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Unique Eu(III) transport selectivity seen using a supported liquid membrane containing a diglycolamide dendrimer ligand

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ABSTRACT

Dendrimers are exotic multi-functional ligands and are expected to give rise to better extraction/transport results as compared to the mono-functional ligands. Diglycolamide (DGA) based dendrimers are scarcely reported and literature on their transport studies are very limited. Transport of Am(III) and Eu(III) across a PTFE (polytetrafluoroethylene) based flat sheet supported liquid membrane containing a generation 1 dendrimer of tris(2-aminoethyl)amine (TREN), containing six diglycolamide (DGA) pendent arms (termed as TREN-G1-DenDGA) was investigated from nitric acid feed solutions. The transport studies involved 5.75×10^{-4} M ligand solution in 5% isodecanol modified *n*-dodecane. Am(III) transport was slower than that of Eu(III) under identical conditions. The transport of both Am(III) and Eu(III) increased with increasing nitric acid concentration from 1 to 6 M HNO_3 suggesting a solvation extraction mechanism with nitrate ions playing a significant role. A unique preferential Eu(III) transport over Am(III) was seen at 3 M HNO_3 with a transport selectivity factor (ratio of permeability coefficient values) of 6.2 which decreased upon changing the acid concentration. Carrier ligand concentration also played a significant role in transport selectivity. Membrane parameters such as permeability coefficient and effective diffusion coefficient (D_{eff}) values were determined experimentally. The liquid membrane stability studies were also carried out.

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Americium; europium; transport; dendrimer; diglycolamide

Introduction

Separation of trivalent actinides/lanthanides from acidic feeds is a challenging area of research.[1] Diglycolamide (DGA) extractants such as TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide, Fig. 1a) are known to be one of the most effective extractants for this purpose.[2–5] The extraction of the *f*-cations by TODGA has been reported to be quite interesting since the trend of extraction is $Am^{3+} > Pu^{4+} > UO_2^{2+}$,[6] which is in sharp contrast to the generally observed trend with most of the other extractant: $Pu^{4+} > UO_2^{2+} > Am^{3+}$ the latter being in line with the ionic potential of the metal ions.[7] Though this was difficult to rationalize, a subsequent study on aggregation by Jensen et al.,[8] suggested that a reverse micellar structure formed by 3–4 TODGA molecules was responsible for this unusual extraction trend. However, this was reported to be favorable in a nonpolar diluent such as *n*-dodecane and may not be feasible in polar diluents where the nature of the extracted species is reported to be entirely different.[2] Keeping this in mind, it was thought of interest to synthesize multiple DGA-containing ligands, so that the diluent polarity effect on metal ion extraction can be discounted. We have reported metal ion extraction with several multiple DGA ligands where the DGA moieties are appended to scaffolds such as calix[4]arene,[9] pillar[5]arene,[10] TREN (tris(2-aminoethyl)amine)[11] or even a central benzene ring leading to a tripodal ligand.[12]

Separation of trivalent actinides from the trivalent lanthanides is one of the most challenging issues due to their similar chemical behavior.[13–15] Due to the large neutron absorption cross-sections of the lanthanides, their separation from the trivalent actinides is mandatory prior to the transmutation of the latter in high flux reactors or accelerator-driven subcritical system.[16] The DGA-based extractants have shown a preference for the trivalent lanthanides as compared to the trivalent actinides thereby helping in the lanthanide – actinide extraction scheme. In case of the multiple DGA ligands, the extraction of both the trivalent lanthanide and actinide ions was highly favored as compared to the simple DGA ligand such as TODGA. This was attributed to cooperative complexation due to the pre-organized structure of these multiple DGA ligands which was the

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possible reason for such efficient extraction ability. While the aggregate formation has a special geometry of a cavity type structure where 3–4 TODGA molecules participate, a recent structural study by the Moyer group[17] suggested complexation of three TODGA molecules in the isolated complexes from chloride or nitrate medium. The flexibility of complexation by the three TODGA molecules (with decreased entropy during complexation) was not there with the multiple DGA-containing ligands mentioned above which formed relatively rigid structures. Therefore, we felt that the superior extraction ability could be due to a rigid structure of the ligand with a pre-organized structure, thus making us believe 'the more the merrier' may be the mantra while designing the ligands. Based on this, DGA-functionalized dendrimers were synthesized, which turned out to be amply efficient like the other multiple DGA-containing ligands.[18] While designing such dendrimers, we found that a TREN-based dendrimer showed interesting extraction as well as complexation properties[19] as compared to the PPI (poly(propylene imine)) based dendrimers, due to the possibility of a 'crab like' stereochemistry of the complex in the case of the former. The structure of the TREN-based generation 1 dendrimer (abbreviated as TREN-G1-DenDGA) is given in Fig. 1b.

Though the solvent extraction studies were quite promising, the multiple DGA-based ligands are quite exotic in nature and hence, the cost of their synthesis can be quite high. On the other hand, if the ligand inventory can be drastically brought down, the process can be cost effective and may have a better applicability. In this context, supported liquid membrane (SLM) based separation methods[20–22] are quite effective, which also have the advantage of simultaneous extraction and stripping possibilities. Moreover, the SLM-based separation methods can alleviate common problems encountered in solvent extraction-based processes such as third phase formation, phase disengagement limitations, phase entrainment, etc.

The present study involves supported liquid membrane transport studies of Am(III) and Eu(III) from nitric acid feed solutions across polytetrafluoroethylene (PTFE) flat sheet membranes containing the TREN-G1-DenDGA in a mixed diluent system of 5% isodecanol and 95% *n*-dodecane. The use of 5% isodecanol as the modifier was needed since the solubility of the ligand is not so good in *n*-dodecane alone. The results are compared with those reported before with TREN-DGA (a tripodal ligand, Fig. 1c) [23] and TODGA.

Experimental

Materials

TREN-G1-DenDGA was synthesized as per a reported method[19] and the purity was ascertained by NMR and HR-MS. *n*-Dodecane (99%) and isodecanol (>99%) were procured from Lancaster and SD Fine Chem, respectively, and were used without further purification. Alpha-hydroxyisobutyric acid (α-HIBA; 99%) was procured from Sigma-Aldrich and was used as obtained. Suprapur nitric acid (Merck) was used for the preparation of all HNO_3 solutions using MilliQ water (Millipore), which were standardized using a standard NaOH (BDH) solution and phenolphthalein (Fluka) indicator. All the other chemicals used in this study were of AR grade.

^{241}Am radiotracer was taken from the laboratory stock solution after fresh purification to get rid of its daughter product, ^{237}Np as mentioned before.[24] ^{152,154}Eu was obtained from the Board of Radiation and Isotope Technology (BRIT) and was used after ascertaining its radionuclidic purity.

PTFE (polytetrafluoroethylene) membrane coupons obtained from Sartorius, Germany, had the following specifications: coupon diameter: 47 mm; coupon thickness: 80 μm; membrane pore size: 0.45 μm; membrane porosity: 64%.

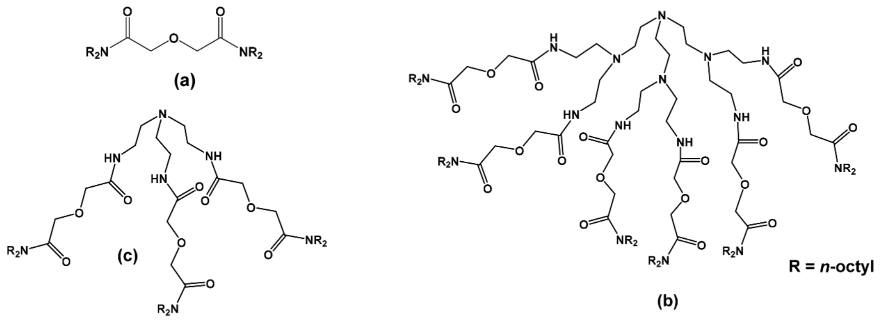
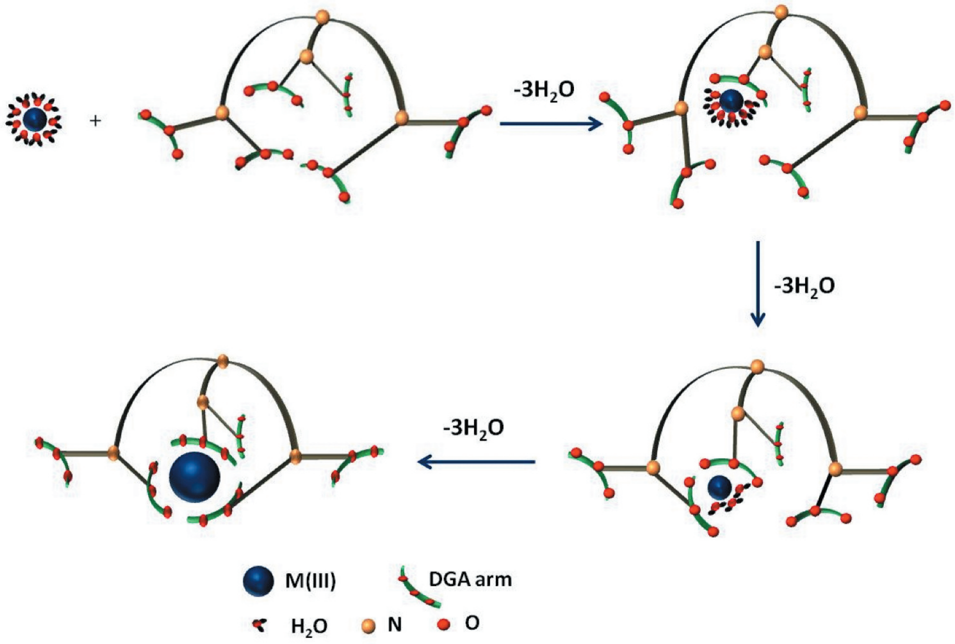


Figure 1. Structural formulae of (a) TODGA, (b) TREN-G1-DenDGA, (c) TREN-DGA.



Scheme 1. Probable extraction mechanism at the feed – membrane interface.

Methods

Distribution studies

The liquid-liquid extraction studies were carried out by taking equal volumes (usually 1 mL) of the organic phase, containing the ligand solution in 5% isodecanol + 95% *n*-dodecane, and the aqueous phase, which usually consisted of tracer spiked nitric acid solutions, in leak-tight Pyrex tubes in a thermostated water bath at 25 ± 0.1°C for 1 h. The tubes were subsequently centrifuged at 3000 rpm for 3 minutes and 0.1 mL aliquots were removed from both the phases for subsequent radiometric assay by gamma ray counting using a NaI (Tl) scintillation detector (Para Electronics) coupled to a multi-channel analyzer (ECIL, India). The distribution ratio (D) is defined as follows:

$$D = \frac{Counts\,per\,minute\,per\,ml\,of\,the\,organic\,phase}{Counts\,per\,minute\,per\,ml\,of\,the\,aqueous\,phase} \quad (1)$$

The D values were obtained in triplicate and the reported data are within <2% error including those due to counting statistics.

Transport studies

The transport studies were carried out as reported before[25] where the transport cell comprised two compartments separated by the PTFE flat sheet membrane. The volume of each compartment was 20 mL, while the exposed surface area of the PTFE membrane coupon was 4.90 cm^2. The membrane was kept dipped in the ligand solution for 10–12 h in a Petri dish. Prior to use, the soaked membrane was taken out, wiped gently with a tissue paper, and was clamped in between the two-compartment transport cell and was fixed using a piece of Para film. The solutions in the two compartments in the transport cell (termed as the feed and receiver compartments) were continuously stirred (stirring speed: 200 rpm) using two small magnetic bars (length: 1 cm; dia: 3 mm). The feed phase contained the required nitric acid solution spiked with the requisite radiotracer, while the receiver phase contained the stripping solution. Samples were taken out from each compartment through the sampling ports at the top side of each compartment at regular time intervals for radiometric assay. The transport of the radiotracer was quantified by the following quantities, *viz.* percent transport (%T) and the permeability coefficient (P).[26]

$$\%T = 100 \times C_{r,t}/C_0 \quad (2)$$

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

where C_0 is the metal ion concentration at the start of the experiment (t = 0) in the feed phase, $C_{r,t}$ and $C_{f,t}$ are the metal ion concentrations at time t in the strip and feed phases, respectively. P, A and V are the permeability coefficient (cm s^{-1}), effective surface area, and the volume of the feed, respectively. The effective area of the membrane was found out to be 3.14 cm^2. The permeability coefficient (P) values were obtained from the slope of the straight line fitting of the ln ($C_{f,t}/C_o$) vs. time (t) plots. The transport studies were carried out at ambient temperature (ca. 24°C). The errors in the transport data presented in this paper are less than 3%.

Results and discussion

Solvent extraction studies

The metal ion transport through a supported liquid membrane (SLM) involves the extraction of the metal ion from the aqueous feed compartment into the liquid membrane phase followed by diffusion through the SLM, and finally, the stripping of the loaded metal ion from the liquid membrane phase into the stripping solution present in the receiver compartment. For a reasonably good metal ion transport rate, the two extraction steps must be reasonably fast to have mass transfer across the membrane. Therefore, it is very important to determine the kinetics of extraction as well as the kinetics of stripping of the metal ions. The extraction kinetics of the metal ions (Am(III), Eu(III)) was followed at 3 M HNO_3 using 0.575×10^{-3} M TREN-G1-DenDGA in 5% isodecanol-95% *n*-dodecane solution, whereas the stripping kinetics was followed by the back extraction studies with the loaded metal ions in the respective organic phases using 1 M α-HIBA as the stripping solution.

As can be seen from Fig. 2, the equilibrium data was obtained after 30 minutes of extraction, whereas stripping kinetics reached equilibrium within 10 minutes of shaking at room temperature. These studies revealed that the extraction kinetics was relatively slower than the stripping kinetics. The extraction involves i) the formation of a chelating complex where the bulky ligand molecules must rearrange itself around the metal ions according to a geometry required for the metal-ligand coordination as well as ii) breaking of the hydration sphere around the metal ion before coordinating with the metal ions, which costs time (Scheme 1). On the other hand, the stripping involves the interaction of the metal ion with comparatively smaller size strippant molecules (Scheme 2). In our earlier investigation with the comparatively less bulky ligand TREN-DGA, it required only two minutes to reach the equilibrium D_M-value,[23] whereas stripping required around ten minutes for that. This suggests that as the bulkiness in the structure of a ligand increases, interaction with a metal ion becomes more difficult resulting in a slower kinetics of extraction.[27

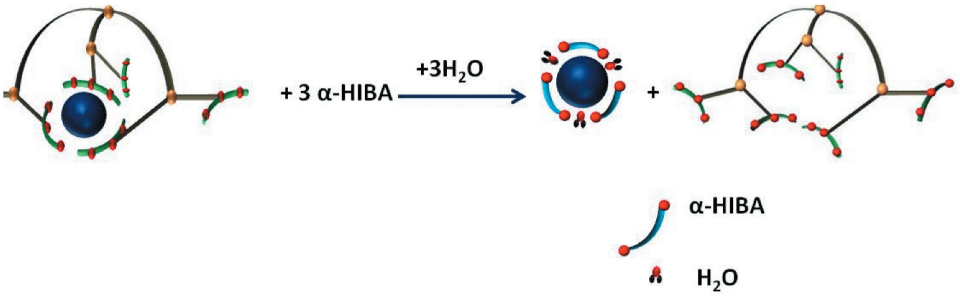
Transport studies

Effect of nitric acid concentration

The acidity of HLW (high-level radioactive waste) is in the range of 3–4 M nitric acid. Nitrate ions play an important role in the metal ion extraction by forming a metal-ligand-nitrate complex according to the following equation, as reported before[19]:

$$M3 + (aq) + L(aq) + 3NO33 - (org)M(NO3)3.L(org) \tag{4}$$

where M is either Am or Eu and L is the TREN-G1-DenDGA ligand. The species with the subscripts '(aq)' and '(org)' represent those in the aqueous and the organic phases, respectively. This metal-ligand-nitrate 'ternary' complex was extracted in the membrane phase at the feed-membrane interface and subsequently transported to the other side of the membrane-strip solution interface (in the receiver compartment) according to the Fick's law of diffusion.[28] Therefore, it is very important to understand the role of nitric acid as well as that of the nitrate ion on the transport of Am(III) and Eu(III) with the time. The transport of these metal ions through the membrane was determined at varying concentrations of nitric acid, viz. 1 to 6 M, with 5.75×10^{-4} M TREN-G1-DenDGA as the carrier ligand and with 1 M α-HIBA as the strippant, present in the receiver compartment. Previously, we



Scheme 2. Probable stripping mechanism at the membrane – receiver interface.

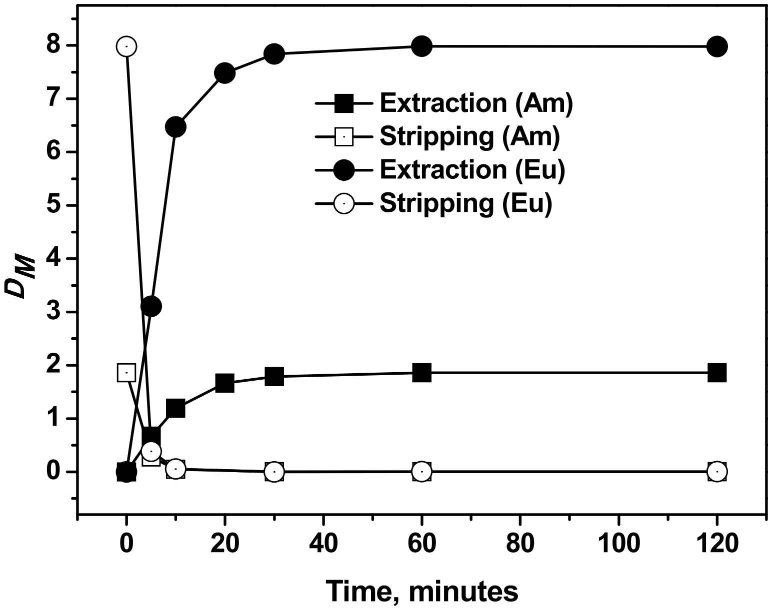


Figure 2. Extraction and stripping kinetics of Am(III) and Eu(III) ions; Extraction: Ligand concentration: 5.75 × 10^{-4} M in 5% isodecanol-95% *n*-dodecane; Aqueous phase: 3 M HNO_3 containing the metal ions; Stripping: Aqueous phase: 1 M α-HIBA.

reported[19] the effect of the nitric acid concentration on the extraction of Am(III) and Eu(III) using TREN-G1-DenDGA as the extractant, which revealed a solvation mechanism for the extraction showing a monotonous increase in the *D*-value with the nitric acid concentration. Therefore, it was expected that the transport of the metal ions would also follow the same trend with the nitric acid concentration.

As can be seen from Fig. 3, the transport of Am(III) and Eu(III) increased with increasing nitric acid concentration and the transport of Eu(III) was higher than that of Am(III) at a given nitric acid concentration, which is in line with the previously reported results.[19] Interestingly, the transport of both Eu(III) and Am(III) at 1 M HNO_3 was very small, which can be due to their smaller *D*-values at lower ligand concentration. The study was therefore conducted at 7.7 times higher ligand concentration (4.42 × 10^{-3} M) though the consequent increase in the metal ion transport at 1 M HNO_3 was not significant (Fig. 4, Table 1). For example, the transport of Eu(III) at 1 M HNO_3 after 300 minutes increased from 1.9% to 7.1%, whereas that of Am(III) after 300 minutes increased from 1.5% to 5.0% when the carrier ligand concentration increased by 7.7 times from 5.75 × 10^{-4} M to 4.42 × 10^{-3} M. On the other hand, when the nitric acid concentration was increased from 1 M to 3 M at a given carrier ligand concentration (5.75 × 10^{-4} M), the percentage transport into the receiver phase expanded from 1.9% to 35.8% for Eu(III) after 5 h of transport. However, under similar conditions, the

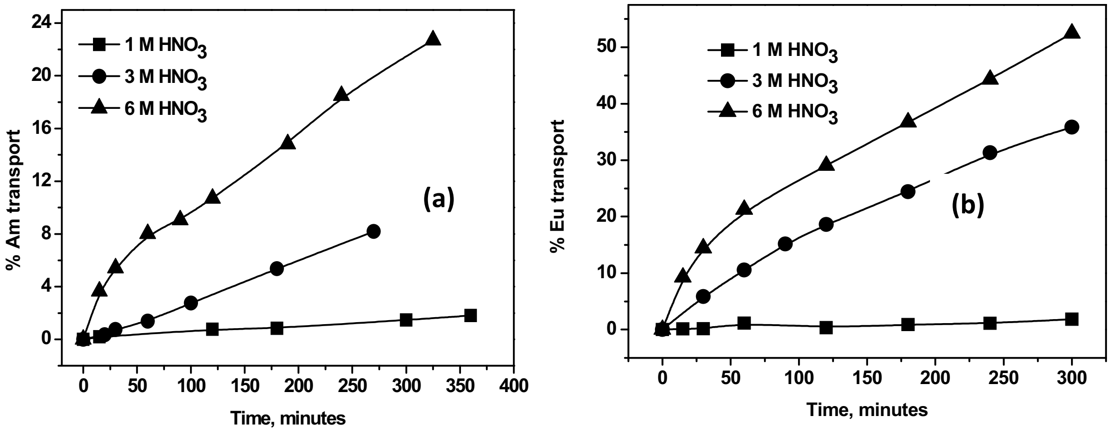


Figure 3. Transport of (a) Am(III) and (b) Eu(III) at different feed nitric acid concentrations; Receiver phase: 1 M α-HIBA; Membrane support: PTFE; [Ligand]: 5.75 × 10^{-4} M TREN-G1-DenDGA in 5% isodecanol-95% *n*-dodecane.

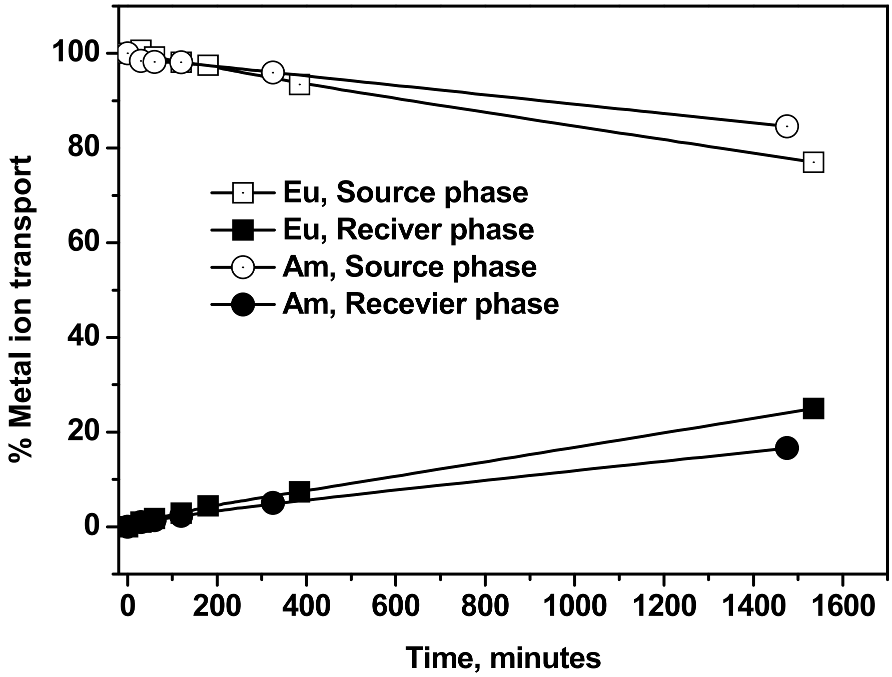


Figure 4. Transport of Am(III) and Eu(III) at 1 M HNO_3 in the source phase; Receiver phase: 1 M AHIBA; Membrane support: PTFE; [Ligand]: 5.75 × 10^{-4} M TREN-G1-DenDGA in 5% isodecanol-95% *n*-dodecane.

Table 1. Transport parameters with 4.42 × 10^{-3} M TREN-G1-DenDGA in 5% isodecanol-95% *n*-dodecane; [HNO_3] = 1 M.

Metal ion	% Feed	% Strip	$P \times 10^3$ (cm/s)
Eu (III)	95.2	6.5	0.019 ± 0.001
Am(III)	95.1	4.9	0.011 ± 0.002

Table 2. Transport of Eu(III) and Am(III) at different feed nitric acid concentrations after 5 h; Receiver phase: 1 M α-HIBA, [Ligand]: 5.75 × 10^{-4} M TREN-G1-DenDGA in 5% isodecanol-95% *n*-dodecane.

Metal ions	[HNO_3], M	% Remained in Feed	% Transport	$P \times 10^4$ (cm/s)
Eu (III)	1	96.3 (91.1)[a]	1.9 (8.2)[a]	0.10 ± 0.04
	3	63.3 (10.6)[a]	35.8 (87.9)[a]	1.59 ± 0.02
	6	49.2 (0.2)[a]	52.5 (99.3)[a]	2.32 ± 0.01
Am(III)	1	97.2 (93.4)[a]	1.5 (4.7)[a]	0.08 ± 0.03
	3	93.7 (73.5)[a]	8.2 (24.2)[a]	0.26 ± 0.03[d]
	6	79.8 (6.1)[a]	21.8[b,c] (94.0)[a]	0.68 ± 0.05

[a] Data between parentheses refer to data after 24 h. [b] Extractant: 2.90 × 10^{-3} M TODGA in 10% isodecanol-90% *n*-dodecane; Aqueous phase: 3 M HNO_3, % Transport: 12.5% after 3 h; $P = 0.86 \pm 0.09 \times 10^{-4}$ cm/s.[25] [c] ~ 15% after 3 h [This work]. [d] $P = 0.95 \pm 0.03 \times 10^{-4}$ cm/s, extractant: 1 × 10^{-3}M TREN-DGA in 5% isodecanol-95% *n*-dodecane, Aqueous phase: 3 M HNO_3.[19]

transport of Am(III) only increased from 1.5% to 8.2%. Therefore, the percentage transport of Eu(III) to the strippant was more than four times of that of Am(III) at 3 M HNO_3, which was only 1.3 times of that of Am (III) at 1 M HNO_3. This can be considered as an 'acid assisted preferential transport' of Eu(III) vis-à-vis that of Am(III). This indicates that nitric acid had a significant role in the transport of metal ions; the effect was more significant with respect to Eu(III) than to Am(III). This is one unique observation seen in this study and may be the carrier ligand is responsible for this behavior. Upon further increase of the feed acidity to 6 M HNO_3, the percentage transport of Eu(III) and Am(III) became 52.5 and 21.8, respectively, after 5 h, the transport of Eu(III) being 2.4 times that of Am(III). The experiment was continued up to 24 h in view of the slower extraction kinetics (*vide supra*). Though the transport rates are somewhat inferior to what has been reported before with the TREN-DGA ligand as the carrier before,[23] the results nonetheless are significant as these are the first reported transport data with the TREN-based DGA dendrimer.

Table 2 shows that at moderate nitric acid concentration (3 M HNO_3), the percentage transport of Eu(III) increased from 35.8% at 5 h to 87.9% at 24 h, whereas under similar conditions, the transport of Am(III) went from 8.2% at 5 h to 24.2% at 24 h. The transport of Am(III) became >90% after 24 h when 6 M HNO_3 was used as the feed. The mass balance loss in the sum of the feed and receiver phase counts (Table 2) was attributed to the activity trapped in the PTFE flat sheet membrane (verified by counting of the membrane). These data suggest that the transport of the metal ion was slow and around 24 h were required for more than 85% transport of Eu(III), whereas for comparable transport of Am(III), higher nitric acid concentration (6 M) in the feed phase was needed. These findings show that the membrane has a tendency of preferential transport of Eu(III) over Am(III) at moderate nitric acid concentration (3 M), however, the selectivity was lost when the nitric acid concentration was either high (6 M) or low (1 M) in the feed compartment. The lower *D*-values of both Eu(III) and Am(III) at 1 M HNO_3 led to the lower extraction of metal ions at the feed-membrane interface and was responsible for the loss of the preferential transport of Eu(III) over Am(III). On the other hand, the higher *D*-values of both Eu(III) and Am (III) at 6 M led to the higher extraction of the metal ions at the feed-membrane interface thereby decreasing the preferential transport of Eu(III) over Am(III). This indicates that the optimization of the nitric acid concentration is required to obtain the maximum separation of Eu(III) over Am(III) in the transport at a given carrier concentration in the liquid membrane phase.

A similar interpretation can be done considering the respective *P* (permeability coefficient) values of the metal ions for the transport at various feed nitric acid concentrations (Table 2). The P values for transport of Eu(III) were (0.10 ± 0.04) × 10^{-4} cm s^{-1}, (1.59 ± 0.02) × 10^{-4} cm s^{-1} and (2.32 ± 0.01) × 10^{-4} cm s^{-1}, while that for Am(III) were (0.08 ± 0.03) × 10^{-4} cm s^{-1}, (0.26 ± 0.03) × 10^{-4} cm s^{-1} and (0.68 ± 0.05) × 10^{-4} cm s^{-1} at 1, 3 and 6 M HNO_3, respectively. The ratio of the *P*-values of Eu(III) over Am(III) (termed as the transport selectivity factor) was maximum at 3 M HNO_3 and with a value of 6.2 is quite unique. The transport selectivity factor for analogous SLM transport system using TREN-DGA as the carrier extractant was ca. 2.[23]

Table 3. Transport of Eu(III) and Am(III) at different concentrations of TREN-G1-DenDGA in the membrane at varying ligand concentrations in 5% isodecanol-95% *n*-dodecane. Feed: 3 M HNO_3, Receiver: 1 M α-HIBA; Transport time: 5 h; Membrane: PTFE.

Metal ions	[L] × 10^{-3}, M	% Feed	% Transport	*P* x 10^3 (cm/s)
Eu(III)	0.575	63.3	35.8	0.159 ± 0.002
	2.21	45.0	55.0	0.287 ± 0.007
	4.42	21.7	76.7[a]	0.524 ± 0.01
Am(III)	0.575	93.7	8.2	0.026 ± 0.003
	2.21	77.4	25.0	0.096 ± 0.003
	4.42	56.7	43.0[a]	0.191 ± 0.007

[a] Extractant: 4.0 × 10^{-3} M TREN-DGA in 5% isodecanol-95% *n*-dodecane; Feed: 3 M HNO_3, % Transport Eu(III): 89.0% and % Transport Am(III): 52.9 after 3 h; Strippant: H_2O.[19]

Calculation of the ratio of the *P*-values of Eu(III) at 3 M HNO_3 to that at 1 M HNO_3, gave a value of around 16, whereas that of Am(III) was around 3. Similarly, the ratio of the *P*-values of Eu(III) at 6 M HNO_3 to that at 3 M HNO_3 was around 1.4, while this ratio for Am(III) was around 2.6. This demonstrates that changing the feed acidity from 1 to 3 M HNO_3, the transport of Eu (III) is more facilitated compared to that of Am(III) with a most favorable transport selectivity factor at 3 M HNO_3 leading to maximum mutual separation. However, a corresponding change from 3 to 6 M HNO_3 affected the transport of Am(III) more than that of Eu(III) leading to a decrease in the transport selectivity factor values and the mutual separations.

Effect of the carrier ligand concentration on the metal ion transport

As described above, the effect of the feed nitric acid on the transport of Am(III) and Eu(III) and their mutual separation was maximum at 3 M HNO_3 when the ligand concentration was 5.75 × 10^{-4} M in 5% isodecanol-95%

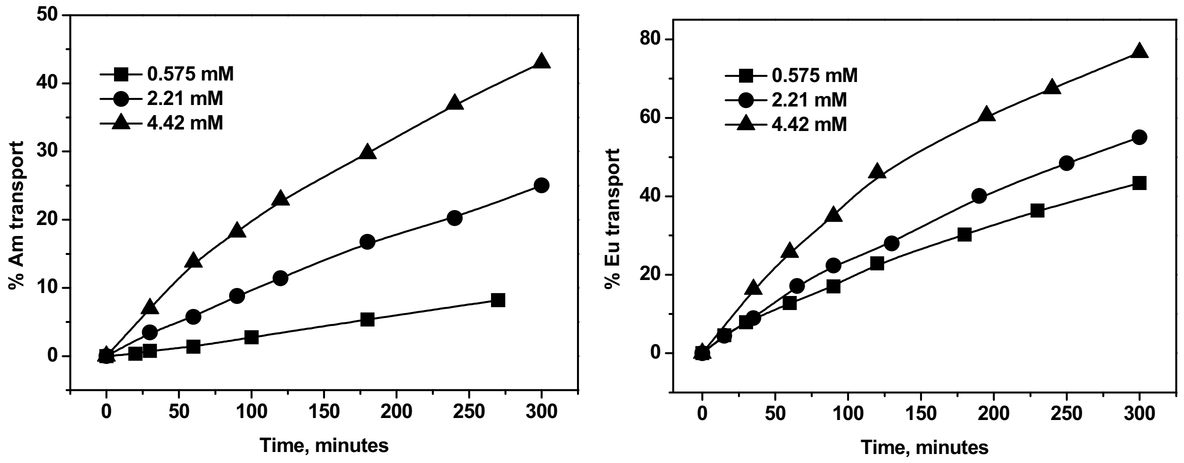


Figure 5. Transport of (a) Am(III) and (b) Eu(III) at different ligand concentrations in the membrane; Source phase: 3 M HNO_3; Receiver phase: 1 M α-HIBA; Membrane support: PTFE.

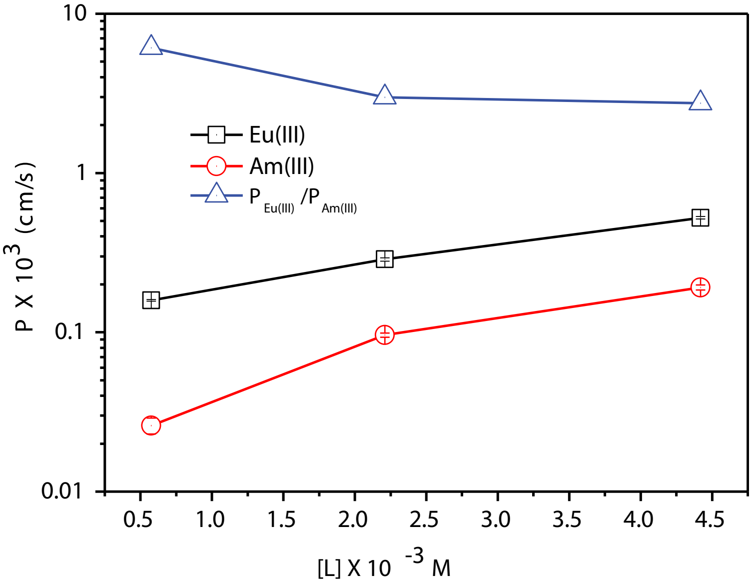
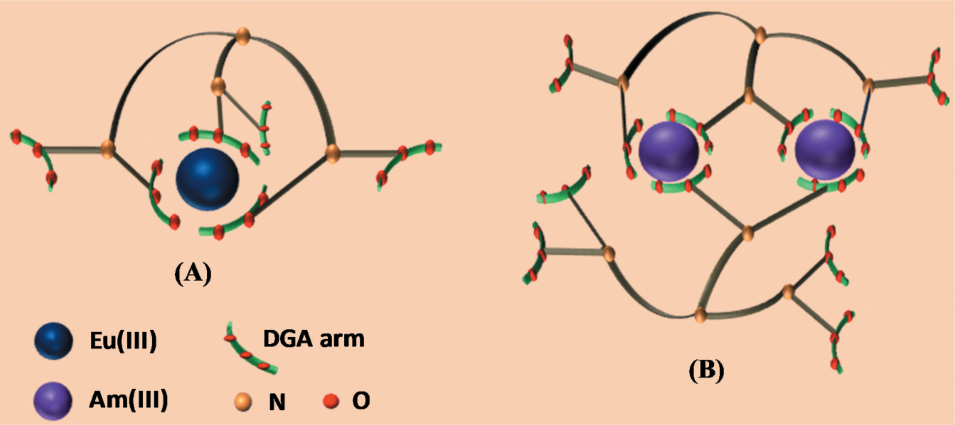


Figure 6. Transport of Am(III) and Eu(III) at different ligand concentrations in the membrane; Feed: 3 M HNO_3, Receiver phase: 1 M α-HIBA; Membrane support: PTFE; [Ligand]: varying amount of TREN-G1-DenDGA in 5% isodecanol-95% *n*-dodecane.

n-dodecane. It was, therefore, important to understand the effect of ligand concentration variation on the transport of Am(III) and Eu(III) since it is directly involved in the formation of the metal-ligand complex (Equation 1). We have earlier reported that one molecule of TREN-G1-DenDGA was involved in the formation of the metal-ligand complex with Am(III) and Eu (III) in nitric acid medium.[19] The effect of ligand concentration variation on the transport of Am(III) and Eu (III) was studied at 3 M HNO_3 by varying the carrier concentration in the membrane from 5.75 × 10^{-4} M to 4.42 × 10^{-3} M in 5% isodecanol-95% *n*-dodecane (Table 3 and Fig. 5).

The transport of both Am(III) and Eu(III) increased at higher ligand concentrations in the membrane, which is obvious due to the increased extraction at the feed-membrane interface. For example, the transport of Eu (III) increased from 35.8% to 76.7%, and that of Am(III) from 8.2% to 43%, when the ligand concentration was increased from 5.75 × 10^{-4} M to 4.42 × 10^{-3} M, respectively (Table 3). On the other hand, for both the metal ions there was also a rise in the *P*-values, but not to the same extent, at higher ligand concentrations, which can be correlated to the increase of the respective *D*-values (Fig. 6). However, a decrease in the transport selectivity factor was noticed when the ligand concentration was increased from 5.75 × 10^{-4} M to 2.21 × 10^{-3} M followed by a plateau up to 4.42 × 10^{-3} M. This suggests that a mutual separation of Eu(III) over Am(III) is possible at the lower ligand concentration. Further lowering of the ligand concentration to obtain an even higher selectivity was not attempted in view of the decreased mass transfer coefficient at low ligand concentrations. This data showed that, despite a better mass transfer at higher ligand concentration in the membrane, the selectivity in the mutual separation of the metal ions decreased. Thus, optimization of the ligand concentration was also equally important as like optimization of the feed nitric acid concentration in the mutual separation of Eu(III) and Am(III) using TREN-G1-DenDGA as the carrier ligand from nitric acid feed (*vide supra*).

Comparison of the transport behavior of TREN-G1-DenDGA after 5 h and that of TREN-DGA after 3 h, showed 43.0% and 52.9% transport of Am(III), respectively, to the strip solution (Table 3). From extraction studies with 4 × 10^{-3} M TREN-DGA in 5% isodecanol-95% *n*-dodecane, a $D_{\mathrm{Am(III)}}$ of 5.17 was obtained at 3 M HNO_3,[23] while that of 5.75 × 10^{-4} M TREN-G1-DenDGA was 1.86 (*vide infra*). Extrapolation to a concentration of 4 × 10^{-3} M TREN-G1-DenDGA (M: L = 1:1) results in a $D_{\mathrm{Am(III)}}$ of 12.9. This indicates that in view of the increased bulkiness of the ligand, the transport of the metal ion decreases due to slower diffusion of the complex. This was also proven by measuring the diffusion coefficient of the metal ion complexes (*vide supra*). The possible transported species can be given as those presented in Scheme 3 which is on the basis of the detailed solvent extraction and luminescence studies reported before.[19] The extracted species are reported to have a metal: ligand stoichiometry of 1:1 on the basis of solvent extraction based slope analysis studies while it contains no inner-sphere water molecules. Therefore,



Scheme 3. The possible structures of the extracted species with 1: 1 (metal: Ligand) stoichiometry.

Table 4. Diffusion coefficient data for Eu(III)/Am(III) determined using the lag-time; [L]: 5.75 × 10^{-4} M TREN-G1-DenDGA in 5% isodecanol-95% *n*-dodecane.

Ligand	Metal ion	t_{lag} (s)	D_{eff} (cm^2/s)
TREN-G1-DenDGA	Eu(III)	264	1.98 × 10^{-8}
	Am(III)	498	1.05 × 10^{-8}
TREN-DGA[a]	Eu(III)	197	2.45 × 10^{-8}
	Am(III)	206	2.34 × 10^{-8}

[a] Ligand concentration: 4 × 10^{-3} M TREN-DGA in 5% isodecanol-95% *n*-dodecane.

there can be an ‘inclusion’ complex where the metal ion is encapsulated in the ligand with a ‘crab-like’ grip (Structure (A) in Scheme 3). On the other hand, there can be a more ‘relaxed’ 2 metal – 2 ligand complex (Structure (B) in Scheme 3) where the ligating arms are under lesser strain.

Comparative evaluation of transport

A comparative study of transport of metal ion with the present carrier ligand with the other different analogous carrier ligand is important to evaluate the performance of the present carrier ligand. The details of transport of Am(III) with different carrier ligand are included in Table 4 for comparison.

As can be seen from Table 4, TREN-G1-Den DGA has slightly lower transport of Am(III) compared to TREN-DGA which could be attributed to the lower rate of diffusion of metal-ligand complex through the membrane with the comparatively bulkier TREN-G1-DenDGA ligand. On the other hand, the transport efficiency of Am(III) with C-pivoted tripodal DGA is much higher compared to that observed with the present membrane, possibly due to the very high D-value for metal ion extraction. However, when the present membrane performance for metal ion transport was compared with that of TODGA-based membrane,[29] it was found that the transport of Am(III) is superior to that of the present membrane. The *P*-value of Am(III) transport found with the TODGA-based membrane at the TODGA concentration of 2.90 × 10^{-3} M was (0.086 ± 0.009)× 10^{-3} cm s^{-1} (Table 2) whereas that with TREN-G1-DenDGA membrane was (0.096 ± 0.003)× 10^{-3} cm s^{-1} at 2.21 × 10^{-3} M concentration of the ligand (Table 3) which is 0.8 times lesser concentration than TODGA. Thus the present membrane shows better trans-membrane transport characteristic for metal ion when compared with TODGA-based membrane, however compared with the other multiple-DGA-based carrier (Table 4), the present membrane shows slower trans-membrane transport for metal ion and therefore longer time (ca. 24 h) is required for >90% transport of Am(III) under similar conditions. Although, the present membrane shows slower mass transfer rate when compared with TREN-DGA membrane, however the selectivity (P_{Eu}/P_{Am}) found with the present membrane was 2.74 which was better than that found with TREN-DGA membrane (ca. 2.40),[23] this certainly shows the better performance of the present membrane for trivalent actinide/lanthanide separation.

Diffusion coefficient measurements

The effective diffusion coefficient values of Am(III) and Eu(III) were determined by the lag-time method using the following formula.

$$D_{eff} = {d_0}^2 \varepsilon / 6 t_{lag} \qquad (5)$$

where d_o is the membrane thickness (cm), ε is the membrane porosity and t_{lag} is the lag-time. The membrane thickness was 0.007 cm; ε was reported to be 0.64.[25] The lag-time (t_{lag}[28]) is the time required for the metal ion complex to be detected first in the receiver compartment from the start of the experiment. The lag-time plot for Am(III) and Eu(III) is shown in Fig. 7

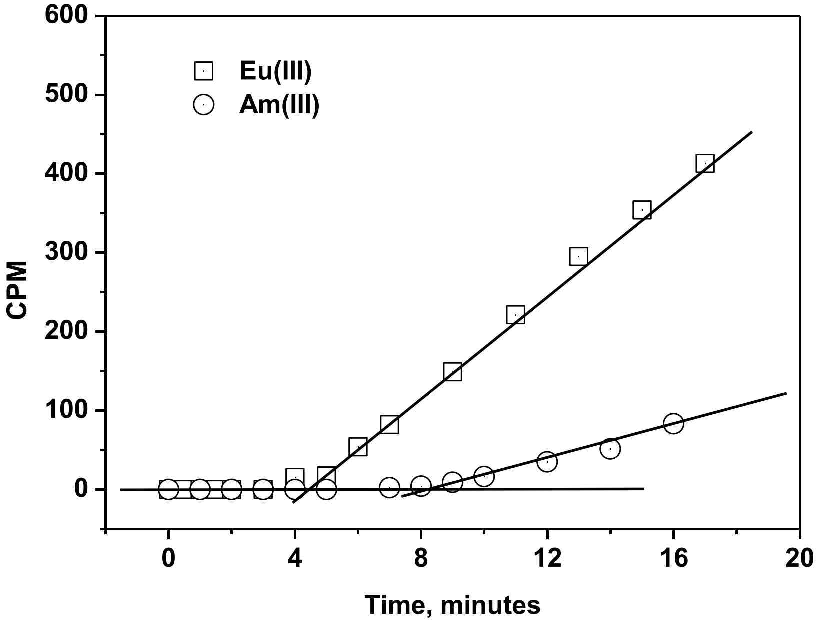


Figure 7. Lag-time determination in the transport of Eu(III); Feed: 3 M HNO_3, Receiver: 1 M α-HIBA; Membrane: PTFE soaked with 0.575×10^{-3} M in 5% isodecanol-95% *n*-dodecane.

Table 5. Transport of Eu(III) at different days of the experiment; Feed: 3 M HNO_3, Receiver: 1 M α-HIBA; Membrane: PTFE membrane soaked with 0.575×10^{-3} M in 5% isodecanol-95% *n*-dodecane; Feed and receiver solutions are changed on the start of each day experiment.

Day	% Feed	% Strip	$P_{Eu(III)} \times 10^3$ (cm/s)
1	63.3	35.8	0.159 ± 0.002
2	79.9	20.9	0.082 ± 0.001
6	95.9	3.7	0.014 ± 0.002

where the breakthrough transport lines are indicated with varying slopes. The slopes of the breakthrough transport lines were reported to be parallel in case of TREN-DGA ligand suggesting that the diffusing species to be similar for both Am(III) and Eu(III). On the other hand, the breakthrough line for Am(III) is having much lower slope in the present case as compared to that obtained for Eu(III) suggesting that the diffusing species

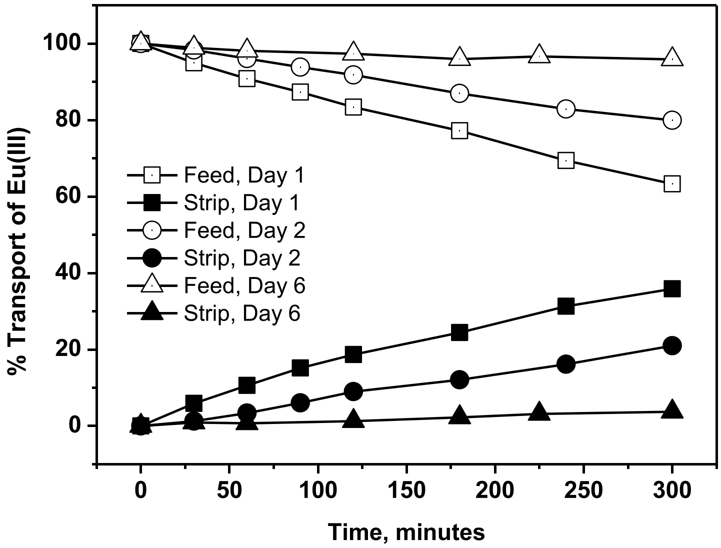


Figure 8. Transport of Eu(III) at different days of the experiment; Feed: 3 M HNO_3, Receiver: 1 M α-HIBA; Membrane: PTFE membrane soaked with 0.575×10^{-3} M in 5% isodecanol-95% *n*-dodecane; Feed and receiver solutions are changed on the start of each day experiment.

may be quite different. As shown in Scheme 3, it may be suggested that while structure (A) may be valid for Eu(III) transport, structure (B) may be the diffusing species for Am(III) leading to a slower transport rate as reported above.

The diffusion coefficient values determined by the lag-time method are given in Table 5. For comparison purposes, the diffusion coefficient values for the TREN-DGA ligand are also included in the table.

Stability of the membrane

The stability of a liquid membrane is an important issue while scaling up the membrane work for industrial purpose. Generally, SLMs are not stable and as the number of cycles of operations increases, the flux decreases. Therefore, it is of importance to investigate the stability of the present SLM containing 5.75×10^{-4} M TREN-G1-DenDGA as the carrier ligand in 5% isodecanol-95% *n*-dodecane. The stability of the membrane was tested by determining the transport of Eu(III) with time. Before the start of the experiment, on each day the feed and strip solutions were changed with the respective fresh solutions keeping the membrane intact. Figure 8 and Table 5 clearly show that the transport of Eu(III) decreased sharply already from day 1. For example, on days 1, 2 and 6 the percentage of transport after 5 h became 35.8, 20.9 and 3.7, respectively, which demonstrates the poor stability of the membrane. A similar poor stability of the membrane was also noticed with TREN-DGA.[23]

Though one would expect that the large carrier extractant molecule cannot be easily dislodged from the membrane pores, the observation made above is in the contrary. The exact reason for this has not been clearly understood by us. However, the membrane stability issue can be alleviated by replenishing the carrier solvent at regular intervals.

Conclusions

In conclusion, the transport of the trivalent actinide Am(III) and lanthanide Eu(III), studied using a TREN-based Gen 1 dendrimer showed a unique transport selectivity for the Eu(III) ion which was dependent on the acid as well as carrier concentrations. Though the transport rates were found to be lower than those reported before with an analogous multiple DGA-containing ligand (TREN-DGA), the transport selectivity reported in this paper can be exploited for a better separation of the metal ions than that reported before. Though the SLM stability was found to decrease with time it can be alleviated as the membrane can be replenished intermittently for continuous operation. Similar loss in stability has been seen before with other multiple DGA-containing ligands.[23,30] The diffusion coefficient values obtained from the lag-time method corroborated the slow diffusion of the complexes, which was enormously large due to the many DGA groups present in the dendrimer and the diffusing species with Am(III) and Eu(III) could be quite different. From application point of view, the mass transfer rates can be improved with thinner membranes and low viscosity diluents.

Finally, though the separation of Am(III) and Eu (III) has been a challenging topic of research and some DGA ligands have shown promising results by having better Eu(III) transport than that of Am(III), the objective of the present work was not just this and as shown from the results higher selectivity can be obtained by proper tuning of the experimental conditions. It is proposed to use complexing agents for selective binding to Am(III) in the feed phase to result in a better separation efficiency.[31]

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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