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Pertraction of americium(III) through supported liquid membranes containing benzene-centered tripodal diglycolamides (Bz-T-DGA) as an extractant/carrier

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ABSTRACT

Two novel benzene-centered tripodal diglycolamide (Bz-T-DGA) ligands with affinity for actinide ions were employed for the solvent extraction as well as flat sheet supported liquid membrane (SLM) transport of trivalent americium (Am^{3+}), considered as one of the most important minor actinide ions in the high level waste (HLW). Bz-T-DGA ligands with isopentyl substituents and varying spacer lengths in the DGA arms, viz. methylene (TPAMTEB) and ethylene (TPAETEB) groups were employed for actinide extraction for possible application in nuclear waste remediation. With both the ligands, the extraction of Am^{3+} increased with the concentration of nitric acid (1–6 M HNO_3), the distribution ratio (D) values being 16.6 and 3.71 at 3 M HNO_3 and 35.1 and 44.4 at 6 M HNO_3 for 6.6×10^{-4} M TPAMTEB and TPAETEB, respectively taken in a 5% isodecanol and 95% *n*-dodecane diluent mixture. A stripping study showed a relatively slow stripping of Am^{3+} from the loaded membrane with TPAETEB even in the presence of a complexing agent. Am^{3+} transport rates were rather slow in polypropylene (PP) flat sheets as compared to previous, analogous studies suggesting slow migration of the complexed ions. Am^{3+} transport was 4.8 times slower in TPAETEB than in TPAMTEB with diffusion coefficients of 4.5×10^{-8} and 2.16×10^{-7} cm^2/s, respectively.

1. Introduction

The high level waste (HLW) emanating from the spent fuel reprocessing by the PUREX (Plutonium Uranium Redox Extraction) process contains almost the entire fission and activation products generated during the fission reaction. Though most of the fission and activation products are short-lived, some of the long-lived fission product radionuclides such as ^{93}Zr (1.3×10^6 y), ^{99}Tc (2.1×10^5 y), ^{107}Pd (6.5×10^6 y), ^{129}I (1.57×10^7 y), ^{135}Cs ($t_{1/2}$: 2.0×10^6 y), and a host of minor actinides, viz. Am, Np, Cm, are of great environmental concern due to their long half-life ranging up to millions of years (Pfennig et al., 2006). The minor actinides are also considered hazardous due to their high radiotoxicities (IAEA, 2004). Therefore, it is proposed to separate the minor actinides from the HLW prior to the vitrification of the latter in glass matrices, considered a standard waste management practice, and burial in deep geological repositories. If these minor actinides are not separated from the HLW, it would require prolonged surveillance of the vitrified waste blocks for a long period (up to millions of years) which itself is a huge burden on the economy.

The strategy to separate minor actinides from the HLW is termed as 'Actinide Partitioning' (IAEA, 2004; Ansari et al., 2011) and it employs tailor made ligands with very high extraction efficiencies for the minor actinides. Among the different ligands studied world-wide for the partitioning of the minor actinides such as CMPO (carbamoylmethyl

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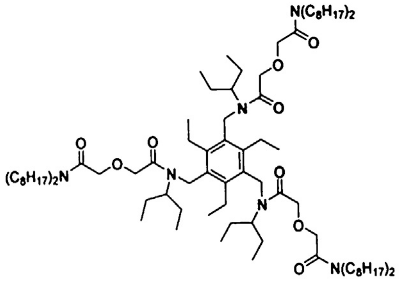
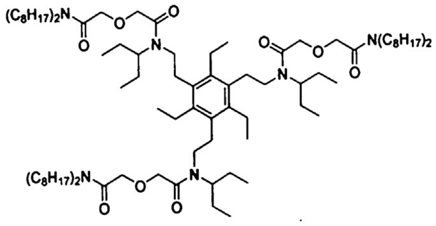


(a) TPAMTEB



(b) TPAETEB

Fig. 1 – Structural presentation of the two Bz-T-DGA ligands TPAMTEB (a) and TPAETEB (b).

phosphine oxide), DIDPA (di-iso-decyl phosphoric acid), TRPO (trialkyl phosphine oxide), etc. (Ansari et al., 2011), diamides are found to be very promising extractant in view of the factors such as (i) their ability to extract minor actinides from HLW solution, (ii) efficient back extraction, (iii) complete incinerability and (iv) innocuous nature of their radiolytic degradation products (Cuillerdier et al., 1993). Subsequent research and development efforts have indicated that incorporating an etheric oxygen atom in between the two amide groups increases the extraction efficiency for the minor actinides due to the tridentate nature of the ligand, termed as diglycolamide (DGA). *N,N,N′,N′*-tetra-*n*-octyl diglycolamide, (TODGA), one of the most studied DGA ligands, has shown very high extraction efficiency for the trivalent actinide and lanthanides from acidic feeds (Ansari et al., 2012; Gujar et al., 2010; Sasaki et al., 2001). Several studies have indicated that TODGA extracts the trivalent actinide/lanthanide ions preferentially over tetra- as well as hexa-valent actinide ions (Ansari et al., 2005) by forming reverse micellar structures in non-polar diluents in the presence of nitric acid (Jensen et al., 2007; Pathak et al., 2013). Though the exact nature of binding is not known, it is considered that multiple DGA moiety participation may be taking place as 3–4 TODGA molecules are reported to participate in the formation of the reverse micellar structure (Jensen et al., 2007). In view of this, we have investigated multiple DGA–functionalized ligands, containing 3–4 DGA arms, for actinide ion extraction from acidic feeds. Our studies with DGA-functionalized calix[4]arenes (Iqbal et al., 2012; Mohapatra et al., 2012, 2013) and several tripodal DGA ligands (Janczewski et al., 2008; Mohapatra et al., 2011a; Leoncini et al., 2016) have shown encouraging results. Recently, several benzene-centered tripodal DGA ligands (Bz-T-DGA) have been evaluated for actinide ion extraction and the results were highly encouraging (Leoncini et al., 2017; Ansari et al., 2017a). In order to study the effect of substituents and also that of the spacer length, two novel Bz-T-DGA ligands were synthesized with iso-amyl groups and also with methylene and ethylene spacers termed as TPAMTEB (Fig. 1a) and TPAETEB (Fig. 1b), respectively.

Though these ligands are expected to be highly efficient for the extraction of the trivalent actinide/lanthanide ions, solvent extraction studies require large inventories. However, supported liquid membrane-based separation methods have many advantages, which include a very low ligand inventory (Mohapatra and Manchanda, 2003; Kocherginsky et al., 2007; Boyadzhiev and Lazarova, 1995; Sulaiman et al., 2018; Sulaiman and Othman, 2017). Though many DGA and multiple DGA ligands are studied for their extraction and liquid membrane transport behaviour, the science is still evolving and newer ligands with better extraction/transport properties are needed. Furthermore, these new ligands can also have interesting structural properties in their uncomplexed as well as complexed forms. In view of this, the two Bz-T-DGA ligands mentioned above were evaluated for the extraction of actinide ions and were subsequently subjected to studies involving flat sheet supported liquid membranes.

The present study deals with a detailed investigation on the extraction of U(VI), Pu(IV) and Am(III) by both TPAMTEB and TPAETEB dissolved in a 5% isodecanol-95% *n*-dodecane diluent mixture. In view of the importance of the separation of Am from HLW, subsequent studies were focused on the transport of Am(III) using these two ligands as the carrier extractant using PP (polypropylene) flat sheets. The different parameters, e.g., effective diffusion coefficient (D_{eff}), permeability coefficient (P), were evaluated for Am(III) by these extractants and the results are compared. The results may be helpful in designing suitable liquid membrane based separation methods for the remediation of environmental samples contaminated with actinide elements such as Am. To the best of our knowledge, no work has been reported regarding the study on the liquid membrane transport of actinide ion (including americium (III)) using any benzene-centered tripodal DGA.

2. Experimental

2.1. *Reagents*

The benzene-centered tripodal DGAs TPAMDGA and TPAEDGA (Fig. 1) were synthesized by the reaction of the corresponding 1,3,5-tris(*N*-(1-ethylpropyl)aminoalkyl)-2,4,6-triethylbenzene derivatives with *p*-nitrophenyl-acitvated DGA (Ansari et al., 2018). The ligands were characterized by NMR (Nuclear Magnetic Resonance) and HR-MS (High Resolution Mass Spectrometry). *n*-Dodecane (99%, Lancaster, UK) and isodecanol (99%, SD Fine Chemicals, India) were used as procured. Polypropylene (PP) membrane (pore size: 0.45 μm, porosity: 80%, thickness: 9×10^{-3} cm) were obtained from Sterlitech, USA. Suprapur HNO_3 (Merck, Germany; 65%) was used for the preparation of dilute HNO_3 using Millipore water at a given dilution, which was standardized volumetrically using phenolphthalein (Merck) as the indicator. All the other reagents were of AR grade. Ligand solutions (6.6×10^{-4} M) were prepared using 5% isodecanol + *n*-dodecane as the diluent mixture. Addition of isodecanol (which acts as a phase modifier) to *n*-dodecane increases the polarity of the medium and therefore, increases the solubility of the ligands as otherwise the ligands of this class have limited solubility in pure *n*-dodecane (Iqbal et al., 2012).

2.2. *Radiotracers*

^{233}U, Pu (mainly ^{239}Pu) and ^{241}Am were used from laboratory stock solutions after checking their radiochemical purities. ^{233}U was purified from its daughter products using a reported method based on ion-exchange (Rattan et al., 1981). Pu (mainly ^{239}Pu) was purified from its decay product (mainly ^{241}Am) by the HTTA (2-thenoyltrifluoroacetone) solvent extraction method (Sajun et al., 1981), while ^{241}Am tracer was purified from ^{237}Np by selective solvent extraction of Np using HTTA as described elsewhere (Mohapatra, 1993). Radiochemical purity of the solutions was checked by alpha spectrometry as well as by gamma ray spectroscopy.

Since Pu can co-exist in different oxidation states in dilute HNO_3, adjustment of its oxidation state to the +4 state was freshly done using $NaNO_2$ (Sajun et al., 1981). To a Pu solution in 1 M HNO_3, a few drops of $NaNO_2$ solution (5×10^{-3} M) were added followed by its extraction into 0.5 M HTTA in xylene.

The extracted Pu was stripped from the organic phase using 7 M HNO_3 (Mohapatra et al., 2002) and was used as the Pu^{4+} stock solution. Typically, the concentration of Pu, Am and U taken for the studies were about 10^{-6} M, 10^{-7} M and 10^{-5} M, respectively.

2.3. *Methods*

2.3.1. *Distribution ratio measurement*

Distribution ratio (D) measurements were done by mixing equal volumes (usually 1 mL) of an organic phase containing 6.6×10^{-3} M ligand in 5% isodecanol-95% *n*-dodecane and an aqueous phase (spiked with the radiotracer) containing the required concentration of HNO_3 in Pyrex glass stoppered equilibration tubes in a thermostated water bath maintained at 24 ± 1 °C for nearly 60 min. As shown in Fig. 2, only 10 min were needed to attain equilibrium D values and hence, the equilibration time of 60 min was considered sufficient. Subsequently, the tubes were centrifuged at 5000 rpm for 3 min and aliquots (100 μL) were removed from both phases for radiometric assay. ^{241}Am was assayed by gamma ray counting employing a NaI(Tl) well type scintillation counter (Para Electronics) coupled with a multichannel analyser (ECIL, India), whereas Pu and ^{233}U were assayed using a liquid scintillation counter (Hidex, Finland) employing a toluene-based extractive scintillator. All the experiments were done in duplicate and the relative standard deviation of the data was found to be within 5%. The distribution ratio (D) was determined using Eq. (1).

$$D = \frac{[C]_o}{[C]_{Aq.}} \qquad (1)$$

where $[C]_O$ and $[C]_{Aq}$ are the concentration of the metal ion (expressed as counter per minute per unit volume) in the organic and the aqueous phases, respectively.

2.3.2. *Transport studies*

The supported liquid membrane (SLM) studies were carried out using a PP membrane whose pores were filled with the carrier ligand solution (6.6×10^{-3} M ligand in 5% isodecanol-95% *n*-dodecane). The membrane was soaked in the ligand solution for 15 min (standardized in a previous study (Ansari et al., 2006)) prior to the start of the experiment. Subsequently, the membrane was taken out from the solution using a tweezer and the excess ligand solution was wiped out from the surface of the membrane using tissue paper. It was mounted in between the two-compartment transport cell and fixed firmly using parafilm to prevent leakage of the solutions from the transport cell. The volume of each compartment of the transport cell was 20 mL and while one of the compartments was filled with the acidic feed solution containing the required radiotracer, the other compartment was filled with the strippant solution. The solutions of both the compartments were stirred at 200 rpm using a magnetic stirrer equipped with precise speed control which ensured a minimal thickness of the aqueous boundary layer (Sriram et al., 2000). Transport of the radionuclide from the source phase to the receiver phase was monitored at different time intervals by assaying the radioactivity of the source and the receiver phases. The SLM studies were carried out at ambient temperature (24 ± 1 °C) and the duplicate runs were reproducible within ±5%.

2.3.3. *Transport equations*

The permeability coefficient (P), which measures the speed of transport of the metal ion, was determined from the slope of the linear fitted plot of $\ln(C_t/C_0)$ vs. time by using the following equation:

$$-\ln\left(\frac{C_t}{C_0}\right) = P\left(\frac{A}{V}\right).t \qquad (2)$$

where A is the effective area (4.16 cm^2) of the membrane (determined from the exposed area of the membrane (Q) multiplied by the porosity (ε) of the membrane), 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 cumulative percentage transport of the radionuclide to the receiver phase at a given time t was determined using the following formula:

$$\%\,\text{Transport} = \frac{C_{r,t}}{C_{f,0}} \times 100 \qquad (3)$$

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). Similarly, the percentage removal of the radionuclide from the source phase was determined using the following formula:

$$\%\,\text{Removal} = \frac{(C_{f,0} - C_{f,t})}{C_{f,0}} \times 100 \qquad (4)$$

where $C_{f,t}$ is the concentration of the radionuclide in the source phase at time t. The other symbols in Eq. (4) stand the same meaning as given above. Both equations were used for obtaining the transport data.

3. Results and discussion

3.1. *Solvent extraction studies*

3.1.1. *Extraction kinetics and stripping*

It is important to study the kinetics of the extraction of a metal ion in solvent extraction studies because it gives an idea about the attainment of equilibrium which varies in different extraction systems. For example, around 10 min were required to get equilibrium D_{Am} values when the extraction of Am(III) from the aqueous feed (3 M HNO_3) was studied using TODGA (Panja et al., 2012), whereas nearly 50% higher equilibration time was needed for the same purpose when a multiple DGA-functionalized ligand (Ansari et al., 2017b) was used as the extractant. The slower kinetics in the latter case was attributed to stereochemical constraints associated with the binding of more than one DGA groups in the concerning ligand due to the formation of relatively bulkier metal/ligand complexes. In the present study, the extraction kinetics of Am(III) was investigated with both TPAMTEB and TPAETEB at 3 M HNO_3 as the feed acid concentration. The plots of D_{Am} versus equilibration time are given in Fig. 2 showing that around 10 min were required to reach the equilibrium D_{Am} value in both cases which is comparable to the time required with TODGA as reported previously (Panja et al., 2012). The back extraction kinetics, i.e., the kinetics of stripping of the loaded Am(III) from the organic phase was investigated in the presence of dilute nitric acid (0.01 M HNO_3) as the strippant. As can be seen from Fig. 2, around 10 min were required to reach the equilibrium D_{Am} value upon stripping of metal ion

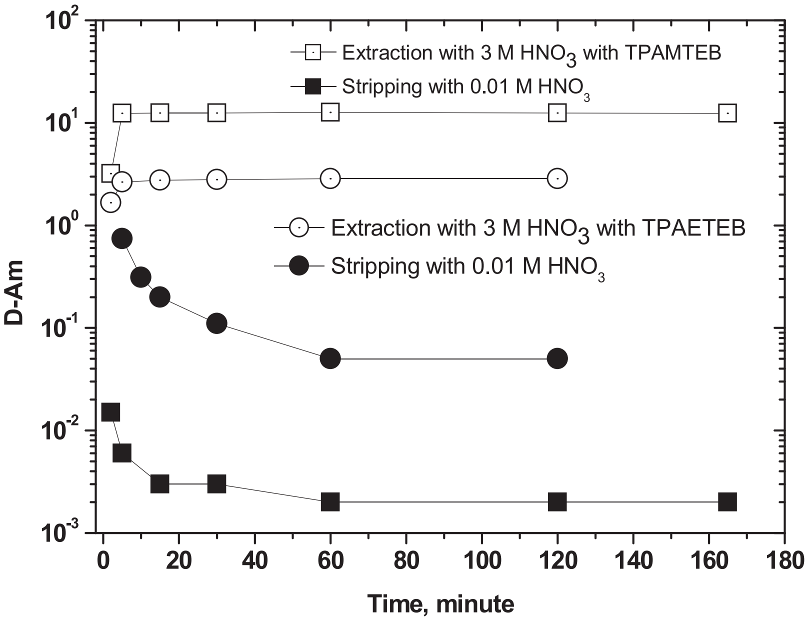


Fig. 2 – Extraction and stripping kinetics of Am^{3+} using 3 M and 0.01 M HNO_3, respectively. Ligands: 6.6 × 10^{-4} M Bz-T-DGA ligands in 5% isodecanol-95% *n*-dodecane. Temperature: 25 °C.

loaded TPAMTEB, whereas it took about 60 min for TPAETEB. The relatively slower back extraction kinetics with TPAETEB may be due to the formation of a cage like structure around the metal ion involving all three of its relatively ‘relaxed’ DGA moieties as compared to that with TPAMTEB which has a rather ‘stressed’ structure due to the shorter methylene spacer groups. The relatively fast forward extraction and back extraction kinetics involving TPAMTEB indicate that this ligand can be used in SLM for metal ion transport studies. It was also required to understand the transport behaviour of Am^{3+} ion using TPAETEB as the carrier extractant as well. However, before carrying out the SLM transport studies, the extraction behaviour of $Am^{3+}$was studied as a function of the feed HNO_3 concentration.

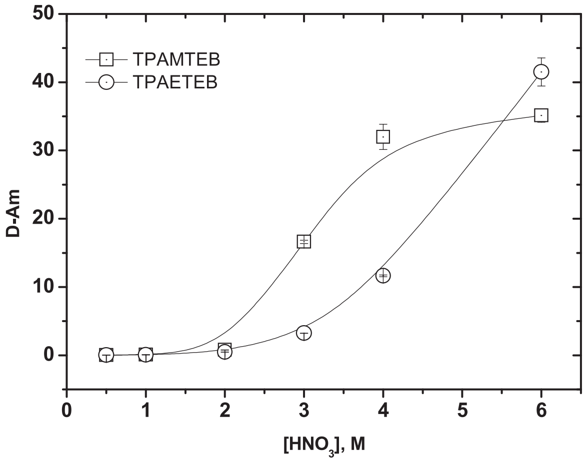
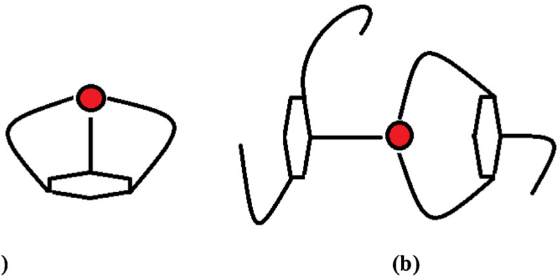


Fig. 3 – Effect of D_{Am} with nitric acid concentration; [Bz-T-DGA] = 6.6 × 10^{-4} M in 5% isodecanol-95% *n*-dodecane. Temperature: 25 °C.



Scheme 1 – Pictorial representation of (a) 1:1 complex where all three DGA arms are binding to the metal ion and (b) 1:2 complex where one DGA from one ligand and two DGA arms from the other one are coordinating.

3.1.2. *Effect of concentration of nitric acid in the feed*

The effect of the HNO_3 concentration on the D_{Am} was investigated with both TPAMTEB and TPAETEB at their fixed concentration, while the HNO_3 concentration of the feed solution was varied from 0.5 M to 6 M. The D_{Am} versus HNO_3 concentration plots are presented in Fig. 3 showing an increasing trend of the D_{Am} values with the HNO_3concentration for both ligands. However, though a monotonous increase in the D_{Am} values was seen for TPAETEB, the profile for TPAMTEB appears less steep at higher HNO_3 concentrations. In addition, the D_{Am} values for TPAMTEB are generally higher than those for TPAETEB in the acidity range studied. In case of TPAMTEB the less steep increase in the D values at higher HNO_3 concentration may be due to a higher acid uptake by the ligand as compared to that with TPAETEB. This preferential acid uptake vis-à-vis metal ion extraction by TPAMTEB can be attributed to binding of the metal ion with either one or two DGA arms, while all the three DGA arms may be binding to Am^{3+} in the case of TPAETEB. This can be explained if one considers a 1:2 M:L complex for TPAMTEB, while an 1:1 complex appears appropriate for TPAETEB (Scheme 1). This model conforms to the higher extraction of the TPAMTEB complex on the basis of a more hydrophobic ML_2 type of complex. The extraction efficiency of the ligands was found to be significantly higher than that with TODGA (D_{Am} = 0.09) under comparable extraction conditions (Panja et al., 2012). In a previous report, a simple C-pivot tripodal DGA yielded a marginally higher D_{Am} value than those reported in the present study (Mohapatra et al., 2011a).

Table 1 – Distribution coefficients of actinides from feed solution at 3 M HNO_3 using 6.6 × 10^{-4} M ligand in 95% *n*-dodecane + 5% isodecanol as the extractant. Temperature: 25 °C.

Ligand	Metal ion	Distribution coefficient
TPAMTEB	Pu^{4+}	25.6 ± 0.8
	UO_2^{2+}	0.060 ± 0.001
	Am^{3+}	16.61 ± 0.25
TPAETEB	Pu^{4+}	11.0 ± 0.1
	UO_2^{2+}	0.010 ± 0.001
	Am^{3+}	3.71 ± 0.01

3.1.3. *Separation behaviour*

In view of the importance of Pu and U in the nuclear fuel cycle, the extraction of U(VI) and Pu(IV) was also studied at 3 M HNO_3 with both ligands and the results were compared with those with Am(III). Table 1 shows the trend being $D_{Pu(IV)} > D_{Am(III)} \gg D_{U(VI)}$, while the metal ion extraction was higher with TPAMTEB than with TPAETEB. The higher $D_{Pu(IV)}$ compared to $D_{Am(III)}$ is due to the higher ionic potential of the former, whereas the very low value of $D_{U(VI)}$ is possibly due to the stereochemical restriction arising from the presence of two axial oxygen atoms on the uranyl ion. Though Am(III) extraction was reported to be higher than that of Pu(IV) in TODGA, when the aqueous phase nitric acid concentration was >2 M (Ansari et al., 2005). It was also reported in the same report that the Pu(IV) extraction was higher than that of Am(III) at <1 M HNO_3. This could be explained on the basis of reverse micellar aggregate formation at nitric acid concentrations >2 M (Jensen et al., 2007) which makes the extraction of Am(III) with ionic radius of 1.09 Å (Shannon, 1976) more effective (Zhu et al., 2004) than that of Pu(IV) with an ionic radius of 0.96 Å (Shannon, 1976). The separation factors (S.F.) of Pu (IV) with respect to Am (III) (S.F. = $D_{Pu(IV)}/D_{Am(III)}$) were found to be 1.5 and 3.0, whereas those of Am(III) with respect to U(VI) (S.F. = $D_{Am(III)}/D_{U(VI)}$) were 276.8 and 371 with TPAMTEB and TPAETEB, respectively. This indicates that if one can convert Pu(IV) into Pu(VI), then it may be possible to selectively extract Am(III) from a mixture containing U, Pu and Am at 3 M HNO_3 using these Bz-T-DGA ligands.

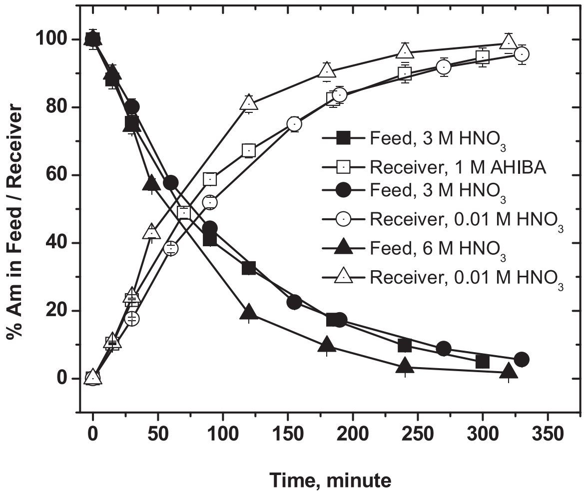


Fig. 4 – Transport of Am(III) using with 6.6 x 10^{-4} M TPAMTEB in 5% isodecanol-95% *n*-dodecane as the carrier; feed: 3 M HNO_3. Temperature: 25 °C.

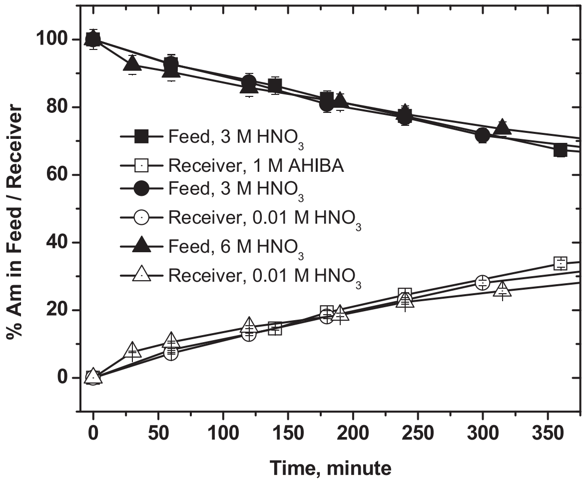


Fig. 5 – Transport of Am(III) using with 6.6 x 10^{-4} M TPAETEB in 5% isodecanol-95% *n*-dodecane as the carrier; feed: 3 M HNO_3. Temperature: 25 °C.

3.2. *Supported liquid membrane studies*

3.2.1. *Effect of feed acidity on the transport of Am(III)*

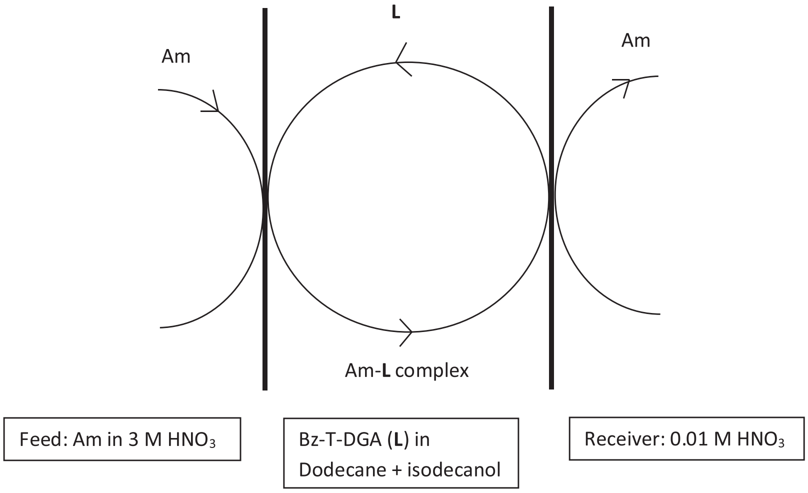
The transport of Am(III) was studied at two different HNO_3 concentrations in the feed phase, i.e. 3 and 6 M with both ligands and the corresponding percentage transport data are given in Table 2. The concentration of nitric acid in the feed phase was not kept lower than 3 M in view of the lower $D_{Am(III)}$ obtained with TPAMTEB and TPAETEB in 5% isodecanol + 95% *n*-dodecane being 0.08 and 0.04 at 1 M HNO_3, respectively. Based on the results presented in Fig. 4 as well as Table 2, the percentage transport of Am(III) in the receiver solution (0.01 M HNO_3) increased marginally at higher HNO_3 concentration of the feed acid in case of TPAMTEB as the carrier ligand. For example, around 93.8% and 98.8% transport of Am(III) was observed after 5 h for the feed HNO_3 concentrations of 3 M and 6 M, respectively. However, when similar experiments were carried out with TPAETEB, the respective Am(III) transport rates were 28.3% and 25.2% (Fig. 5, Table 2). A slight decrease in the transport of Am(III) at higher concentration of HNO_3 with TPAETEB may be due to the higher transport of HNO_3 to the receiver solution at 6 M HNO_3 as the feed. Acid transport studies indicated that after 5 h, around 2.1% of HNO_3 was transported to the receiver side at 6 M HNO_3, whereas 0.4% HNO_3 was transported at 3 M HNO_3. A comparable behavior was obtained for TPAMTEB where around 2.5% HNO_3 was transported to the receiver side at 6 M HNO_3. However, as the stripping kinetics is different for both ligands, it is expected to have a different impact on the transport of Am(III) in the presence of a comparable HNO_3 concentration in the receiver solution. In view of the higher $D_{Am(III)}$ for TPAETEB at 6 M HNO_3, its Am(III) transport is expected to be higher since the acid transport is nearly comparable for both the extractants at 6 M HNO_3 as the feed. However, the significantly lower transport of Am(III) with TPAETEB (as compared to that observed with TPAMTEB) at 6 M HNO_3 as the feed was attributed to a slow stripping kinetics of the ligand with longer spacer groups (vide supra).

The transport of the metal ion through the SLM takes place in three steps, viz. (i) metal ion extraction into the membrane phase at the source-membrane interphase, (ii) diffusion of the metal-ligand complex across the membrane pores, and (iii) stripping of the metal ion at the membrane-receiver interphase (Mohapatra and Manchanda, 2003). A schematic of the mechanism of Am transport is depicted in Scheme 2. As the

Table 2 – Transport data of Am(III) with Bz-T-DGA ligands as carrier extractant (6.6×10^{-4} M ligand in 5% isodecanol-95% *n*-dodecane). Feed: 3 M HNO_3, Receiver: 0.01 M HNO_3. Temperature: 25 °C.

Membrane	Feed acidity, M	% Am(III) in feed at 5 h (24 h)	% Am(III) in strip at 5 h (24 h)	$P_{Am(III)} \times 10^3$ (cm/s)
TPAMTEB	3	7.3	93.8	45.6 ± 0.9
	6	1.7	98.8	68.3 ± 2.2
	3[a]	4.9	94.7	50.6 ± 0.7
TPAETEB	3	71.6 (25.0)[b]	28.3 (74.2)[b]	5.6 ± 0.1
	6	74.4 (25.7)[b]	25.2 (67.7)[b]	4.6 ± 0.3
	3[a]	71.6 (35.6)[b]	29.3 (66.0)[b]	5.5 ± 0.1

[a] Feed: 3 M HNO_3, Receiver: 1 M α-HIBA.
[b] 24 h data.



Scheme 2 – Transport mechanism for Am(III) transport using Bz-T-DGA (L) in Dodecane + isodecanol as the carrier.

kinetics of the extraction of a metal ion into the organic phase is relatively fast with both ligands (vide supra), then the rate of the transport of a metal ion into the receiver phase depends either on the rate of the transport of a metal ion through the membrane or on the rate of back extraction at the membrane-receiver solution interphase. With TPAETEB as the carrier, the back extraction is relatively slower than that with TPAMTEB. This indicates that a slight increase in the HNO_3concentration in the receiver phase would further enhance the difficulty in the stripping of the metal ion from the membrane phase using TPAETEB as the carrier. This may be the reason why the percentage transport of Am(III) into the receiver phase is lower with TPAETEB even though the $D_{Am(III)}$ with the ligand was higher than that with TPAMTEB at 6 M HNO_3 (Fig. 3). The transport of Am (III) with TPAETEB after 24 h was found to be 74.2% and 67.7% using 3 and 6 M HNO_3 in the feed solution, respectively. The P (permeability coefficient) values for Am(III) transport were $(45.6 \pm 0.9) \times 10^{-3}$ cm s^{-1} and $(5.6 \pm 0.1) \times 10^{-3}$ cm s^{-1} with TPAMTEB and TPAETEB for 3 M HNO_3 feed, while that with 0.1 M TODGA was reported to be 2.10×10^{-3} cm s^{-1} (Ansari et al., 2006). This clearly shows that higher P values were obtained with TPAMTEB and TPAETEB even at 150 times lower concentrations which may be attributed to the cooperative complexation due to the presence of multiple DGA arms in the Bz-T-DGA ligands. The P value for Am(III) with TPAMTEB increases upon increasing the concentration of the feed acid from 3 M to 6 M HNO_3, whereas it decreases slightly in the case of TPAETEB, which was also reflected in the transport of Am(III). This could be due to the slower stripping kinetics and higher acid transport with TPAETEB as mentioned above. The P values were larger than that reported with a C-pivot tripodal DGA ligand ($(2.39 \pm 0.07) \times 10^{-3}$ cm s^{-1}) (Mohapatra et al., 2011a).

The transport behavior of the Bz-T-DGA extractants were compared with the commonly used DGA extractants TODGA as well as some of the previously investigated C-pivot and N-pivot tripodal DGA ligands termed as T-DGA (Mohapatra et al., 2011b) and DGA-TREN (Mahanty et al., 2018), respectively (Table 3). The results indicated that the present set of ligands, are much superior to the T-DGA while the TPAMTEB displayed P value one order higher than that of TPAETEB as well as T-DGA. Though DGA-TREN was reported (Mahanty et al., 2018) to be far superior to both T-DGA (Mohapatra et al., 2011a) and also TPAETEB, it was found to be inferior as compared to TPAMTEB.

3.2.2. *Effect of complexing agent on stripping*

The stripping of the metal ion was studied using 0.01 M HNO_3 which resulted in slow stripping (particularly in the case of TPAETEB) and hence, complexing agents could be used for this purpose. In order to investigate the effect of a complexing agent on the stripping of Am(III), transport studies were carried out using 1.0 M α-HIBA (hydroxyisobutyric acid) as the complexing agent in the receiver solution, while the feed solution contained Am(III) tracer in 3 M HNO_3. Complexing agents have been previously used for the transport of Am(III) using T-DGA ligand (Mohapatra et al., 2011b). As the pH of the receiver phase was not controlled, the α-HIBA was completely dissociated to form strong complexes. It was expected that the presence of a complexing agent would expedite the rate of Am(III) transport with TPAETEB as the carrier extractant. However, as can be seen from Table 2 and Fig. 5, in case of TPAETEB there was only a marginal increase in the metal ion transport in the presence of the complexing agent in the receiver

Table 3 – Comparison of DGA based extractants for Am^{3+} ion transport using flat sheet supported liquid membranes (Temperature: 25 °C). The role of complexing agents are discounted here.

Extractant	Extractant concentration	Feed	Receiver	$P \times 10^3$ (cm/s)	Reference
TODGA	0.1 M	1 M HNO_3	Distilled water	2.10 ± 0.05	Ansari et al. (2006)
TODGA[a]	0.1 M	3 M HNO_3	0.01 M EDTA	3.67 ± 0.06	Mohapatra et al. (2011b)
T-DGA[a]	2.9×10^{-3} M	3 M HNO_3	0.01 M EDTA	2.39 ± 0.07	Mohapatra et al. (2011b)
DGA-TREN[b]	4×10^{-3} M	3 M HNO_3	0.01 M HNO_3	16.0 ± 0.29	Mahanty et al. (2018)
TPAMTEB[b]	6.6×10^{-4} M	3 M HNO_3	0.01 M HNO_3	45.6 ± 0.9	This work
TPAETEB[b]	6.6×10^{-4} M	3 M HNO_3	0.01 M HNO_3	5.6 ± 0.1	This work

Note: [a]in 90% *n*-dodecane + 10% isodecanol; [b]in 95% *n*-dodecane + 5% isodecanol.

solution. This suggests that even a strong complexing agent like α-HIBA is not able to increase the stripping of Am(III) with TPAETEB. A similar observation was made with TPAMTEB indicating that the stripping kinetics is not the rate-limiting step (Fig. 4). We have reported a similar slower mass transfer of Am(III) with a C-pivot tripodal ligand when 0.01 M HNO_3 was used as the receiver solution (Mohapatra et al., 2011a), which improved considerably when the receiver contained 0.01 M EDTA (ethylenediaminotetraacetic acid) at pH 3.0. Other complexing agents were not considered here as these ligands were previously reported by us to make easy comparisons.

The P-value obtained for Am(III) transport with 3 M HNO_3 as the feed and 1.0 M α-HIBA as the receiver solution showed a slight increase on changing the receiver composition in the case of TPAMTEB, whereas it remains unchanged in case of TPAETEB (Table 2). Normally, one would expect better transport rate with α-HIBA as the receiver solution (compared to 0.01 M HNO_3) in view of the complexing action of the former. As mentioned above, complexing agents have been used for the efficient transport of Am(III) (Mohapatra et al., 2011b). On the other hand, the slow stripping kinetics in case of TPAETEB appears to control the transport behavior and the complexing agent has a negligible role.

3.3. Determination of diffusion coefficient (D_{eff})

The slow mass transfer rates could be quantified by the determination of the diffusion coefficient (D_{eff}) values which were determined by the lag-time method (Crank, 1975). The lag-time is defined as the time (t_{lag}) required for the metal ion to appear in the receiver solution from the source solution from the start of the experiment. It is determined graphically from the plot of the counts in the receiver solution versus the time elapsed in the experiment.The D_{eff} was calculated using the following equation:

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

where d_0 is the thickness (cm) of the membrane, ε is the membrane porosity and t_{lag} is the lag-time (seconds). The D_{eff} for Am(III) transport was determined for both ligands using 6.6×10^{-4} M concentrations, while using 3 M and 0.01 M HNO_3 solutions as the source and receiver phases, respectively. The lag-time plots are given in Fig. 6 and the corresponding lag-time and D_{eff}–values are summarized in Table 3. As can be seen from Fig. 6, the lag-time for Am(III) transport in the case of TPAETEB is 4.8 times higher than that of TPAMTEB indicating a slower transport of Am(III) with the former. The D_{eff} value for TPAETEB is about one order of magnitude lower than that calculated for TPAMTEB (Table 4). The kinetic inertness of the Am(III)-TPAETEB complex for the release of Am(III) to the receiver solution is reflected in the low value of D_{eff}. The D_{eff}-values for the C-pivot tripodal DGA ligand (Mohapatra et al., 2011a) and TODGA (Panja et al., 2012) were reported as 3.28×10^{-6} cm^2 s^{-1} and 5.1×10^{-6} cm^2 s^{-1}, respectively.

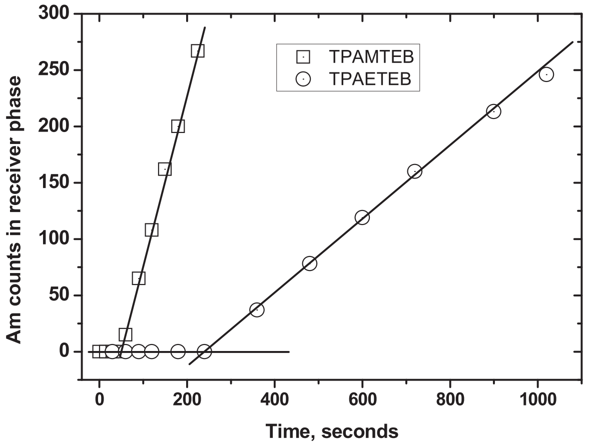


Fig. 6 – Lag-time plot for Am^{3+} ion transport. Feed: 3 M HNO_3; Receiver: 0.01 M HNO_3. Carrier solvent: 6.6×10^{-4} M TPAETEB (or TPAMTEB) in 5% isodecanol-95% *n*-dodecane. Temperature: 25 °C.

Table 4 – Diffusion coefficient data for the transport of Am^{3+} by the Bz-T-DGA ligands; Carrier concentration: 6.6×10^{-4} M in 5% isodecanol-95% *n*-dodecane.

Transport system	Lag-time (s)	D_{eff} (cm^2/s)
Am^{3+}-TPAMTEB	50	2.16×10^{-7}
Am^{3+}-TPAETEB	238	4.5×10^{-8}

3.4. Stability of the membranes

The reusability of the SLM is one of the major issues for the sustainability of the separation process. In view of this, studying the stability of the membrane is very important. The SLM stability was experimentally studied by carrying out the transport studies repeatedly and measuring the transport parameters. Here, the SLM stability study with both the extractants was carried out using PP membranes soaked with 6.6×10^{-4} M solutions of the carrier extractants, while the source and the receiver phases contained 3 M and 0.01 M HNO_3 solutions, respectively. The transport data were recorded up to 5 h. Figs. 7 and 8 show that the stability of the SLMs was rather poor. Fig. 7 suggests slow deterioration of the TPAMTEB-based SLM as the Am(III) transport data after 5 h were 95%, 50% and 25% in the repetitions carried out on days 1, 2 and 8, respectively. The results of the stability studies with TPAETEB were

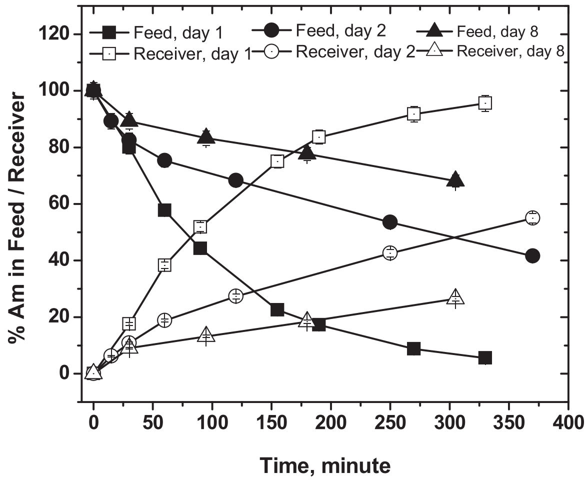


Fig. 7 – Transport of Am(III) using with 6.6 x 10^{-4} M TPAMTEB in 5% isodecanol-95% *n*-dodecane as the carrier; feed: 3 M HNO_3, strip: 0.01 M HNO_3. Temperature: 25 °C.

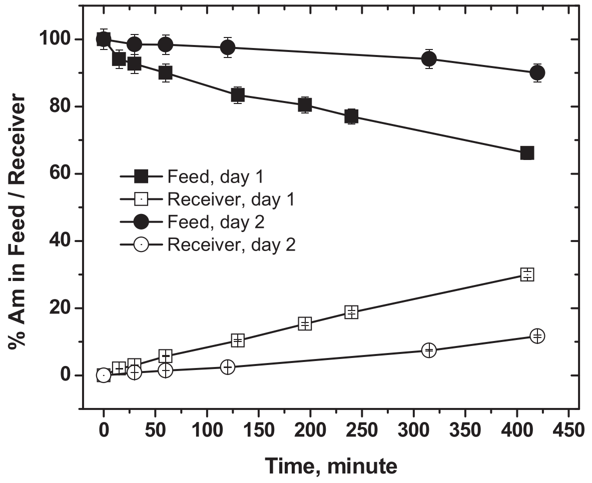


Fig. 8 – Transport of Am(III) using with 6.6 x 10^{-4} M TPAETEB in 5% isodecanol-95% *n*-dodecane as the carrier; feed: 3 M HNO_3, receiver: 0.01 M HNO_3. Temperature: 25 °C.

in the same line as 22% and 10% Am(III) transport was found in the experiments carried out on two consecutive days, respectively. The drastic decrease in the transport rate from day 1 may be due to the loss of carrier extractant from the membrane phase into the solution of the source and the receiver phases. This could be due to the shear forces which can cause leaching out of the carrier molecules. A similar, poor stability of the membrane was found in our earlier study with an *N*-pivot tripodal extractant as the carrier (Mahanty et al., 2018).

4. Conclusions

Solvent extraction of the actinide ions Pu(IV), U(VI) and Am(III) was investigated using two benzene-centered ligands, viz. TPAMTEB and TPAETEB, in a diluent mixture containing 5% isodecanol and 95% n-dodecane. The extraction of Am(III) was higher with TPAMTEB as compared to TPAETEB, which could be based on an 'inclusion' complex formation in the latter, having longer spacers resulting in a more 'relaxed' structure. Extraction studies indicated the order of extraction as: Pu(IV) > Am(III) ≫ U(VI) in case of both ligands. The selectivity of Am(III) and Pu(IV) with respect to U(VI) was found to be better with TPAETEB as compared to TPAMTEB. Supported liquid membrane studies, using PP flat sheet membranes, were carried out for Am(III) alone and indicated a significantly faster mass transfer with TPAMTEB than with TPAETEB. The Am(III) transport was >90% after 5 h with the former when the source compartment contained 3 M HNO_3 and the receiver phase 0.01 M HNO_3. On the other hand, the transport of Am(III) was only 28.3% under identical conditions in case of TPAETEB. The permeability data indicated that the present set of ligands, especially TPAMTEB, is far more efficient as compared to previously used tripodal DGA ligands such as T-DGA and DGA-TREN. Use of a complexing agent did not affect the transport rate to any significant extent. The diffusion coefficient values were determined for Am(III) transport by the lag-time method, the values being one and two orders of magnitude lower than that reported for TODGA with TPAMTEB and TPAETEB, respectively. The stability of the liquid membranes was poor with both membranes, which was attributed to the loss of carrier from the membranes.

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