



Evaluation of three novel benzene-centered tripodal diglycolamide ligands for the pertraction of americium(III) through flat sheet membranes for nuclear waste remediation applications



Bholanath Mahanty^a, Prasanta K. Mohapatra^{a,*}, Andrea Leoncini^b, Jurriaan Huskens^b, Willem Verboom^b

^a Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

^b Laboratory of Molecular Nanofabrication, MESA⁺ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands

ARTICLE INFO

Keywords:

Diglycolamide
Americium
Plutonium
Radioactive waste
Membrane transport

ABSTRACT

Three benzene-centered tripodal diglycolamide (Bz-T-DGA) ligands were evaluated for the pertraction of Am³⁺ across PTFE flat sheet membranes. The feed phase contained a tracer spiked nitric acid solution (3 M), while the receiver phase contained 1 M α -hydroxyisobutyric acid (AHIBA). The transport of Am³⁺ was quantitative with ligand L_I, with ethyl groups appended to the benzene ring at the 1,3,5-positions and two spacer atoms between the ring and the DGA group. Ligand L_{III}, with a butoxy tether between the ring and the DGA unit, displayed a much better transport efficiency than ligand L_{II} having an ethylamide linkage, although in both cases the transport rates are lower than that of L_I. The transport efficiency of the actinide ions was Am³⁺ > Pu⁴⁺ >> UO₂²⁺ suggesting that Am and Pu can be easily decontaminated from U in a mixture. The membrane stability was reasonably good with L_I, while it was poor for the other two ligands.

1. Introduction

Separation of trivalent actinide/lanthanide ions from acidic feeds, prevailing in high level waste (HLW), is a challenging task. Due to their lower ionic potential, these ions are not as well extracted with common extractants such as TBP (tri-*n*-butyl phosphate) from nitric acid solutions [1]. In sharp contrast, UO₂²⁺ and Pu⁴⁺ ions are very well extracted from acidic feeds [1]. However, tailor made extractants such as CMPO (carbamoymethyl phosphine oxide) [2], malonamides [3] and more recently diglycolamides [4] are found to be very good extractants for the trivalent actinide as well as lanthanide ions from moderate concentrations (2–6 M) of nitric acid. Interestingly, while the ease of extraction with CMPO and malonamides follow the trend: Pu⁴⁺ > UO₂²⁺ > Am³⁺ (Am taken as a representative trivalent actinide / lanthanide element) an entirely different trend of Am³⁺ ~ Pu⁴⁺ >> UO₂²⁺ was reported with diglycolamide (DGA) extractants like TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) [5]. This has been attributed to aggregate formation in non-polar diluents in the presence of nitric acid [6,7]. In a separate study, size selective extraction of metal ions was reported where metal ions with 100 pm ionic radii were found to be extracted preferentially with TODGA [8], which may be considered to be based on reverse micelle formation [6]. In

view of this, it appears logical that multiple DGA extractants with three to four DGA pendent arms might be quite efficient for the extraction of trivalent actinide ions such as Am³⁺.

Multiple DGA-functionalized extractants where DGA groups are appended to a calix[4]arene resulted in very high extraction of the trivalent actinides and lanthanides [9]. Similarly, a tripodal DGA ligand where the DGA arms are bound to a central carbon atom (termed as T-DGA) has also been evaluated with highly encouraging results [10]. In a separate study, an N-pivot tripodal DGA ligand (termed as TREN-DGA) showed interesting extraction behavior towards trivalent lanthanide/actinide ions [11]. In view of the flexibility of the T-DGA ligand, it was thought of interest to functionalize the DGA pendent groups to a planar scaffold such as benzene. Recently, we have synthesized several benzene-centered tripodal (Bz-T-DGA) extractants which were found to be highly efficient for the extraction of actinides as the extraction of Am³⁺ was comparable to that reported with 0.1 M TODGA even with millimolar concentrations of the tripodal ligands [12,13]. The Bz-T-DGA extractants were reported to be quite efficient for metal ion extraction in view of the pre-organized conformation imparted by the benzene scaffold. In view of the very high efficiency of these extractants one would like to employ 'green' separation methods which utilize markedly low ligand inventory.

* Corresponding author.

E-mail address: mpatra@barc.gov.in (P.K. Mohapatra).

<https://doi.org/10.1016/j.seppur.2019.115846>

Received 2 May 2019; Received in revised form 18 July 2019; Accepted 21 July 2019

Available online 22 July 2019

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Supported liquid membrane (SLM) based separation methods have quite a few advantages over the solvent extraction based separation methods, which include very low ligand inventory, simultaneous extraction and stripping as well as alleviation of problems such as third phase formation, phase disengagement issues, etc. [14–17]. SLM-based studies with DGA-based ligands as the carrier extractants were evaluated by us for the transport of Am^{3+} from acidic feeds and the results were highly encouraging [18–20]. We have also used several tripodal DGA ligands, viz. T-DGA and TREN-DGA, for analogous studies [21,22] and while the transport efficiency of the ligands was encouraging, the SLM stability was poor. Recently, we have used two benzene-centered tripodal DGA ligands [23] for Am^{3+} transport where the spacer length effect was investigated. Interestingly, the extractant with a longer spacer length, expected to form a stronger complex, showed poor transport efficiency. It was thought that the isopentyl groups appended to the amidic 'N' atom closer to the benzene ring might be causing steric congestion leading to poor metal ion transport. Therefore, no substitution at the aforementioned 'N' atom may result in better transport efficiency.

In this study, it is intended to investigate the SLM transport of Am^{3+} across PTFE flat sheets containing three Bz-T-DGA ligands with ethylene spacers attached to one of the 'N' atoms of the DGA group which is closer to the benzene ring. It is expected to impart flexibility to the DGA pendent arms. Furthermore, the above mentioned 'N' atom of the DGA group is not substituted with any alkyl group to discount any steric constraints during metal ion binding. Finally, another novelty factor is to employ different functional groups in between the benzene ring and the amide linkage of the DGA closer to the benzene ring. In the present study, one of the Bz-T-DGA has ether groups, while the other has amide groups tethered to the benzene ring and these functional groups are in addition to the ethylene spacer thereby leading to additional flexibility to the extractants. The structural formulae of the three Bz-T-DGA ligands are presented in Fig. 1. Apart from investigation on the extraction and transport of Am^{3+} , transport of other metal ions such as UO_2^{2+} and Pu^{4+} was also investigated. SLM stability studies were also carried out and diffusion coefficients were determined using the 'lag time' method.

2. Experimental

2.1. Materials

2.1.1. Chemicals

The Bz-T-DGA extractants L_I – L_{III} were synthesized following a procedure reported earlier [12]. The ligands were characterized by elemental analysis, NMR, FTIR and MS and were found to be reasonably

pure. HTTA (2-thenoyltrifluoroacetone) was obtained from Sigma Aldrich (USA) and was used after checking its purity (m.p. = 43 °C). *n*-Dodecane (99%; Lancaster) and isodecanol (> 99%; SRL, Mumbai) were used as procured. α -Hydroxyisobutyric acid (AHIBA) was obtained from Fluka (Switzerland) and was used in the strippant solutions. Suprapur nitric acid (Merck, Germany) was used along with MilliQ water (Millipore, USA) for preparation of HNO_3 stock solutions. All other reagents were of AR grade.

2.1.2. Membrane

PTFE flat sheet membrane filters (47 mm dia) were procured from Sartorius (Germany) with 0.45 micron pore size and 80 micron thickness and were used in the SLM transport studies as detailed below. The pore size was confirmed from Hg porosimetry, while the thickness was measured using a Mututoya digital micrometer.

2.1.3. Radiotracers

^{241}Am , Pu (mainly ^{239}Pu) and ^{233}U radiotracers were used from the laboratory stock after the usual purification of the stocks prior to their use [23]. The purity of radiotracers was confirmed prior to their use by alpha and gamma ray spectrometry. While ^{241}Am was assayed radiometrically by gamma ray counting using a NaI(Tl) scintillation counter, Pu and ^{233}U were assayed by liquid scintillation counting using a counting system supplied by Hidex (Finland). Ultima gold scintillation cocktail (Perkin Elmer) was used for the scintillation counting.

2.2. Methods

2.2.1. Plutonium valency adjustment

Pu extraction / transport studies were carried out using the metal ion in the +4 oxidation state which was done by a literature method [24] where a few drops of $5 \times 10^{-2} \text{ M NaNO}_2$ solution were added to a Pu solution in 1 M HNO_3 . Though the major part of Pu is converted to the +4 state, there could be some amounts of Pu in the +3 and +6 state. In view of this, Pu^{4+} was extracted preferentially by 0.5 M HTTA in xylene, followed by its back extraction using 8 M HNO_3 . The Pu^{4+} in the stripped fraction was stable for more than a month [25] and hence, was used for all subsequent experiments. The oxidation state of Pu was established by an HTTA concentration variation experiment carried out at 1 M HNO_3 and a slope value of ca. +4 for the $\log D_{\text{Pu}}$ and $\log [\text{HTTA}]$ indicated that Pu predominantly existed in the +4 state.

2.2.2. Solvent extraction studies

The solvent extraction studies were carried out by equilibrating equal volumes (usually 1.0 mL) of organic and aqueous phases in leak-

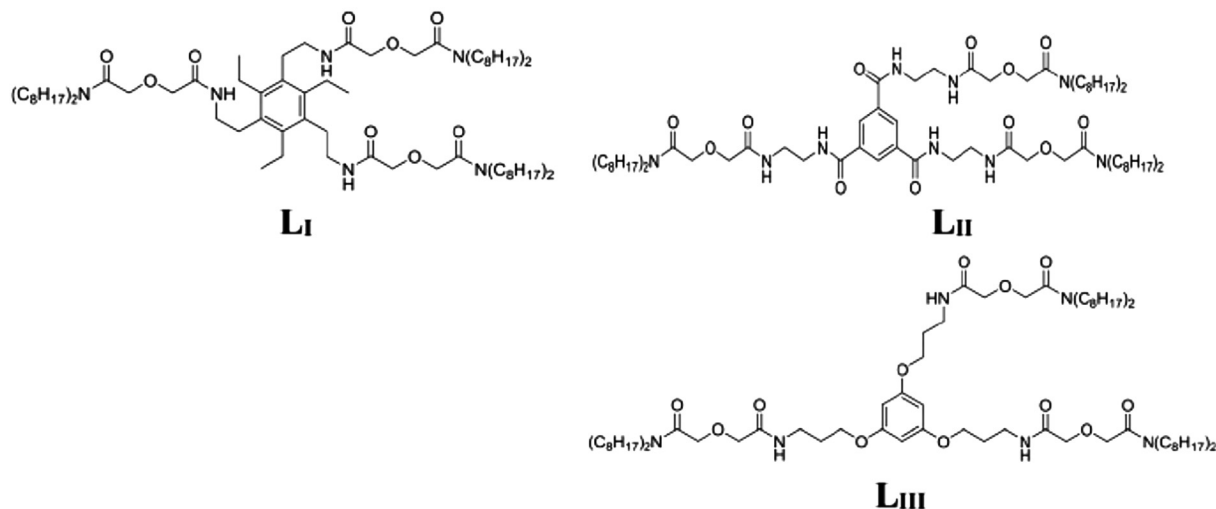


Fig. 1. Structural formulae of the three Bz-T-DGA extractants L_I , L_{II} and L_{III} .

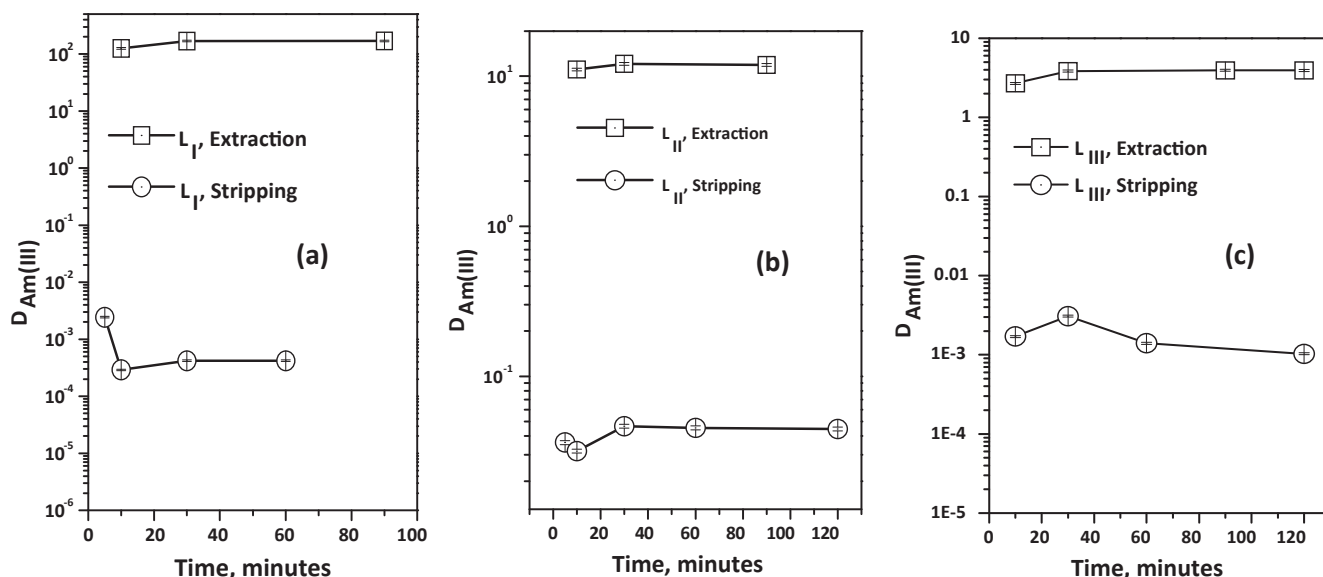
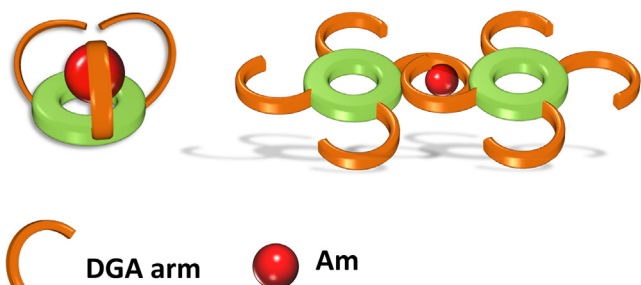


Fig. 2. Extraction and stripping kinetics of Am(III); Feed: 3 M HNO₃; Strip: 1 M AHIBA; [Ligand]: 1 × 10⁻³ M in 5% isodecanol-95% *n*-dodecane.



Scheme 1. Pictorial representation of (a) 1:1 and (b) 1:2 complexes.

tight Pyrex glass tubes and vortexed in a constant temperature bath at 25 ± 0.1 °C. The organic phase contained the extractant solutions (1 mM) in a diluent mixture of 5% isodecanol + 95% *n*-dodecane, while the aqueous solutions contained the required radiotracer in a solution of nitric acid at the desired concentration. The equilibration time was varied as the objective of the solvent extraction experiment was to find out the time required to attain equilibrium *D* values. The tubes were removed from the water bath after the required time interval and were centrifuged at 3000 rpm for 5 min for clear phase separation. Aliquots (usually 100 µL) were taken out from the aqueous as well as the organic phases and were assayed radiometrically as mentioned above. The distribution ratio (*D*) was defined as:

$$D = \frac{\text{Activity per unit volume in the organic phase}}{\text{Activity per unit volume in the aqueous phase}} \quad (1)$$

The mass balance in the solvent extraction studies was better than 2% and the data points with a poor mass balance were rejected.

2.2.3. Supported liquid membrane studies

The supported liquid membrane transport studies were carried out using a two-compartment transport cell with glass flanges within which the PTFE flat sheet membrane was held using stainless steel clips. The PTFE flat sheet membrane was wetted by dipping the same overnight in a Petri dish containing about 2 mL of the extractant solution (1 mM in 5% isodecanol + 95% *n*-dodecane). Prior to the transport experiment, the wet membrane, pores filled with the ligand solution, was removed from the Petri dish and wiped gently with a tissue paper to remove the sticking organic solution. The feed and the receiver compartments

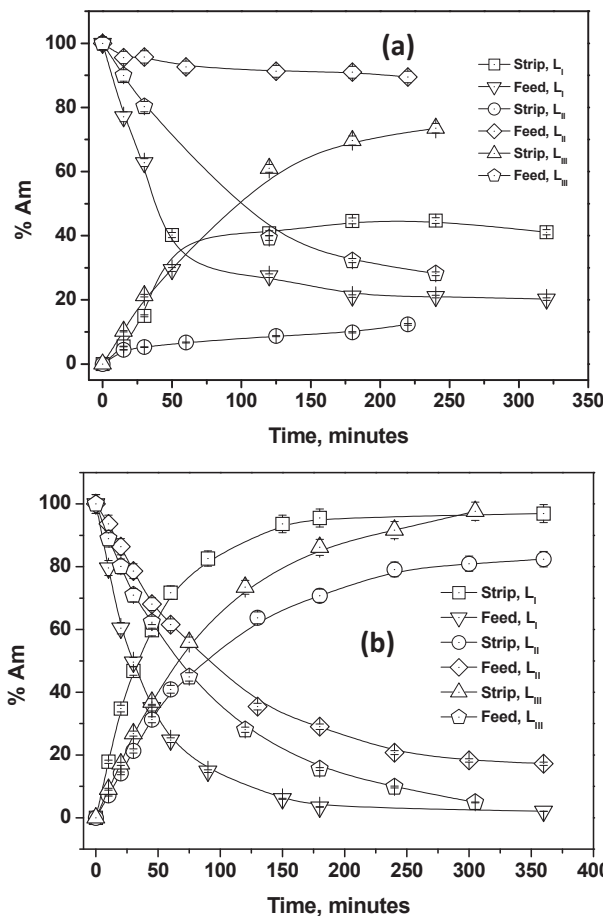


Fig. 3. Transport profile of Am(III) across flat sheet supported liquid membranes from 3 M HNO₃ feed solutions using 1 × 10⁻³ M Bz-T-DGA ligands in 5% isodecanol-95% *n*-dodecane. Stripping solutions in receiver are (a) 0.01 M HNO₃ and (b) 1 M AHIBA.

(20 mL capacity each) were filled with the radiotracer solution in 3 M HNO₃ and 1 M AHIBA, respectively. The compartments of the transport cell were stirred vigorously by Teflon coated magnetic stirring bars at 200 rpm to make the phases homogeneous and also to break the

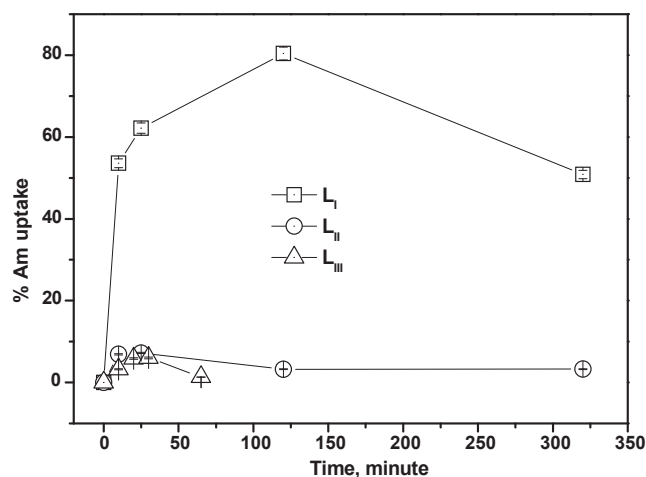


Fig. 4. Uptake profile of Am(III) by a PTFE membrane soaked with the ligand solution; [Ligand]: 1×10^{-3} M in 5% isodecanol-95% *n*-dodecane; weight: L_I 2.9 ± 0.1 mg, L_{II} 3.1 ± 0.1 mg, L_{III} 3.0 ± 0.1 mg.

aqueous diffusion layers close to the membrane surface. Aliquots were removed from the feed and the receiver compartments at regular intervals to get an idea on the mass transfer. The %transport of the metal ion from the feed to the receiver compartment was calculated using the following equation:

$$\% \text{Transport} = \frac{C_{r,t}}{C_{f,0}} \times 100 \quad (2)$$

where $C_{r,t}$ and $C_{f,0}$ are the concentration of the radionuclide at the receiver phase at time t and that of the radionuclide at the source phase at the start of the experiment ($t = 0$). The permeability coefficient (P) was calculated from the following equation:

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

where A is the active transport surface area, V is the total volume of the feed solution, while C_t and C_0 are the concentration of the metal ion in the source phase at time t and at initial $t = 0$, respectively. The active transport area is given by the product of the exposed membrane area (4.90 cm^2) and porosity (64%). For the present set of PTFE membrane filters, A is 3.14 cm^2 , while V is 20 mL. With the values of A and V known, the permeability coefficient for a given metal ion was obtained from the negative slope of straight line plots between $\ln(C_t/C_0)$ vs ' t '. The SLM transport studies were carried out at ambient temperature ($24 \pm 1^\circ \text{C}$).

3. Results and discussion

3.1. Solvent extraction studies

There was negligible extraction ($D < 0.0001$) of the metal ion

Table 1

Transport data of actinide across flat sheet supported liquid membrane with [Ligand]: 1×10^{-3} M in 5% isodecanol-95% *n*-dodecane; Feed: 3 M HNO_3 ; Receiver: 1 M AHIBA; data at 2 h.

Membrane	L_I		L_{II}		L_{III}	
	% in Feed	% in Strip	% in Feed	% in Strip	% in Feed	% in Strip
Am(III) ^a	10.6 ± 0.3	87.7 ± 2.6	39.1 ± 1.2	60.5 ± 1.8	29.3 ± 0.9	72.2 ± 2.2
Pu(IV) ^b	52.6 ± 1.6	18.4 ± 0.5	45.9 ± 1.4	30.9 ± 0.9	33.0 ± 1.0	59.0 ± 1.8
U(VI) ^a	98.7 ± 3.0	< 2	99.4 ± 3.0	< 2	98.3 ± 2.9	< 2

^a Mass balance (total of feed and receiver phase counts) close to 100%.

^b Mass balance in the range of 92–71%.

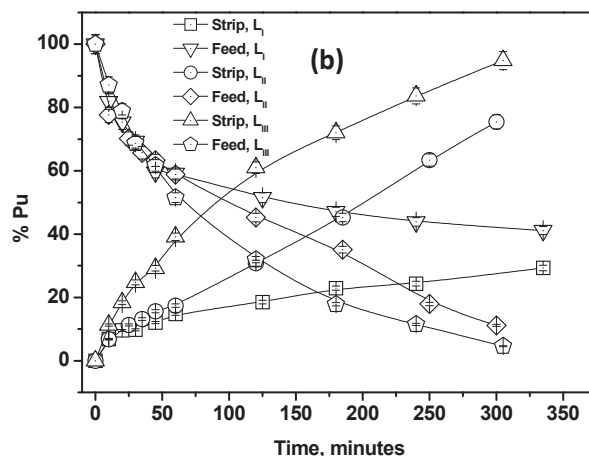
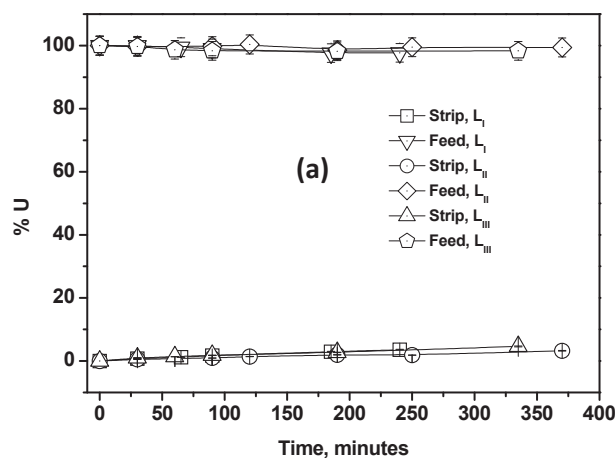
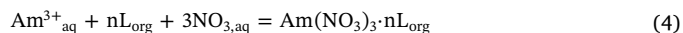


Fig. 5. Transport profile of (a) U(VI) and (b) Pu(IV) across flat sheet supported liquid membranes; Feed: 3 M HNO_3 ; Strip: 1 M AHIBA, [Ligand]: 1×10^{-3} M in 5% isodecanol-95% *n*-dodecane.

when the diluent mixture of 5% isodecanol + 95% *n*-dodecane without any extractant was contacted with solutions of Am^{3+} in 3 M HNO_3 . On the other hand, the extraction of the metal ion increased enormously as the D values of Am were obtained as 170, 11.9 and 3.9 in the presence of 1×10^{-3} M ligand solutions of L_I , L_{II} and L_{III} , respectively. This suggested strong complexation of the metal ions though their extraction efficiencies were widely different. It is reported [13] that the following mechanism is operative for Am^{3+} extraction:

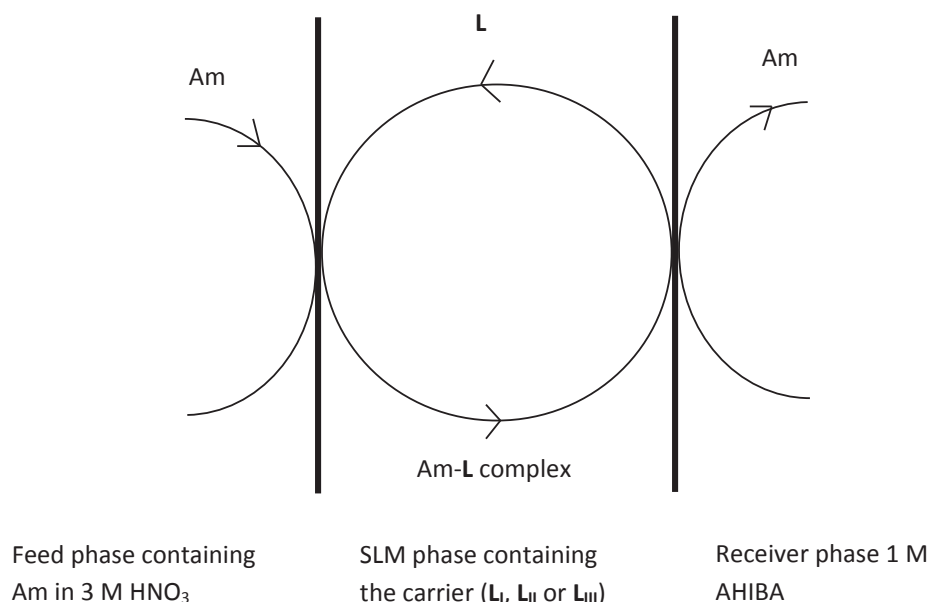


where L represents the Bz-T-DGA ligands used in the present study, n the number of ligands associated in the extracted species and the subscripts 'aq' and 'org' represent the species present in the aqueous and the organic phases, respectively. A previous report suggested [12] that two molecules of the Bz-T-DGA are associated with the extracted

Table 2

Transport data of Am(III) across flat sheet supported liquid membrane with [Ligand]: 1×10^{-3} M in 5% isodecanol-95% *n*-dodecane; Feed: 3 M HNO₃; Receiver: 1 M AHIBA; data at 2 h.

Day	L _I			L _{II}			L _{III}		
	% in Feed	% in Strip	$P \times 10^3$ (cm/s)	% in Feed	% in Strip	$P \times 10^3$ (cm/s)	% in Feed	% in Strip	$P \times 10^3$ (cm/s)
1	10.6 ± 0.3	87.7 ± 2.6	1.94 ± 0.06	39.1 ± 1.2	60.5 ± 1.8	0.76 ± 0.03	29.3 ± 0.9	72.2 ± 2.2	1.04 ± 0.01
2	10.7 ± 0.3	87.8 ± 2.6	2.07 ± 0.13	65.1 ± 1.9	35.0 ± 1.0	0.30 ± 0.01	40.8 ± 1.2	59.0 ± 1.8	0.73 ± 0.01
6	72.9 ± 2.2	29.5 ± 0.9	1.09 ± 0.01	84.3 ± 2.5	18.1 ± 0.5	0.09 ± 0.01	59.1 ± 1.8	39.9 ± 1.2	0.38 ± 0.01



Scheme 2. Transport mechanism for Am(III) transport using Bz-T-DGA (L) ligands in 5% isodecanol-95% *n*-dodecane as the carrier.

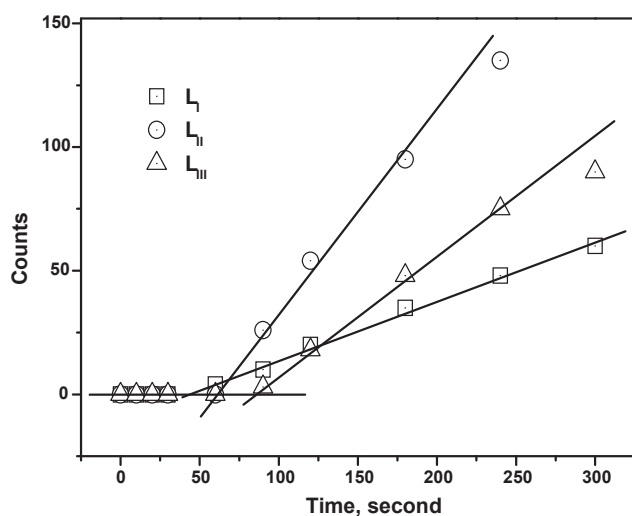


Fig. 6. Lag-time plot of Am(III): Feed: 3 M HNO₃; Strip: 1 M AHIBA, [Ligand]: 1×10^{-3} M in 5% isodecanol-95% *n*-dodecane; Support: 0.45 μ PTFE.

Table 3

Diffusion coefficient of Am(III); [Ligand]: 1×10^{-3} M in 5% isodecanol-95% *n*-dodecane; Feed: 3 M HNO₃; Receiver: 1 M AHIBA.

Membrane	t_{lag} , s	D_{eff} , cm ² /s
L _I	43 ± 1	$(1.58 \pm 0.04) \times 10^{-7}$
L _{II}	86 ± 1	$(7.93 \pm 0.09) \times 10^{-8}$
L _{III}	61 ± 1	$(1.12 \pm 0.02) \times 10^{-7}$

species making it as Am(NO₃)₃·2L_{org} for L_{II} and L_{III} in a molecular diluent. In another report [13], such ML₂ type species were reported to be extracted for all the three ligands. In view of this, the extracted species of ML₂ will be considered throughout this paper.

As reported previously [12], the extraction efficiency followed the trend: L_I > L_{III} > L_{II}. The extraction kinetics data are plotted in Fig. 2, which indicate that about 30 min was enough for attaining extraction equilibrium. Though a pre-organized structure of the ligand is expected to form a complex through the three DGA pendent arms instantaneously (Scheme 1), it is not the case. Apparently, the binding of the metal ions may be to two molecules of the extractant [13], which is possible through the participation of one DGA arm each from the two ligands as shown in Scheme 1 and this may be the reason for the relatively slow attainment of extraction equilibrium. On the other hand, the stripping kinetics was rather fast and only 10 min were needed for quantitative stripping of the metal ion. The stripping efficiency of AHIBA for the three different Bz-T-DGA ligands followed the trend: L_{III} > L_{II} > L_I. The solvent extraction studies indicate that though the extraction of the metal ion from the feed phase into the SLM is rather slow, it may not be reflected in the transport data as the *D* values are quite high. On the other hand, rapid back extraction into the receiver phase suggested good transport efficiency as the carrier extractant is readily available for one more cycle of metal ion transport from the feed into the SLM phase.

3.2. Transport studies

3.2.1. Nature of the stripping solution

Studies on the transport of Am³⁺ were carried out with the three Bz-T-DGA ligands L_I-L_{III} as the carrier extractant, while keeping 3 M HNO₃

Table 4
Comparison of DGA-based extractants for Am³⁺ ion transport from 3 M HNO₃ feeds using PTFE flat sheet supported liquid membranes.

Extractant	Extractant concentration	Receiver	Am transport (3 h)	Reference
TODGA ^a	2.9 × 10 ⁻³ M	0.01 M EDTA	15%	21
T-DGA ^a	2.9 × 10 ⁻³ M	0.01 M EDTA	ca. 97%	21
TREN-DGA ^b	4 × 10 ⁻³ M	0.01 M HNO ₃	ca. 40%	22
TPAMTEB ^{b,c}	6.6 × 10 ⁻⁴ M	0.01 M HNO ₃	ca. 80%	23
L _I	1.0 × 10 ⁻³ M	1 M AHIBA	95.5	Present work
L _{II}	1.0 × 10 ⁻³ M	1 M AHIBA	70.7	Present work
L _{III}	1.0 × 10 ⁻³ M	1 M AHIBA	86.2	Present work

^a In 10% isodecanol-90% *n*-dodecane.

^b In 5% isodecanol-95% *n*-dodecane.

^c The ligand contains isopentyl substituents.

as the feed. Two different strippants, viz. 0.01 M HNO₃ and 1 M AHIBA, were used as the strippant solution in the receiver compartment and the data are compiled in Fig. 3. With 0.01 M HNO₃ as the strippant in the receiver phase, the transport efficiency as detected from disappearance from the feed phase followed the trend: L_I > L_{III} > L_{II} which was surprisingly different from the transport efficiency as detected from the receiver phase as: L_{III} > L_I > L_{II}. Though the mass balance, as defined by the sum of the Am activity in the feed and the receiver phases, was good for L_{II} and L_{III}, it was about 40% off for L_I. Apparently, the Am³⁺ uptake from the feed into the SLM phase was fast for L_I, while the diffusion inside the membrane was slow suggesting a huge chunk of the activity being trapped inside the SLM. This was confirmed by counting the SLM after the transport experiment. The uptake kinetics was proven by carrying out a sorption experiment while using pieces of the SLM impregnated with the carrier extracts. As shown in Fig. 4, the uptake kinetics was far superior for L_I as compared to L_{II} or L_{III}.

It was interesting to note that while 0.01 M HNO₃ as the stripping agent in the receiver compartment effected relatively poor transport of Am³⁺ (Fig. 3a), changing the strippant to AHIBA resulted in a much improved metal ion transport (Fig. 3b). This is in sharp contrast to our observation with other analogous extractants where there was no difference seen with the nature of the stripping agents [23]. Comparative transport data of Am³⁺ pertraction through the PTFE membranes using the three extractants are presented in Table 1. As seen from the table, the transport efficiency of the Bz-T-DGA ligands with 0.01 M HNO₃ followed the trend: L_I > L_{III} > L_{II}, which marginally changed to L_I > L_{III} > L_{II} with AHIBA as the strippant, suggesting a sharp rise in the transport efficiency even with L_{II}. Furthermore, the mass balance (sum of Am activity in the feed and the receiver) improved dramatically to suggest no trapping of the Am activity inside the SLM. We have also carried out acid transport studies (Supporting Information; Table S1) which indicated negligible (< 0.03% in 3 h) transport of the nitric acid into the receiver compartment. In view of this, the transport studies were carried out with 1 M AHIBA in all subsequent studies.

3.2.2. Transport of other actinide ions

Apart from Am, many radioactive feeds from nuclear fuel cycle operations also contain U and Pu and hence, it was of interest to carry out the transport studies using these metal ions. In view of the most stable oxidation states being +6 and +4 for U and Pu, respectively, the next set of transport studies was carried out using UO₂²⁺ and Pu⁴⁺ ions. The results of the transport studies involving these metal ions are given in Fig. 5. As seen in Fig. 5a, the transport of UO₂²⁺ ion is very poor and only 2.9%, 1.9% and 2.7% are transported to the receiver phase with L_I, L_{II} and L_{III}, respectively, even after 3 h when the Am transport is 95.5%, 70.7% and 86.2% in the same time period using the same set of extractants. On the other hand, Pu⁴⁺ ion transport was quite significant (Fig. 5b) with all the three carrier extractants. However, as seen from Table 2, the mass balance for Pu is not satisfactory and about 10–15% mass loss was observed, attributed to the metal ion being trapped inside the SLM in a manner similar to that observed for

Am³⁺ with 0.01 M HNO₃ as the stripping solution. Table 2 gives the permeability coefficient data for Am³⁺ transport obtained from the straight line plots of ln(C_v/C₀) vs time (Supporting Information).

3.2.3. Determination of diffusion coefficients

The diffusion coefficient is a measure of the transport efficiency of the extracted complex in the SLM phase. As mentioned above in section 3.1, species of the type Am(NO₃)₃·2L_{org} are extracted which makes it a bulky structure. This is the reason for the slow transport of the species across the SLM. The transport mechanism can be simplistically put in three distinct steps, viz. (i) extraction of the metal ion at the feed – membrane interface, (ii) diffusion of the extracted species inside the membrane phase and (iii) back extraction of the metal ion at the membrane – receiver interface. Fig. 2 shows relatively fast extraction (from the feed phase) and stripping of the metal ion (from the organic phase), suggesting that the rate-determining step in the transport profiles is due to the slow diffusion of the extracted species, Am(NO₃)₃·2L_{org}. The extraction mechanism can be pictorially represented by Scheme 2. The effective diffusion coefficient (D_{eff}) can be determined by the lag time method [26] described by the following equation:

$$D_{\text{eff}} = \frac{d_0^2 \varepsilon}{6t_{\text{lag}}} \quad (5)$$

where d_0 is the thickness (cm) of the membrane, ε is the membrane porosity and t_{lag} is the lag-time (seconds). Experimental results on the metal ion transport as detected in the receiver compartment as a function of time is presented in Fig. 6 and the calculated D_{eff} data are presented in Table 3. As shown in the table, the diffusion coefficient values followed the trend L_I > L_{III} > L_{II}, which is same as the transport efficiency of the extractants.

3.2.4. Comparative transport performance

As mentioned above, several tripodal DGA ligands have been studied by us for their SLM transport efficiency. It is imperative to make a comparative evaluation of the transport behavior of the present set of extractants with those reported earlier. Table 4 gives the transport data of these extractants along with that reported with TODGA, a well-studied DGA ligand by many research groups around the world [4]. As seen from the table, the transport data indicate that the highest transport efficiency is obtained with the present set of extractants, especially with L_I. This is to note that though the extractant concentration is marginally higher than the analogous extractant used in our recent study [23], the transport efficiency involving L_I is significantly larger (Table 4). Furthermore, other tripodal DGA extractants such as T-DGA and TREN-DGA are found to be markedly inferior in their transport efficiencies (Table 4). This suggests that the present transport system can be employed efficiently for radioactive waste remediation indicating minimum ligand inventory resulting in maximum transport.

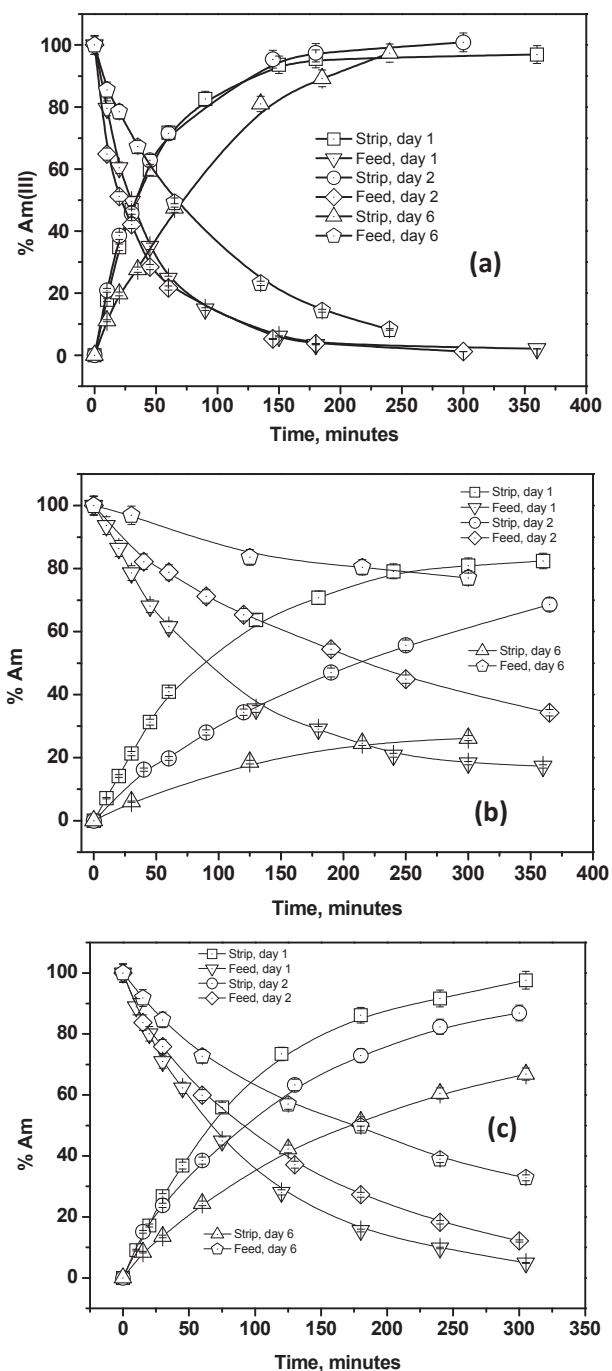


Fig. 7. Stability of the SLMs for Am transport studies using (a) L_I , (b) L_{II} and (c) L_{III} . Feed: 3 M HNO_3 ; Strip: 1 M AHIBA, [Ligand]: 1×10^{-3} M in 5% isodecanol-95% *n*-dodecane; Support: 0.45 μ PTFE.

3.2.5. Membrane stability

Any long term application of a supported liquid membrane system requires that the stability of the membrane should be reasonably good. There are a host of factors responsible [27] for the long term stability of the SLM which include (i) trans-membrane pressure difference, (ii) solubility of the carrier extraction in the aqueous phases, (iii) wetting of support pores by the aqueous phase sometimes leading to water channel formation, (iv) pore blockage by either emulsion formation or by solid precipitation, etc. We have found that the nature of the diluent used in the carrier solvent also has a significant role. While *n*-dodecane is reported to have a better SLM stability, use of chloroform and nitrobenzene led to a poor stability of the SLMs [28,29]. The diluent

mixture of *n*-dodecane and isodecanol has been used in some studies and has been reported to lead to reasonably good SLM stability [21].

The SLM stability studies were carried out by using the same SLM over a period of six days while replacing the feed and the receiver solutions each time. The results of the transport behavior of Am^{3+} with the three Bz-T-DGA extractants L_I – L_{III} are presented in Fig. 7. The transport rates of the metal ion decreased drastically over the time period for both L_{II} and L_{III} , while the SLM, containing L_I , displayed a better stability. The permeability coefficient (P) values of the stability studies are listed in Table 2 and though the P value obtained on the 6th day of continuous operation with the L_I -containing SLM has become nearly half the value obtained on the 1st day, the transport efficiency is still satisfactory. Regarding the SLMs containing L_{II} and L_{III} , it appears that the presence of hydrophilic amide groups (L_{II}) and ether atoms (L_{III}) render partial leaching of these ligands into the aqueous phase. In summary, this study suggested that the L_I -containing SLM can be employed for the remediation of radioactive feeds containing Am over the period of several days up to maybe one week.

4. Conclusions

In conclusion, though multiple DGA extractants are far superior to the commonly employed DGA extractants such as TODGA, the presence of substituents and the spacer length play a very relevant role in the metal ion extraction/transport. Though increasing spacer length is expected to induce more flexibility, the coordination apparently involves more bending of the pendent arms and hence, is not favourable. On the other hand, though substituents attached to the benzene ring can enhance the lipophilicity of the complex thereby enhancing the extraction possibility, linear short alkyl chains are preferred as it poses least stereochemical constraints during metal ion coordination. In view of this, ligand L_I showed better extraction and higher transport rates than the extractants L_{II} and L_{III} as well as the Bz-T-DGA ligands with isopentyl groups reported in a recent study [23].

The poor transport of U can be used for the separation of Am and Pu from a mixture of actinides containing Am, Pu and U. The reasonably good SLM stability in case of L_I indicates that the transport system has potential in the remediation of radioactive wastes. It is required to scale up using hollow fiber contactors for a more efficient mass transfer rate and improved throughput.

Acknowledgement

Two of the authors (BM and PKM) are thankful to Dr. P.K. Pujari, Head, Radiochemistry Division, Bhabha Atomic Research Centre, for his keen interest and constant encouragement.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.115846>.

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