



# Diglycolamide-functionalized dendrimers: Studies on Americium(III) pertraction from radioactive waste



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## ABSTRACT

Diglycolamide (DGA)-functionalized poly(propylene imine) diaminobutane dendrimers were evaluated as the carrier in supported liquid membranes (SLMs) for selective recovery of trivalent actinides over uranium. The 0, 1st, and 2nd generation dendrimers with 2, 4, and 8 DGA moieties, termed as **L<sub>I</sub>**, **L<sub>II</sub>**, and **L<sub>III</sub>**, respectively, gave  $D_{Am}$  values of  $0.11 \pm 0.02$ ,  $41.9 \pm 3.21$  and  $109.4 \pm 6.22$  in solvent extraction studies using 1 mmol/L ligand solutions in a diluent mixture of 95% *n*-dodecane + 5% *iso*-decanol. SLM studies using polytetrafluoroethylene flat sheet membrane filters impregnated with 1 mmol solutions of **L<sub>II</sub>** and **L<sub>III</sub>** suggested quantitative mass transfer of  $Pu^{4+}$ ,  $Am^{3+}$ , and  $Eu^{3+}$  from 3 mol/L  $HNO_3$  in about 5 h. Various diffusional parameters affecting SLM transport have been calculated for better understanding the transport data. The stability of the SLM was also studied over a period of five days.

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## 1. Introduction

Global acceptability of the nuclear energy as an alternative source of energy can be increased enormously if public concerns regarding the hazards associated with the radioactive wastes can be mitigated in an efficient manner [1]. The radioactive waste remediation is proposed to be efficiently handled by a strategy called 'Partitioning & Transmutation', which dwells upon selective separation of the minor actinides (such as Am, Cm, and Np) from the high level waste (Table 1), followed by their transmutation in high flux reactors or accelerator driven sub-critical systems [2–8]. The minor actinide separation can be taken up conveniently using actinide selective extractants such as CMPO (carbamoyl methylene phosphine oxide), trialkyl phosphine oxides, DIDPA (di-*iso*-decyl phosphoric acid) or malonamides [9,10]. However, the most efficient separation of the minor actinides has been accomplished using diglycolamide (DGA) extractants [11]. Amongst the DGA extractants, TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) [12–14] and T2EHDGA (*N,N,N',N'*-tetra-2-ethylhexyl diglycolamide) [15,16] have been studied extensively for the separation of minor actinides, and have been tested in hot runs in several laboratories [17–19]. The major features of the

DGA-based extractants include a drastic change in the general extraction trend of the actinide ions from  $Pu^{4+} > UO_2^{2+} > Am^{3+}$  to  $Am^{3+} > Pu^{4+} > UO_2^{2+}$  favoring better extraction of minor actinides over uranium.

The extraction efficiency of DGA extractants was reported to increase manifold when multiple DGA-containing extractants such as tripodal DGA (T-DGA) [20–22], DGA-functionalized calix[4]arenes [23–25], and pillar[5]arenes [26] were used. Furthermore, the extraction of  $UO_2^{2+}$  decreased significantly with these extractants translating into a high selectivity of  $Am^{3+}$  in the presence of a large excess of  $UO_2^{2+}$  ions. In view of this, another class of multiply DGA-functionalized extractants, namely DGA-dendrimers (Fig. 1), was recently synthesized by us and evaluated for the complexation of trivalent actinides and lanthanides [27]. These DGA-dendrimers are a special class of ligands prepared by grafting DGA moieties onto the propylene imine-diaminobutane (PPI-DAB) skeleton. In view of the novelty of these ligands and their exceptionally high metal ion extraction efficiency, a thorough investigation on radioactive waste processing is warranted.

Liquid membrane-based separation methods are known to be 'green' alternatives to solvent extraction-based separation methods in view of high ligand inventory and generation of large amounts of secondary waste in the latter case [28–30]. In contrast, liquid membrane-based separation methods offer numerous advantages over conventional solvent extraction such as simultaneous extraction and stripping, generation of low volume

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**Table 1**

Composition of a typical high level waste of pressurized heavy water reactor origin. Acidity: ~3 mol/L HNO<sub>3</sub>; Spent fuel burn up of ~6500 MWd/Te and 3 years cooling; Volume of waste is 800 L/tonne of spent fuel.

Element	Concentration (g/L)	Element	Concentration (g/L)
Na	5.50	Pd	0.03
K	0.22	Mo	0.14
Cr	0.12	Ba	0.06
Mn	0.43	Y	0.06
Fe	0.72	La	0.18
Sr	0.03	Ce	0.06
Cs	0.22	Pr	0.09
Zr	0.09	Nd	0.12
Ru	0.04	Sm	0.09

of volatile organic carbons and low operating cost, etc. The supported liquid membrane (SLM) technique has been evaluated successfully for the selective removal of radiotoxic elements from radioactive waste solutions [31–34]. Here the selectivity is achieved by selective complexation of the target metal with a ligand (known as carrier), followed by mass transfer of the metal-ligand complex across the membrane from the feed phase to the receiver phase. Such transport processes are, therefore, referred to as “carrier facilitated transport” processes. It is worth evaluating the transport of minor actinides from radioactive waste solutions using these novel DGA-dendrimers (Fig. 1).

The present study involves the investigation of three DGA-functionalized dendrimers, namely, zero generation (L<sub>I</sub>), 1st generation (L<sub>II</sub>), and 2nd generation (L<sub>III</sub>) (Fig. 1) as the carrier in SLMs for separation of Am<sup>3+</sup> ion from dilute nitric acid feed solutions. Batch solvent extraction studies were performed to investigate the selectivity of the ligands for Am<sup>3+</sup> over other metal ions present in the radioactive waste, viz. high level waste (HLW). Solvent extraction data were also obtained to optimize different parameters for efficient transport of Am<sup>3+</sup> in SLMs. Various diffusional parameters affecting SLM transport were calculated for a better understanding of the transport data. Finally, the stability of the SLM was studied over a period of five days. Though we have

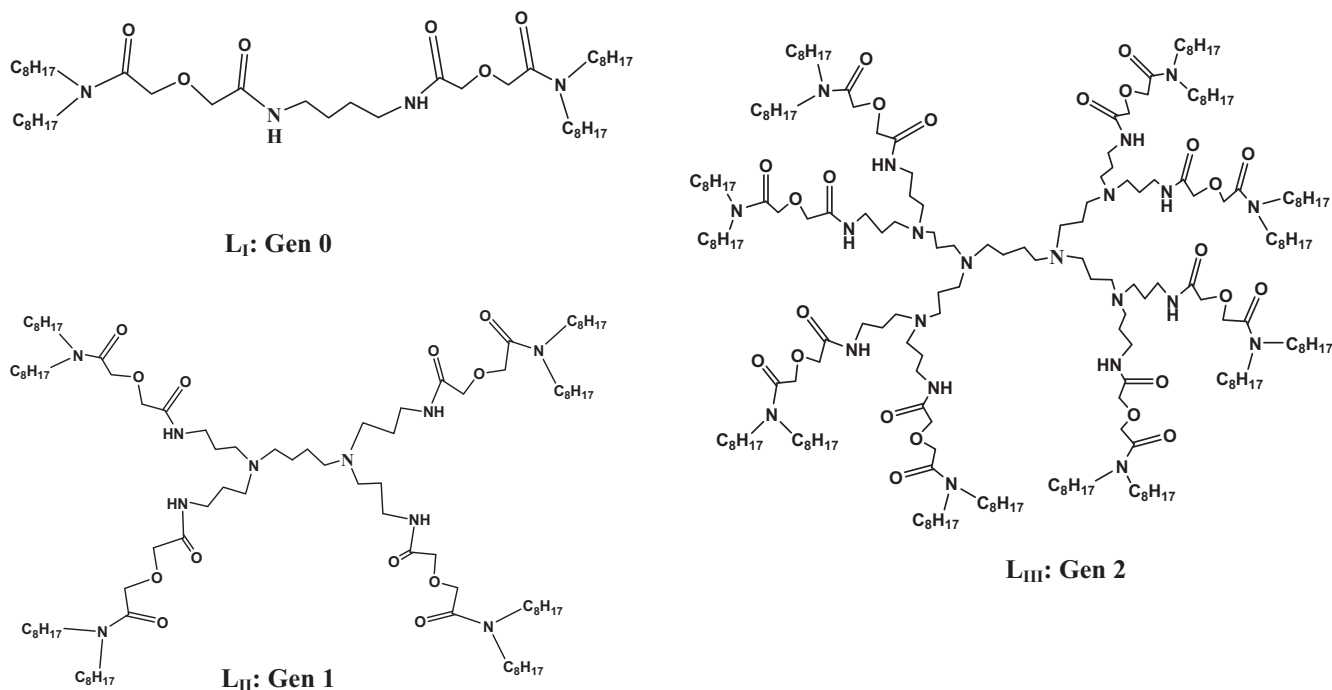
previously reported liquid membrane transport studies involving DGA-functionalized calix[4]arenes, the dendrimers are of great interest to study in view of their less flexible conformation compared to the calixarenes as well as their special ‘tree like’ structure. To our knowledge, this is the first report on the transport behavior of actinides using DGA – functionalized dendrimers.

## 2. Experimental section

### 2.1. Materials

The DGA-dendrimers (L<sub>I</sub>–L<sub>III</sub>, Fig. 1) were synthesized by reaction of 1,4-diaminobutane or the appropriate PPI-DAB dendrimers with *p*-nitrophenyl-activated DGA in refluxing toluene as described recently [27]. The ligands were characterized by <sup>1</sup>H 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. Polytetrafluoroethylene (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 the solutions were prepared using Milli Q deionized water (18.2 M Ω cm).

<sup>241</sup>Am from laboratory stock was used after purification (from its decay product, <sup>237</sup>Np) using the HTTA (2-thenoyltrifluoroacetone) extraction method and checking its radiochemical purity by alpha as well as gamma ray spectroscopy [35]. <sup>233</sup>U was purified from its daughter products using a reported method [36], while Pu (mainly <sup>239</sup>Pu) was purified from its decay products (mainly <sup>241</sup>Am) by the HTTA extraction method [37]. The oxidation state of Pu (taken in 1 mol/L HNO<sub>3</sub>) was adjusted to the +4 state by adding a few drops of 5 mmol/L NaNO<sub>2</sub> followed by selective extraction of Pu<sup>4+</sup> by 0.5 mol/L HTTA in xylene. <sup>239</sup>Np was prepared by neutron activation of <sup>238</sup>U followed by its purification as described earlier [38]. The neptunium valency was adjusted to the +4 state by the addition of hydroxylamine hydrochloride and ferrous sulphamate (at 1 mol/L HNO<sub>3</sub>) followed



**Fig. 1.** Structures of the DGA-functionalized PPI-DAB dendrimers L<sub>I</sub>–L<sub>III</sub>.

by HTTA extraction.  $^{152,154}\text{Eu}$ ,  $^{85,89}\text{Sr}$ , and  $^{137}\text{Cs}$  were procured from BRIT (Board of Radiation and Isotope Technology), Mumbai, and were used after checking their radiochemical purity.

## 2.2. Distribution measurements

The distribution ratio measurements in solvent extraction were carried out by equilibrating equal volumes of the aqueous phase (usually 1 mL, spiked with the required metal ion tracers), and the organic phase containing ligands in 5% *iso*-decanol + 95% *n*-dodecane. It is important to note that due to the limited solubility of the ligands in pure *n*-dodecane, 5% *iso*-decanol was added to increase the polarity of the medium, thereby giving free solubility to all the ligands. Equilibration was performed in Pyrex glass stoppered tubes in a thermostated water bath maintained at  $25 \pm 0.1$  °C for about 60 min. Subsequently, the tubes were centrifuged and aliquots (usually 100  $\mu\text{L}$ ) were removed from the aqueous and the organic phases for radiometric assay.  $^{241}\text{Am}$ ,  $^{239}\text{Np}$ ,  $^{152,154}\text{Eu}$ ,  $^{85,89}\text{Sr}$ , and  $^{137}\text{Cs}$  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,  $^{239}\text{Pu}$  and  $^{233}\text{U}$  were assayed by liquid scintillation counting using a toluene-based extractive scintillator (Hidex, Finland). The distribution ratio of metal ions ( $D_M$ ) was calculated as the ratio of counts per unit time per unit volume of the organic phase to that in the aqueous phase. All the experiments were carried out in duplicate and the accepted data were within the error limits of  $\pm 5\%$ .

## 2.3. Supported liquid membrane studies

The supported liquid membrane (SLM) studies were carried out using PTFE flat sheet membranes as a support whose pores were filled with the carrier solution (1 mmol/L ligand solutions in 5% *iso*-decanol/*n*-dodecane). The PTFE membranes were soaked overnight in the carrier solution to yield reproducible results [31]. Subsequently, the submerged membranes were removed from the solution and wiped carefully with a tissue paper to clear it of the excess fluid at the outside of the support, and mounted on the two compartments (20 mL capacity each) of the glass transport cell. The solutions in feed (3 mol/L  $\text{HNO}_3$  spiked with metal tracer) and the receiver (0.01 mol/L  $\text{HNO}_3$ ) compartments were stirred at 200 rpm using a magnetic stirrer equipped with precise speed control, which ensured a minimal thickness of the aqueous boundary layers [39]. The transport of the metal ion was estimated by taking out 100  $\mu\text{L}$  samples from both the compartments at regular intervals and assaying them radiometrically (*vide supra*). The cumulative percent transport (%T) of the metal ions at any given time  $t$  was calculated as:

$$\%T = \left( \frac{C_f - C_t}{C_f} \right) \cdot 100 \quad (1)$$

where  $C_o$  and  $C_t$  are the concentrations of metal ion in the feed at  $t = 0$ , and at time  $t$ , respectively. The SLM transport experiments were carried out at ambient temperatures ( $24 \pm 1$  °C) and duplicate runs were reproducible within  $\pm 5\%$ .

## 3. Results and discussion

### 3.1. Solvent extraction studies

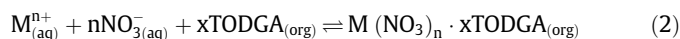
#### 3.1.1. Extraction kinetics

The extraction kinetics of  $\text{Am}^{3+}$  with all the three DGA-dendrimer ligands  $\text{L}_{\text{I-III}}$  was investigated at 3 mol/L  $\text{HNO}_3$ . The reason for using 3 mol/L  $\text{HNO}_3$  was the feed acidity of HLW (Table 1), which is the source of minor actinides. As shown in Fig. 2a, about

15 min were required to obtain equilibrium  $D_{\text{Am}}$  values in the extraction cycle. In contrast, the attainment of the forward extraction equilibrium with TODGA was found to be only 10 min [40]. The slower extraction kinetics with the DGA-dendrimers  $\text{L}_{\text{I-III}}$  might be due to binding of more than one DGA group of the same ligand molecule, and the formation of a relatively bulkier metal/ligand complex. At the same time, stripping kinetics studied with 0.01 mol/L  $\text{HNO}_3$  shows a marginally slower attainment of the equilibrium (20 min, Fig. 2b), which may be attributed to the difficulty in breaking the metal/ligand complexes. The relatively fast extraction and stripping kinetics suggests that the SLM technique can be used effectively for separation of minor actinides with the DGA-dendrimers  $\text{L}_{\text{I-III}}$ .

#### 3.1.2. Effect of feed acidity

The effect of the nitric acid concentration on the distribution of  $\text{Am}^{3+}$  by the three DGA-dendrimer ligands  $\text{L}_{\text{I-III}}$  was investigated from feed acidities of 0.1–6 mol/L  $\text{HNO}_3$ , and the results are shown in Table 2. In the case of bare DGA ligands like TODGA, the extraction of the metal ion increases with increasing  $\text{HNO}_3$  concentration due to the fact that the metal ion extraction has a direct correlation with the aqueous phase nitrate ion concentration as per the following equation [12]:



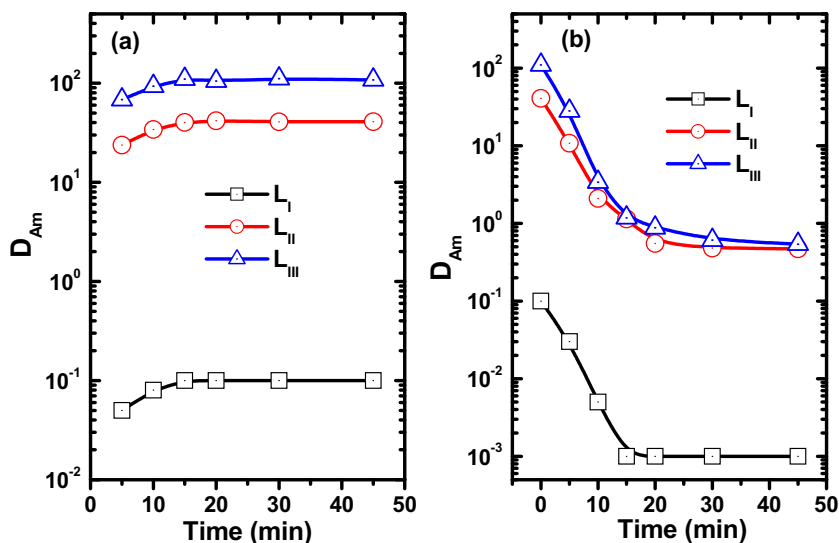
A similar extraction behavior is also expected with the DGA-dendrimers  $\text{L}_{\text{I-III}}$  used in the present work as well. Table 2 shows a monotonous increase in the extraction of  $\text{Am}^{3+}$  with all the three dendrimer ligands  $\text{L}_{\text{I-III}}$  conforming to a solvation mechanism, similar to that observed with TODGA [12]. The co-extraction of  $\text{HNO}_3$  was negligible even up to 6 mol/L  $\text{HNO}_3$ , indicating that the transport of metal ions will not be affected as the transport of acid from feed to the receiver phase will be insignificant (*vide infra*).

#### 3.1.3. Nature of the extracted species

The nature of the extracted species was determined by the slope analysis method where the distribution ratio of  $\text{Am}^{3+}$  was measured as a function of ligand concentrations. The  $\log D_{\text{Am}}$  vs.  $\log [\text{Ligand}]$  plots yielded a slope value of  $2.04 \pm 0.17$ ,  $1.05 \pm 0.05$ , and  $1.05 \pm 0.05$  for  $\text{L}_{\text{I}}$ ,  $\text{L}_{\text{II}}$ , and  $\text{L}_{\text{III}}$ , respectively, suggesting the participation of two molecules of  $\text{L}_{\text{I}}$  and one molecule of both  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$  in the  $\text{Am}^{3+}$  bearing extracted complex. Scheme 1 shows a pictorial representations of the 1:2 as well as 1:1 (M:L) complexes with  $\text{L}_{\text{I}}$  and  $\text{L}_{\text{II}}$ , respectively. As there are only two coordinating DGA moieties present in  $\text{L}_{\text{I}}$ , one can reasonably assume that, in all probability, only one DGA moiety from each ligand may be participating in the complexation. On the other hand,  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$  have four and eight coordinating DGA sites, respectively, and participation of more than one ligand in complex formation may lead to unusually high crowding at the metal centre resulting in highly unstable systems. Therefore, 1:1 complex formation appears reasonable for both  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$ , and has been confirmed by spectroscopic measurements [27]. Though only 1:1 metal/ligand complexes are formed with  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$ , the overall lipophilicity of the complex with  $\text{L}_{\text{III}}$  will be higher, which is reflected in the large enhancement of the  $\text{Am}^{3+}$  extraction.

#### 3.1.4. Separation behavior

The extraction of  $\text{Am}^{3+}$  was carried out from 3 mol/L  $\text{HNO}_3$  feed, which is the feed acidity of HLW (Table 1), the major source of minor actinides and fission product elements. As shown in Table 3, while the extraction of  $\text{Am}^{3+}$  was very low with 1.0 mmol/L  $\text{L}_{\text{I}}$ , it sharply increased when comparable concentrations of  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$  were used (Fig. 2). This indicates that the DGA-functionalization onto dendritic scaffolds increases the extraction efficiency enor-



**Fig. 2.** (a) Extraction kinetics of  $Am^{3+}$  at 3 mol/L  $HNO_3$ ; (b) Stripping kinetics of  $Am^{3+}$  with 0.01 mol/L  $HNO_3$ . Ligands: 1.0 mmol/L DGA-dendrimers  $L_{I-III}$  in 5% *iso*-decanol/*n*-dodecane.

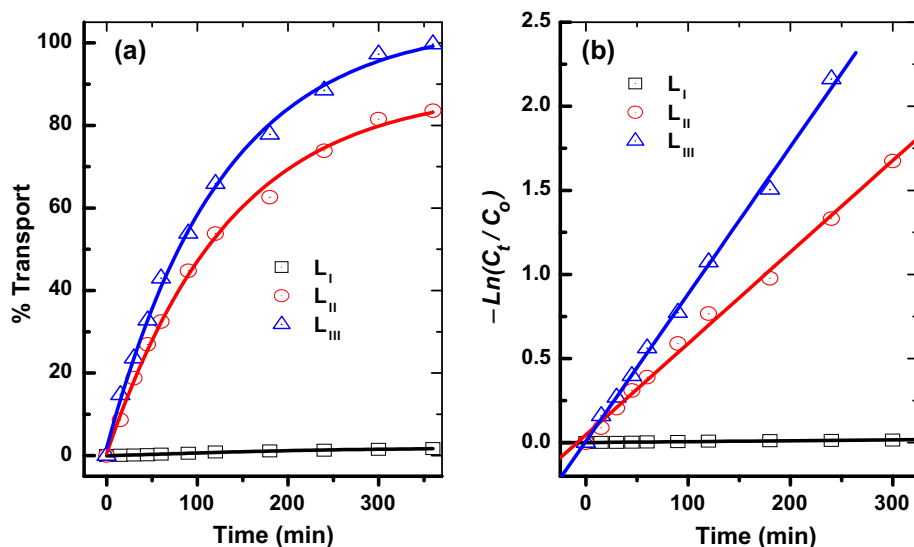
**Table 2**

Distribution ratio of  $Am^{3+}$  with DGA-dendrimers  $L_{I-III}$  as a function of the  $HNO_3$  concentration. [Ligand]: 1.0 mmol/L in 5% *iso*-decanol/*n*-dodecane.

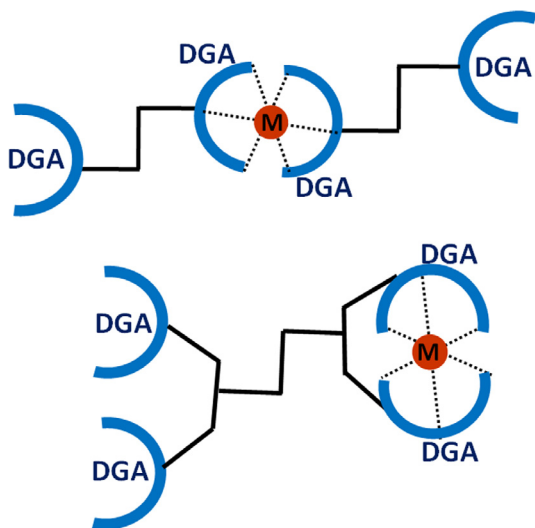
[ $HNO_3$ ], mol/L	Distribution ratio of $Am^{3+}$		
	$L_I$	$L_{II}$	$L_{III}$
0.1	<0.001	$0.17 \pm 0.01$	$0.21 \pm 0.02$
1	$0.01 \pm 0.005$	$8.05 \pm 0.38$	$12.7 \pm 0.94$
3	$0.11 \pm 0.02$	$41.9 \pm 3.21$	$109.4 \pm 6.22$
6	$0.63 \pm 0.05$	$161 \pm 8.95$	$413 \pm 35.8$

ously. The extraction of  $Eu^{3+}$  also followed a similar trend to that of  $Am^{3+}$ . Bare DGA ligands such as TODGA are reported to preferentially extract  $Eu^{3+}$  over  $Am^{3+}$ , and a separation factor ( $S.F. = D_{Eu}/D_{Am}$ ) of ca.10 has been reported [12]. It is interesting to note that, in the present work, the  $S.F.$  values were poor and

did not improve upon increasing the generation of DGA dendrimers. However, the  $S.F.$  values with respect to  $UO_2^{2+}$  ( $S.F. = D_{Am}/D_U$ ) were highly promising as a value of 11, 380, and 500 were obtained with  $L_I$ ,  $L_{II}$ , and  $L_{III}$ , respectively. Similarly, the  $S.F.$  values with respect to  $Cs^+$  were:  $>100$ ,  $>4 \times 10^4$ , and  $>1.1 \times 10^5$  and those with respect to  $Sr^{2+}$ : 5.5, 1393, and 5500 were highly promising for  $L_I$ ,  $L_{II}$  and  $L_{III}$ , respectively. These high selectivities are quite encouraging for these ligands and hence, hold promise for nuclear waste treatment applications.  $Sr(II)$  extraction with TODGA from 3 mol/L  $HNO_3$  was reported to be quite high, leading to its significant extraction along with the trivalent Am [43] and decontamination was possible only at a higher  $HNO_3$  concentration (6 M). The DGA-dendrimers  $L_{II}$  and  $L_{III}$ , on the other hand, showed a very high decontamination from  $Sr^{2+}$  even at 3 mol/L  $HNO_3$ . These results are highly encouraging and give exciting prospects for the selective recovery of trivalent actinides over  $UO_2^{2+}$ ,  $Sr^{2+}$ , and  $Cs^+$ .



**Fig. 3.** Transport of  $Am^{3+}$  by DGA-dendrimers  $L_{I-III}$ . [Ligand]: 1.0 mmol/L in 5% *iso*-decanol/*n*-dodecane; Feed: 3 mol/L  $HNO_3$  (20 mL); Strippant: 0.01 mol/L  $HNO_3$  (20 mL). (a) Transport profile of  $Am^{3+}$ , (b)  $\ln(C_t/C_0)$  vs. time for calculation of permeability coefficient.



**Scheme 1.** Pictorial representation of the complexation of  $L_I$  (1:2) and  $L_{II}$  (1:1) with the metal ion.

**Table 3**  
Distribution behavior of metal ions and their ionic size by DGA-dendrimers  $L_{I-III}$ . [Ligand]: 1.0 mmol/L in 5% iso-decanol/*n*-dodecane; Aqueous phase: 3 mol/L  $HNO_3$ .

Metal ions	Ionic size (Å) <sup>a</sup>	$D_M$		
		$L_I$	$L_{II}$	$L_{III}$
$Am^{3+}$	1.09	0.11	41.8	110
$Eu^{3+}$	1.066	0.21	147	300
$UO_2^{2+}$	1.4; 2.35 <sup>b</sup>	0.01	0.11	0.22
$Pu^{4+}$	0.96	2.6	165	145
$Np^{4+}$	0.98	0.30	47.5	95.6
$Sr^{2+}$	1.26	0.02	0.03	0.02
$Cs^+$	1.74	<0.001	<0.001	<0.001

<sup>a</sup> Ionic radii data refer to coordination number 8 and are used from Ref. [41].

<sup>b</sup> Uranyl ion is reported to have an elliptical shape with radius along the minor axis as 1.4 and that along the major axis as 2.35 [42].

### 3.2. Supported liquid membrane studies

#### 3.2.1. Permeation of $Am^{3+}$

Permeation of  $Am^{3+}$  was measured at 3 mol/L  $HNO_3$  feed solution and water as the receiver phase. As seen in Fig. 3a, the permeation of  $Am^{3+}$  was poor (<1% transport in 5 h) with  $L_I$ , while a significant enhancement in the  $Am^{3+}$  transport was recorded with  $L_{II}$  (81.5% in 5 h), which further increased with  $L_{III}$  (97.3% in 5 h). The permeability coefficient ( $P$ ), which is a parameter to express the transport properties of the given membrane, was calculated graphically by plotting the following permeation equation [39]:

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

where  $V$  is the total volume of the feed solution. The effective surface area ( $A$ ) of the membrane was 3.14 cm<sup>2</sup>, calculated from the actual exposed surface area ( $Q$ ) and the porosity ( $\epsilon$ ) of the membrane. The  $P$  values of  $Am^{3+}$  obtained from the slope of the straight line plots of  $\ln(C_t/C_0)$  vs.  $t$  (Fig. 3b) followed the order of their distribution ratio with these ligands (Table 4). However, the  $P$  value with  $L_I$  was found to be 3 orders of magnitude lower than that reported for TODGA, while that with  $L_{III}$  was somewhat lower than half, which can be attributed to the 100 times higher concentration of TODGA used in the previous study [31]. The  $D_{Am}$  value with  $L_{III}$  was also nearly half of that obtained with TODGA. The extracted complex with TODGA is reported to be  $Am(NO_3)_3 \cdot nTODGA$ , where,  $n$  is close to 4 [12]. On the other hand, 1:2 metal ligand complexes

**Table 4**

Transport and extraction data of  $Am^{3+}$  with DGA-dendrimers  $L_{I-III}$  and TODGA at 3 mol/L  $HNO_3$ . Experimental conditions are the same as in Fig. 3.

Ligand	$D_{Am}$	$P$ (cm/s)	%T (5 h)	Reference
$L_I$	0.11	$5.20 \times 10^{-6}$	0.76	This work
$L_{II}$	41.8	$5.77 \times 10^{-4}$	81.5	This work
$L_{III}$	110	$9.29 \times 10^{-4}$	97.3	This work
TODGA <sup>a</sup>	203	$2.10 \times 10^{-3}$	99.9	Ref. [31]

<sup>a</sup> 0.1 mol/L solution in *n*-dodecane.

are formed with  $L_I$ , while both  $L_{II}$  and  $L_{III}$  give rise to 1:1 complexes (*vide supra*). Even with 1:1 species, very large complexes are expected to be formed with  $L_{III}$  which may lead to very slow diffusion of the extracted complex based on the Wilke-Chang equation [44] given below.

$$D_0 = 7.4 \times 10^8 \cdot \frac{(\chi^{0.5} M^{0.5} T)}{\eta V_m^{0.6}} \quad (4)$$

where  $M$ ,  $\chi$ , and  $\eta$  are the molecular weight, solvent association parameter, and the viscosity of the solvent, respectively, while  $V_m$  is the molar volume of the carrier extractant and  $T$  is the temperature. The association parameters for the diluents are taken as unity [45]. A detailed discussion on the diffusion coefficient of the complex is made in a following section.

DGA-based extractants such as TODGA are known to transport acid from the feed to the receiver side in flat sheet SLM experiments based on the following extraction mechanism:



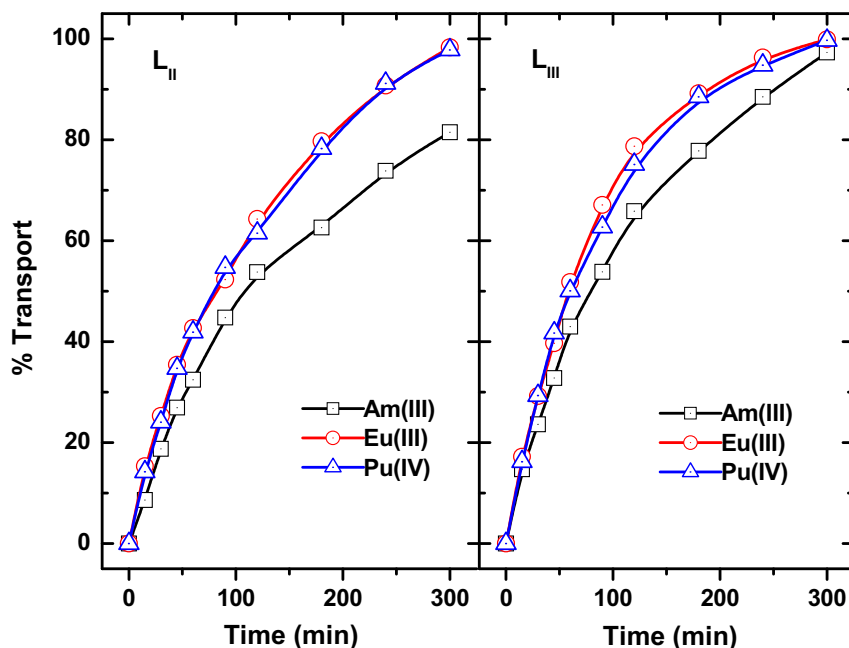
Accordingly, it may be expected that some amount of nitric acid may be transported from the feed to the receiver compartment during the course of the experiment in the present study as well. However, in view of the very low concentration of the extractants used, negligible acid transport took place (<1%) monitored up to 7 h. This assumes great relevance as the metal ion transport rates will not be affected over a period of time as is the case in TODGA [31].

#### 3.2.2. Transport of other metal ions

The transport of other metal ions such as  $Eu^{3+}$  and  $Pu^{4+}$  was also studied in view of their significance in the solvent extraction studies. However, only  $L_{II}$  and  $L_{III}$  were used in these studies since very low transport rates were observed with  $L_I$  (Fig. 3). The transport profiles of the metal ions such as  $Am^{3+}$ ,  $Eu^{3+}$  and  $Pu^{4+}$  as are shown in Fig. 4 which shows the transport trend as:  $Eu^{3+} > Pu^{4+} > Am^{3+}$ , which is in close agreement with their relative extraction trends (Table 3). It is important to mention that for all the metal ions, except  $Pu^{4+}$ , 0.01 M  $HNO_3$  was used as the strippant. However, in case of  $Pu^{4+}$ , 0.2 M mol/L  $HNO_3$  was used to avoid the hydrolysis of plutonium. The permeability coefficient ( $P$ ) values were calculated by plotting the transport data in Eq. (3) and the values are summarized in Table 5. The  $P$  values obtained with  $L_{II}$  and  $L_{III}$  followed the same trend as shown in their transport profiles. It is also important to mention here that the transport of U(VI),  $Sr^{2+}$ , and  $Cs^+$  was negligible even after 5 h, indicating clean and excellent separation of minor actinides over the bulk of uranium and fission product elements such as  $Sr^{2+}$  and  $Cs^+$ .

#### 3.2.3. Calculation of diffusion parameters

The transport rates are dependent on three factors, viz. the extraction rate (at the feed–SLM interface), the diffusion rate of the metal carrier complex (in the SLM phase), and the back extraction rate (at the SLM–receiver phase interface). As the metal ion extraction and back extraction kinetics were reasonably fast (Fig. 2), the rate-deciding factor is the diffusion of the metal-car-



**Fig. 4.** Transport of  $\text{Am}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Pu}^{4+}$  by DGA-dendrimers  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$ . [Ligand]: 1.0 mmol/L in 5% *iso*-decanol/*n*-dodecane; Feed: 3 mol/L  $\text{HNO}_3$  (20 mL); Strippant: 0.01 mol/L  $\text{HNO}_3$  (20 mL). Note: For  $\text{Pu}(\text{IV})$ , 0.2 M  $\text{HNO}_3$  was used as strippant to avoid its hydrolysis.

**Table 5**

Transport of actinides and lanthanides by DGA-dendrimers  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$ . Experimental conditions are the same as in Fig. 4.

Metal ions	$\text{L}_{\text{II}}$			$\text{L}_{\text{III}}$		
	$P$ (cm/s)	%T (2 h)	%T (5 h)	$P$ (cm/s)	%T (2 h)	%T (5 h)
$\text{Am}^{3+}$	$5.77 \times 10^{-4}$	53.7	81.5	$9.29 \times 10^{-4}$	65.8	97.3
$\text{Eu}^{3+}$	$8.55 \times 10^{-4}$	64.3	98.3	$1.24 \times 10^{-3}$	78.7	99.9
$\text{Pu}^{4+}$	$6.85 \times 10^{-4}$	61.5	97.8	$1.04 \times 10^{-3}$	75.1	99.7

U, Sr, and Cs transport was not measured due to their poor extraction.

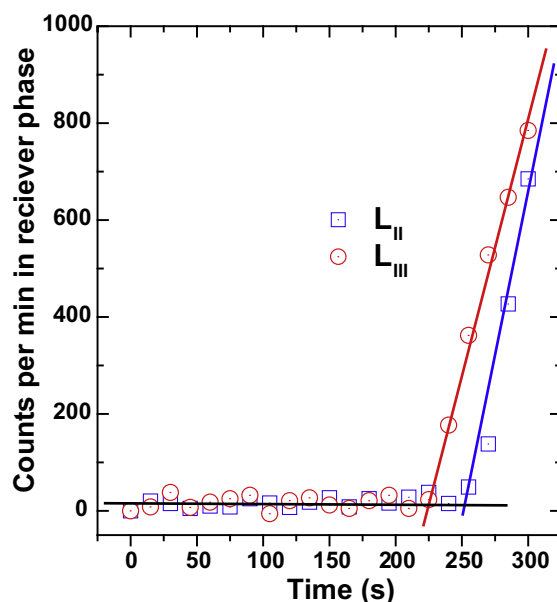
rier complex, which should be deciding the overall transport rates. The diffusion coefficient of the metal–carrier complex in the SLM phase ( $D_o$ ) can be calculated as per the empirical Wilke–Chang equation as given in Eq. (3) [44]. For calculating the  $D_o$  values by the Wilke–Chang method, the molar volume of the complex ( $V_m$ ) was calculated to be 8721 and 37,261 for  $[\text{Am}(\text{NO}_3)_3 \cdot \text{L}_{\text{II}}]$  and  $[\text{Am}(\text{NO}_3)_3 \cdot \text{L}_{\text{III}}]$ , respectively [39]. The  $D_o$  values for both complexes were calculated and are given in Table 6. To compare the bulk diffusion coefficient,  $D_o$ , values obtained by the Wilke–Chang equation, we also obtained the effective diffusion coefficient ( $D_{\text{eff}}$ ) values experimentally using the lag-time ( $t_{\text{lag}}$ ) method [45]. The lag-time plots for the transport of  $\text{Am}^{3+}$  from feed to receiver phase were obtained with  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$  and are presented in Fig. 5. From the experimentally determined time-lag values, the  $D_{\text{eff}}$  values were calculated using the following equation and the results are compared in Table 6.

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

**Table 6**

Diffusion coefficient data for the transport of  $\text{Am}^{3+}$  by DGA-dendrimers  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$  and TODGA. Experimental conditions are the same as in Fig. 3.

Ligand	Diffusion coefficient ( $\text{cm}^2/\text{s}$ )		
	Wilke–Chang method	Lag time method	Reference
$\text{L}_{\text{II}}$	$9.37 \times 10^{-7}$	$2.90 \times 10^{-8}$	This work
$\text{L}_{\text{III}}$	$3.92 \times 10^{-7}$	$3.26 \times 10^{-8}$	This work
TODGA	$5.33 \times 10^{-6}$	$5.10 \times 10^{-6}$	Ref. [46]



**Fig. 5.** Time-lag experiments for the transport of  $\text{Am}^{3+}$  by DGA-dendrimers  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$ . [ligand]: 1.0 mmole/L/5% *iso*-decanol/*n*-dodecane; Feed: 3 mol/L  $\text{HNO}_3$ ; Strippant: 0.01 mol/L  $\text{HNO}_3$ .

In Eq. (6)  $t_{\text{lag}}$  is the lag-time and  $d_o$  is the membrane thickness. As given in Table 6, the bulk diffusion coefficients ( $D_o$ ) calculated from the Wilke–Chang equation for both  $\text{L}_{\text{II}}$  and  $\text{L}_{\text{III}}$  are not consis-

tent with the  $D_{\text{eff}}$  values obtained from the lag-time method. The  $D_{\text{eff}}$  values are about one order of magnitude lower than those obtained by the Wilke-Chang equation (*vide supra*). This is possibly due to the fact that the assumption of a spherical complex is not valid with the dendrimer type ligands, particularly for the Gen 2 dendrimer  $L_{II}$ . On the other hand, TODGA forms near spherical complexes inside reverse micelles [38] and hence, the diffusion coefficient value obtained from the Wilke-Chang model matches very well with that determined by the lag-time method.

### 3.2.4. Membrane stability

In order to make the SLM-based separation studies for possible applications, the stability of the liquid membranes is one of the most important parameters. Though a variety of factors are known to affect the SLM stability, some of the most important ones involve erosion of the SLM due to the shear forces, osmotic pressure difference, aqueous solubility of the carrier, etc. We have recently reported the role of the organic diluent as another important factor affecting the SLM stability. Diluents such as *n*-dodecane [31] and NPOE [47] result in reasonably stable SLMs, while those containing PTMS (phenyltrifluoromethyl sulphone) [48], chloroform [49], nitrobenzene [50], etc., show a poor membrane stability.

The stability of the SLM containing 1 mmol/L  $L_{III}$  in 5% *iso*-decanol/*n*-dodecane was tested by carrying out  $\text{Am}^{3+}$  transport over a period of 5 days and the results are shown in Fig. 6. The transport profiles are almost superimposable over each other suggesting qualitatively that the SLM stability is reasonably good. Quantification of this study was done by calculating the  $P$  values which are presented in Table 7 along with the %T data after 1 h and 2 h. It is clear from the table that the results are nearly reproducible within experimental error limits. Though the studies were not extended beyond 5 days, another study has indicated stability of the SLMs up to 12 days when a mixture of 5% *iso*-decanol/*n*-dodecane was used as the diluent mixture [51]. It is important to add that the diluent used in the present study is mainly responsible for the stability of the membrane as similarly good SLM stability has been reported previously using analogous diluent system [31].

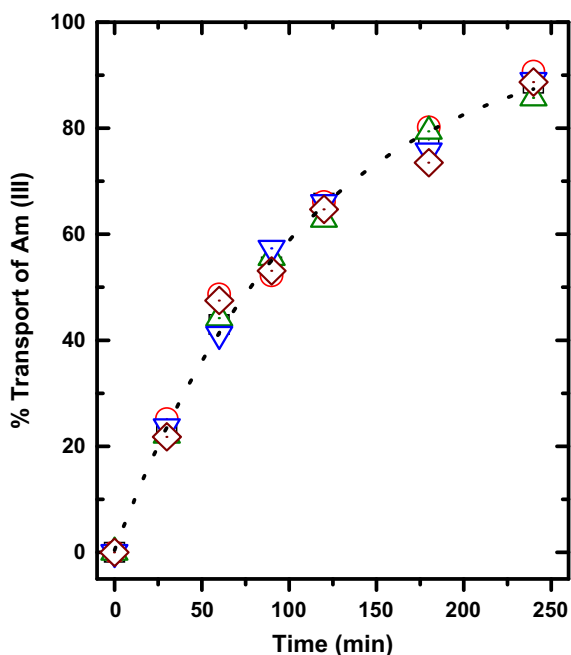


Fig. 6. Transport of  $\text{Am}^{3+}$  using DGA-dendrimer  $L_{III}$  of multiple experiments carried out in 5 consecutive days.  $[L_{III}]$ : 1.0 mmole/L in 5% *iso*-decanol/*n*-dodecane; Feed: 3 mol/L  $\text{HNO}_3$ ; Strippant: 0.01 mol/L  $\text{HNO}_3$ .

Table 7

Stability<sup>a</sup> of SLM containing  $L_{III}$  as seen from the  $\text{Am}^{3+}$  transport studies from a feed containing 3 mol/L  $\text{HNO}_3$ .  $[L]$ : 1 mmol/L ligand  $L_{III}$  in 5% *iso*-decanol + 95% *n*-dodecane.

Day	$P$ (cm/min)	% Transport	
		1 h	2 h
1	$5.17 \times 10^{-2}$	42.9	65.8
2	$5.53 \times 10^{-2}$	48.7	60.1
3	$5.24 \times 10^{-2}$	44.2	62.8
4	$5.38 \times 10^{-2}$	41.1	66.0
5	$5.22 \times 10^{-2}$	47.5	64.7

<sup>a</sup> The stability test was only performed with  $L_{III}$ .

## 4. Conclusions

In conclusion, the DGA-functionalized dendrimers, especially  $L_{II}$  and  $L_{III}$ , were found to be highly efficient extractants for actinide ions. The distribution coefficient values for the actinide and fission product element ions follow the trend:  $\text{Eu}^{3+} > \text{Pu}^{4+} > \text{Am}^{3+} > \text{Np}^{4+} \gg \text{UO}_2^{2+} > \text{Sr}^{2+} > \text{Cs}^+$ . As the  $D$  values for  $\text{UO}_2^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Cs}^+$  are  $<0.25$  and those of  $\text{Eu}^{3+}$ ,  $\text{Pu}^{4+}$ , and  $\text{Am}^{3+}$  are  $>100$ , separation factor values in excess of 400 are obtained, which is very impressive from the radioactive waste management point of view. The nature of the extracted species was investigated by slope analysis and while 1:2 (M:L) species were found to get extracted with  $L_I$ , 1:1 species were found to extract with both  $L_{II}$  and  $L_{III}$ . The SLM studies have shown great promise as quantitative metal ion transport can be carried out with a very small volume of the ligand. The membrane stability was found to be reasonably good over a period of five days and it is expected that the SLM can be used for radioactive waste processing for a long period of time. It is required to carry out scale up studies using hollow fiber contactors for actual process applications using radioactive waste solutions.

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