the transport of the extracted HNO₃ into the receiver phase can affect the stripping reaction (reverse of Eq. (4)). In view of these, the receiver phase HNO₃ concentration had to be monitored against time for all the feed solutions used in these studies (1–6 M HNO₃). As shown in Fig. 6, there is an increase in the acid concentration in the receiver phase with time. However, the total concentration of the acid was rendered insignificant (<1%) to affect the transport of Am³⁺ to the receiver phase.

3.2.2. Transport of other metal ions

The transport behaviour of other metal ions, viz. Eu³⁺, Pu⁴⁺, UO₂²⁺, was investigated using 3 M HNO₃ as the feed solution and 4.0×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol as the carrier solvent. The receiver phase contained 0.01 M HNO₃ for both Eu³⁺ as well as UO₂²⁺, while 0.2 O.1 M HNO₃ was used as the stripant for Pu⁴⁺ in order to avoid its hydrolysis. The transport profiles of the three metal ions along with that of Am³⁺ ion are presented in Fig. 7, which shows that the transport of the metal ions follows the order Eu³⁺ > Am³⁺ ~ Pu⁴⁺ » UO₂²⁺, which is in slight variance with their solvent extraction trend discussed above. In sharp contrast to this observation, the Am³⁺ transport rates are significantly higher than those of Pu⁴⁺ ion when T-DGA was used as the carried extractant [30]. The lower transport of Pu⁴⁺ as compared to Eu³⁺, even though the former has a higher D value, may be due to the different stripping conditions employed in their transport experiments. The low transport of uranyl ion will be due to the very poor extraction of the metal ion (vide supra). The cumulative transport data of all the metal ions studied here are summarized in Table 3. As can be seen from Table 3, after 2 h, the % transport values of Eu³⁺, Am³⁺, Pu⁴⁺ and UO₂²⁺ to the receiver phase are 60%, 30.3%, 28.7% and 2.8%, respectively, from the feed containing 3 M HNO₃. The lower transport rate of the uranyl ion across the membrane indicates that

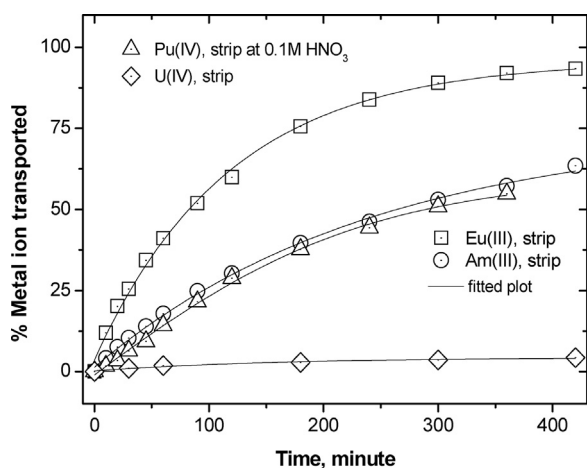


Fig. 7. Transport profiles of metal ions with 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol as the carrier solvent. Feed: 3 M HNO_3 ; Receiver: 0.01 M HNO_3 .

Table 3

Transport data of actinides/lanthanide with 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol as the carrier solvent. Feed: 3 M HNO_3 ; Receiver: 0.01 M HNO_3 .

Actinide ion	% Am(III) in feed at 2 h	% Am(III) in receiver at 2 h	$P \times 10^3$ (cm/s)
Eu(III)	38.9	60.0	38.5 ± 1.4
Am(III)	70.6	30.3	16.0 ± 0.3
Pu(IV)	73.5	28.7	13.4 ± 0.4
U(VI)	97.3	2.8	0.67 ± 0.08

the other metal ions could be separated in the presence of bulk amounts of uranium from acidic feed solutions. The permeability coefficient (P) data for the transport experiments mentioned above were determined using Eq. (3) and are also listed in Table 3. As the P values are a measure of the metal ion transport rates, these follow the same order as the %T values discussed above, i.e., $P_{\text{Eu}} > P_{\text{Am}} \geq P_{\text{Pu}} \gg P_{\text{U}}$ and are, expectedly, in variance with the extraction trend.

These studies indicate that in a mixture containing actinide ions such as Am^{3+} , Pu^{4+} and UO_2^{2+} , the former two can be transported leaving behind U to a large extent. On the other hand, if Pu can be oxidized to the +6 oxidation state, then it may be possible to separate Am from U and Pu. An attempt has been made in this direction and plutonium was oxidized to the +6 state using AgO and the mixture of Am^{3+} , PuO_2^{2+} and UO_2^{2+} was taken in the feed compartment and transport of the metal ions was monitored after 5 h. As shown in Fig. 8 selective transport of ^{241}Am (as indicated by the 5.48 MeV peak) was seen with some contamination from ^{239}Pu (5.16 MeV) and ^{233}U (4.778 MeV) to a much lower extent. These results are encouraging and one can use such membrane separators in series (two or three stage separation) to get a pure ^{241}Am from the actinide mixture.

3.3. Determination of diffusion coefficients

Though the extraction and stripping reactions take 2 and 30 min, respectively, using 3 M and 0.01 M HNO_3 , the transport of Am^{3+} ion under comparable conditions was only 53% even after 5 h. One can split the overall transport process into three parts: i) the metal ion is extracted by the carrier ligand at the membrane-feed solution interface, ii) the metal – carrier ligand complex is then transported from the feed – membrane interface to the membrane – receiver interface through the membrane pores and iii) de-complexation (stripping) takes place at the membrane-receiver interface. This suggests that the transport of the metal ion-carrier

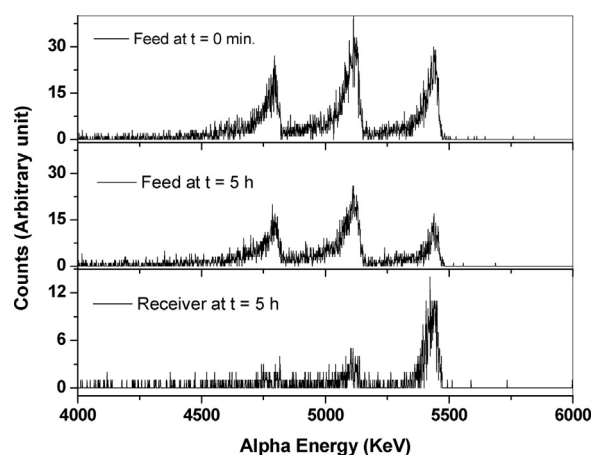


Fig. 8. Alpha spectra of mixture of ^{241}Am , ^{239}Pu (and ^{238}Pu) and ^{233}U in the feed at the beginning of the experiment (top) and those in the feed (middle) and receiver (bottom) after 5 h. Carrier solvent: 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol. Feed: 3 M HNO_3 ; Receiver: 0.01 M HNO_3 .

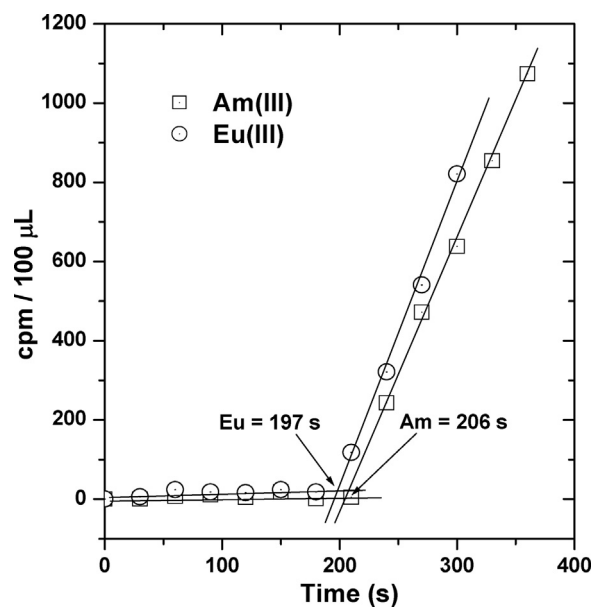


Fig. 9. Lag-time determination for the transport of Am(III)/Eu(III) by TREN-DGA as carrier extractant. [TREN-DGA]: 4×10^{-3} M; Feed: 3 M HNO_3 ; Receiver: 0.01 M HNO_3 .

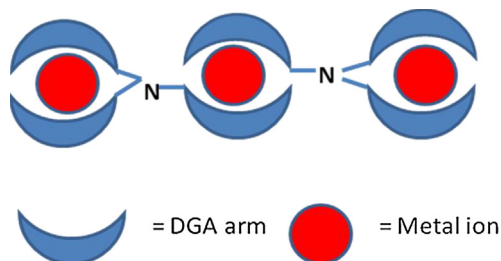
complex through the membrane is the slowest step and hence, the overall process is a diffusion-controlled process. Therefore, it is very important to determine the diffusion coefficient of the metal ion. The effective diffusion coefficient (D_{eff}) value was determined by the 'lag-time method' [31] in which the time required for the metal ion to first appear in the receiver phase is termed as the lag-time (t_{lag}) and is determined graphically. The D_{eff} was determined using the following equation:

$$D_{\text{eff}} = d_0^2 \varepsilon / 6t_{\text{lag}} \quad (6)$$

where d_0 is the membrane thickness (in cm) and ε is the membrane porosity. The lag-time plots for the transport of Am^{3+} and Eu^{3+} from the feed to the receiver phase are given in Fig. 9. The D_{eff} values are determined using Eq. (6) and are included in Table 4. The diffusion coefficient values appear to be about two orders of magnitude lower as compared to those reported with either T-DGA [30] or with TODGA [33]. Though the nature of the extracted species are similar in case of both TREN-DGA and T-DGA (at least in the lower ligand concentration range), the lower diffusion coefficient of the

Table 4
Diffusion coefficient data for the transport of $\text{Am}^{3+}/\text{Eu}^{3+}$ by 4×10^{-3} M TREN-DGA.

Metal ion	Lag-time (s)	D_{eff} (cm^2/s)
Am^{3+}	206	2.34×10^{-8}
Eu^{3+}	197	2.45×10^{-8}



Scheme 1. Schematic presentation of the 3:2 metal ligand complex.

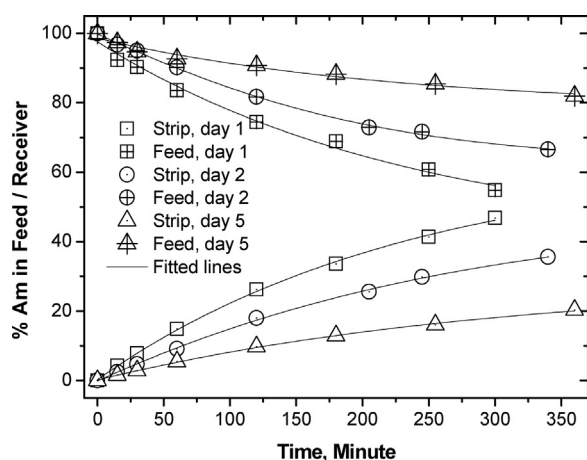


Fig. 10. Transport of $\text{Am}(\text{III})$ using 4×10^{-3} M TREN-DGA in 5% iso-decanol + 95% n-dodecane as the carrier solvent for five consecutive days; Feed: 3 M HNO_3 ; Receiver: 0.01 M HNO_3 .

TREN-DGA complex needs to be investigated in greater detail. In view of participation of two DGA arms from one TREN-DGA and a single DGA arm from another TREN-DGA ligand molecule, possibility of extracted species with two TREN-DGA and three metal ions (3:2 M:L species) is not ruled out (Scheme 1) which can slow down the diffusion rate.

3.4. Stability of the liquid membrane

One of the most important parameters of the supported liquid membrane is the stability of the membrane as this would decide whether it could be used in a continuous manner for a long duration of time or not. There are many factors which affect the membrane stability, e.g., the shear forces, osmotic pressure difference, aqueous solubility of the carrier, etc. [32]. The stability of the SLM containing 4×10^{-3} M TREN-DGA in 95% n-dodecane + 5% iso-decanol was monitored by measuring the percentage transport of Am^{3+} in the receiver phase at different time intervals over a period of several days. Each day, the feed and the receiver compartments were changed with fresh solutions while keeping the same pore-filled PTFE flat sheet. The % transport of Am^{3+} to the receiver phase decreased drastically after day 1 (Fig. 10). For example, transport of Am^{3+} to the receiver phase at 2 h was 26.2% in day 1, while it decreased sharply to 18.0 and 9.7 in days 2 and 5, respectively (Table 5). The permeability coefficient values were also determined for each run and are presented in Table 5. In our earlier study, where

Table 5
Stability studies of SLM by monitoring $\text{Am}(\text{III})$ transport on different days. [TREN-DGA]: 4×10^{-3} M; Feed: 3 M HNO_3 ; Receiver: 0.01 M HNO_3 .

Day	% $\text{Am}(\text{III})$ in feed (2 h)	% $\text{Am}(\text{III})$ in receiver (2 h)	$P_{\text{Am}(\text{III})} \times 10^3$ (cm/s)
1	74.4	26.2	11.9 ± 0.5
2	81.7	18.0	7.9 ± 0.5
5	90.8	9.7	3.2 ± 0.3

the FSSLM contained TODGA as the carrier extractant, the membrane stability was excellent over a period of 20 days [33]. However, analogous studies carried out with multiple DGA-functionalized ligands such as a calix[4]arene scaffold tethered with four DGA moieties [34] and the T-DGA ligand [30] showed poor membrane stability from the beginning itself. However, the loss of stability in the present case was much more pronounced. Though the poor SLM stability in these cases could be attributed to the loss of carrier, the relatively poor stability of the SLM containing TREN-DGA as the extractant may be attributed to the facile leaching out of the ligand from the pores of the PTFE flat sheet membrane due to the formation of the protonated species, TREN-DGA- H^+ . Zha et al. investigated the loss of SLM stability by impedance measurements [35]. Impedance measurements were carried out and the Nyquist plots [36] obtained using 3 M HNO_3 as the aqueous phase (Supporting Information) suggested decrease in the resistance over a period of time which may indicate continuous protonation of the carrier with a subsequent leaching out of the carrier which results in a decrease in the transport rate and hence loss of membrane stability. Though the membrane stability was relatively less, the membrane could be regenerated easily by replenishing the leached out carrier solvent. Though the continuity of the process may be hampered due to relatively lower membrane stability, there was no significant cost concern due to the very low amount of carrier solvent loss.

4. Conclusions

Solvent extraction of actinide ions such as Am^{3+} , Pu^{4+} and UO_2^{2+} and the trivalent Eu^{3+} lanthanide ion was investigated using solutions of TREN-DGA in 95% n-dodecane + 5% iso-decanol, the trend of extraction being: $\text{Pu}^{4+} > \text{Eu}^{3+} > \text{Am}^{3+} \gg \text{UO}_2^{2+}$. The extracted species for the trivalent ions were found to be predominantly ML with small amounts of ML_2 species being extracted as well. The transport of the metal ions across TREN-DGA-containing flat sheet supported liquid membranes was also investigated and conformed to the trend: $\text{Eu}^{3+} > \text{Am}^{3+} \geq \text{Pu}^{4+} \gg \text{UO}_2^{2+}$. Separation of ^{241}Am can be achieved using this carrier extractant when Pu can be oxidized to the +6 oxidation state. The diffusion coefficient values were calculated from lag-time studies involving Am^{3+} and Eu^{3+} ions and were found to be two orders of magnitude slower as compared to those reported with T-DGA. The stability of the SLM was found to be rather poor and reusability options are limited.

Acknowledgements

The authors thank Dr. P.K. Pujari, Head, Radiochemistry Division, BARC, for his keen interest in this work. They are also thankful to Dr. A.K. Satpati, Analytical Chemistry Division, BARC, for his help in carrying out the impedance measurements.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2017.12.068>

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