



# Liquid–liquid extraction and flat sheet supported liquid membrane studies on Am(III) and Eu(III) separation using 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine as the extractant

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## ABSTRACT

Solvent extraction and supported liquid membrane transport studies for the preferential removal of Am<sup>3+</sup> from feeds containing a mixture of Am<sup>3+</sup> and Eu<sup>3+</sup> was carried out using 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (*n*-Pr-BTP) as the extractant. Diluent plays an important role in these studies. It was observed that the distribution coefficients deteriorate significantly for both Am<sup>3+</sup> and Eu<sup>3+</sup> though the separation factors were affected only marginally. The transport studies were carried out at pH 2.0 in the presence of NaNO<sub>3</sub> to result in the preferential Am<sup>3+</sup> transport with high separation factors. Effect of different experimental parameters, viz. feed composition, stripping agents, diluents of the organic liquid membrane and membrane pore size was studied on the transport and separation behaviour of Am<sup>3+</sup> and Eu<sup>3+</sup>. The supported liquid membrane studies indicated about 85% Am<sup>3+</sup> and 6% Eu<sup>3+</sup> transport in 6 h using 0.03 M *n*-Pr-BTP in *n*-dodecane/1-octanol (7:3) diluent mixture for a feed containing 1 M NaNO<sub>3</sub> at pH 2 and a receiver phase containing pH 2 solution as the strippant. Consequently, a permeability coefficient of  $(1.75 \pm 0.21) \times 10^{-4} \text{ cm s}^{-1}$  was determined for the Am<sup>3+</sup> transport. Stability of the *n*-Pr-BTP and its SLM was also studied by carrying out the distribution and transport experiment after different time intervals.

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## 1. Introduction

One of the major drawbacks of nuclear energy programme is the generation of high level liquid wastes (HLLW) containing long lived radionuclides ( $t_{1/2} = 10^2$ – $10^6$  years) such as minor actinides (<sup>237</sup>Np, <sup>241,243</sup>Am and <sup>245</sup>Cm) and fission products (<sup>93</sup>Zr, <sup>99</sup>Tc, <sup>129</sup>I, <sup>135</sup>Cs, etc.). Therefore, safe management of HLLW is required for the public acceptability of the nuclear energy programme. The strategy of vitrification and storage in deep geological repositories is now accepted worldwide for the management of HLLW. It, however, requires surveillance over millions of years to monitor deformation of glass and the migration of the long lived radionuclides to aquatic environment under natural calamities such as earth quake, volcanic eruption, etc. An alternative strategy is to separate the long-lived radionuclides followed by their transmutation in high flux reactors or accelerator driven sub-critical systems (ADSS) and is known as the 'Partitioning and Transmutation' strategy [1]. The partitioning step proposed to selectively extract the minor actinides co-extracts

the lanthanides. Many of the lanthanide isotopes have high neutron capture cross-sections resulting in adverse effect on the transmutation process. It is, therefore, required to carry out separation of lanthanides from the trivalent minor actinides immediately after the partitioning step [2].

Lanthanide–actinide separation is, therefore, a key step in the back end of the fuel cycle. Amongst the early processes employed for the Ln(III)/An(III) separation, the TRAMEX (tertiary amine extraction) process and the TALSPEAK (trivalent actinide lanthanide separation by phosphorus extractants aqueous complexes) process using Alamine-336 and di-2-ethylhexylphosphoric acid (D2EHPA), respectively as the extractants were found to be promising [3–5]. Due to similar charge and ionic size (ionic potential), trivalent actinides and lanthanides show similar chemical behaviour towards the hard 'O' donor ligands. Actinides, however, can form stronger covalent bond with the soft donor ligands because of higher spatial distribution of the '5f' valence orbitals of the actinides as compared to the valence '4f' orbitals of the lanthanides and this property is being exploited for the separation of trivalent actinides and lanthanides. Dithiophosphinic acids with 'S' donor atoms such as bis(2,4,4-trimethyl pentyl)dithiophosphinic acid (Cyanex-301) and bis-(chlorophenyl)dithiophosphinic acid have also been used as selective extractants for the trivalent

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actinides [6,7]. In spite of very high selectivity for the trivalent actinides over the lanthanides, the major disadvantage of Cyanex-301 is its poor extractability at low pH region ( $\text{pH} < 3$ ) [8,9]. Bis-(chlorophenyl)dithiophosphinic acid, however, can extract the trivalent actinides from acidic medium with poor selectivity over the lanthanides [7]. Recently, several 'N' donor reagents such as 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (*n*-Pr-BTP) ligand have been proposed for the selective extraction of trivalent actinides from acidic feeds (0.1–1.0 M  $\text{HNO}_3$ ) with reasonably high S.F. ( $\sim 150$ ) values with respect to the trivalent lanthanides [10,11]. Softer nature of this aromatic 'N' donor ligand is responsible for the selectivity of *n*-Pr-BTP towards trivalent actinides over the lanthanides. A number of reports appeared in the literature on the complexation studies of *n*-Pr-BTP with trivalent actinides and lanthanides and its selectivity towards the actinides over lanthanides was explained on the basis of formation of  $\text{ML}_3 \cdot [\text{NO}_3]_3$  type of species in higher extent in case of actinides [12] due to higher stability constant of this complex in case of actinides [13].

Most of the separation studies of trivalent actinides and lanthanides involving *n*-Pr-BTP as the extractant were carried out using solvent extraction [14]. The major drawback of solvent extraction is the requirement of large solvent inventory and formation of third phase. These problems can be alleviated by the use of alternative methods such as extraction chromatography and liquid membrane. There are very limited reports available using BTP derivatives for lanthanide–actinide separation by extraction chromatography [15–18] and liquid membrane [19,20]. Supported liquid membrane (SLM) based separation methods have received considerable attention by the researchers for various separations and purification of metal ions [21–23]. SLM based techniques are particularly attractive as they involve low inventory of organic extractants and simultaneous extraction and stripping of the metal ion [21]. It is, therefore, pertinent to evaluate supported liquid membranes (SLMs) using *n*-Pr-BTP as the carrier extractant for the selective transport of trivalent actinides. The present study involves the synthesis of *n*-Pr-BTP derivative and its evaluation for the extraction and supported liquid membrane transport studies of Am(III) and Eu(III) using PTFE flat sheets of different pore size and a variety of feed and strip conditions, viz. varying the  $\text{NaNO}_3$  concentration in the feed solution and using different stripping agents (pH 2.0 and 0.01 M EDTA). Effect of organic diluent was also studied on the extraction and transport behaviour of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$ .

## 2. Experimental

### 2.1. Reagents

#### 2.1.1. Synthesis of *n*-Pr-BTP

The synthesis of the bis-triazinyl pyridine **4** is depicted in Scheme 1. Stetter reaction of butanal in the presence of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride and triethylamine in ethanol under reflux gave the hydroxy ketone **1** (68%) which under Swern oxidation conditions gave the diketone **2** in very good yield (87%). The required dihydrazide partner **3** was prepared from commercially available 2,6-dicyanopyridine by treating with excess of hydrazine hydrate at room temperature in a quantitative yield. The desired *n*-Pr-BTP **4** was prepared by refluxing a 1:2 mixture of hydrazide **3** and the diketone **2** in ethanol. The crude product was crystallized from 2-propanol to give pure **4** in 88% yield. The following are the NMR characterization data.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.93$ – $1.12$  (m, 12H,  $4 \times \text{CH}_3$ ),  $1.77$ – $2.0$  (m, 8H,  $4 \times \text{CH}_3$ – $\text{CH}_2$ – $\text{CH}_2$ ),  $2.87$ – $2.95$  (m, 4H,  $4 \times \text{CH}_3$ – $\text{CH}_2$ – $\text{CH}_2$ –),  $2.99$ – $3.07$  (m, 4H,  $4 \times \text{CH}_3$ – $\text{CH}_2$ – $\text{CH}_2$ –),  $8.08$  (t, 8.0 Hz, 1H,  $\text{H}^4$  of Py),  $8.7$  (d, 8.0 Hz, 2H,  $\text{H}^3$ ,  $\text{H}^5$  of Py).  $^{13}\text{C}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.9$  (2C),  $14.0$  (2C),  $21.1$  (2C),  $21.7$  (2C),  $34.3$  (2C),  $35.9$  (2C),  $125.1$  (2C),  $138.0$ ,  $153.9$  (2C),  $159.7$  (2C),  $161.1$  (2C),  $161.9$  (2C).

### 2.2. Methods

#### 2.2.1. Distribution studies

Distribution studies were carried out with  $^{241}\text{Am}$  and  $^{152}\text{Eu}$  as the tracers in different aqueous phase conditions using different organic phases containing Et-BTP as the extractant. Equal volumes (0.5 mL) of the organic phase and the aqueous phase containing the required tracer were taken in stoppered glass tubes and agitated in a thermostated water bath at  $25.0 \pm 0.1$  °C for 1 h. The two phases were then centrifuged and assayed by taking suitable aliquots (usually 0.1 mL) from both the phases. The gamma activities were measured using a NaI(Tl) scintillation detector when only one radiotracer was used and using HPGe detector when a mixture of radiotracers was used. The distribution ratio ( $D_M$ ) was calculated as the ratio of counts per minute per unit volume in the organic phase to that in the aqueous phase. The separation factor (S.F.) is defined as the ratio of  $D_{\text{Am}}$  to  $D_{\text{Eu}}$ . All the experiments were carried out in duplicate and the accepted data points have material balance with in  $\pm 5\%$ .

#### 2.2.2. Transport studies

The transport studies were carried out in a two-compartment glass cell, each of 20 mL capacity. The feed and the receiver compartments were separated by microporous PTFE filters ( $0.45 \mu\text{m}$ ) containing the liquid membrane. The supported liquid membranes were prepared by soaking the PTFE filters with the solutions of *n*-Pr-BTP in different organic diluent mixtures (*vide infra*). The compositions of the feed, strip solution and carrier concentration were varied and the transport of Am and Eu were measured. The feed, containing the required radiotracers, and the strip compartments were stirred using magnetic stirrer at a constant speed of 200 rpm, which was found to be adequate in an earlier communication [24]. Aliquots were withdrawn at regular intervals and the radioactivity was assayed by gamma counting as mentioned above.

### 2.3. Transport equations

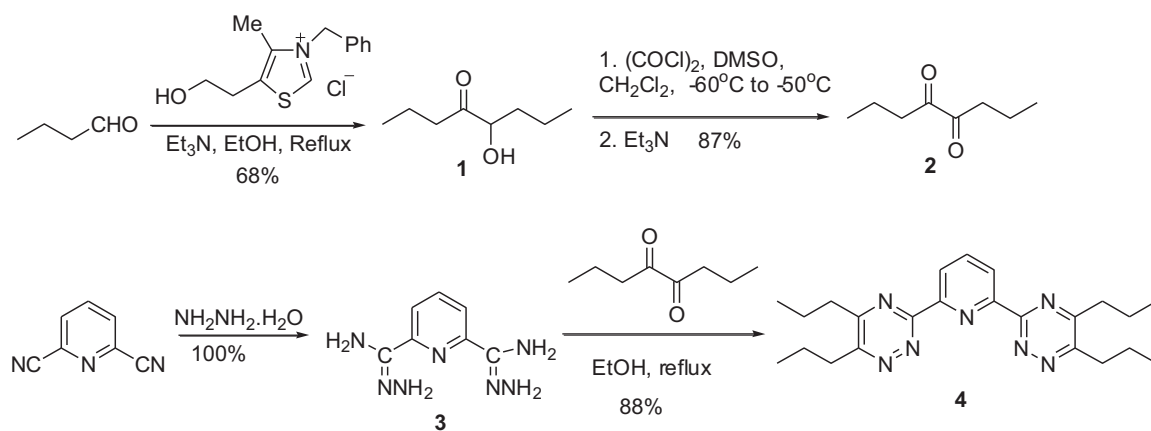
The transport of a metal ion using a carrier solution as the supported liquid membranes usually involves five distinct steps, viz. (1) diffusion of the metal ion from the bulk feed phase to the feed–membrane interface; (2) extraction of the metal ion by the carrier molecule at the feed–membrane interface; (3) diffusion of the metal–carrier complex inside the membrane phase; (4) stripping of the metal ion at the membrane–receiver interface; and (5) diffusion of the stripped metal ion from the membrane–receiver interface. The transport experiments are carried out under the conditions that the distribution coefficient (symbolized as  $D$ ) is much larger at the feed–membrane interface as compared to that at the membrane–receiver interface. Under steady state condition, by ignoring the concentration of the metal ion in the receiver phase one can get the flux ( $J$ ) from the following equation [25]:

$$J = PC_f \quad (1)$$

where  $P$  is the permeability coefficient at the feed–membrane interface and  $C_f$  is the concentration of the metal ion at the feed side. The flux can alternatively be expressed as

$$J = - \left( \frac{1}{Q} \right) \cdot \frac{dV_f C_f}{dt} \quad (2)$$

where  $V_f$  is the feed volume and  $Q$  is the exposed area of the membrane. Assuming that the volume of the feed does not change



Scheme 1. Synthesis scheme for *n*-Pr-BTP followed in the present study.

significantly with time and after combining Eqs. (1) and (2), and integrating one obtains,

$$\ln \left( \frac{C_{f,0}}{C_{f,t}} \right) = \frac{QPt}{V_f} \quad (3)$$

where  $V_f$ ,  $C_{f,0}$  and  $C_{f,t}$  represent the volume of the feed and concentrations of feed at starting time and after time ' $t$ ', respectively.  $Q$  is expressed as the product of the geometrical surface area ( $A$ ) and the porosity ( $\varepsilon$ ). The permeability coefficient ( $P$ ) values were calculated using Eq. (3). The cumulative percent transport (% $T$ ) of the metal ions at a given time is determined by the following equation,

$$\%T = 100 \times \frac{C_{r,t}}{C_{f,0}} \quad (4)$$

where  $C_{r,t}$  is the concentration of the metal ion in the receiver phase at a given time ' $t$ '. The data treatment that follows generally includes plots of % $T$  vs time as well as calculations of permeability coefficient using Eq. (3). All the experiments were repeated and the accepted data were within the error limits of  $\pm 5\%$ .

### 3. Results and discussion

#### 3.1. Distribution studies

##### 3.1.1. Effect of equilibrium time

The attainment of equilibrium of  $\text{Am}^{3+}$  extraction by *n*-Pr-BTP was investigated as a function of equilibration time and the results are plotted in Fig. 1. A continuous increase in the  $D_{\text{Am}}$  value was observed up to 60 min beyond which no change was seen suggesting that 1 h equilibration time is sufficient. All subsequent experiments were carried out with 2 h equilibration time to ensure attainment of equilibrium. It has been reported earlier that  $\text{Am}^{3+}$  extraction rate is linearly dependent on the free *n*-Pr-BTP concentration. As in the presence of 1 M  $\text{HNO}_3$  in the aqueous phase, the free *n*-Pr-BTP concentration is very less,  $\text{Am}^{3+}$  extraction is, therefore relatively less in the present case [26]. Studies have been carried out at low acidity to ensure higher  $\text{Am}^{3+}$  extraction and efficient separation from  $\text{Eu}^{3+}$ .

##### 3.1.2. Effect of organic diluents

Low volatile hydrocarbon solvents, viz. *n*-dodecane, kerosene or TPH are ideal for the solvent extraction or liquid membrane based separation processes. The BTP derivatives are generally insoluble in hydrocarbon solvents and can be solubilized by using polar solvent as modifiers along with the hydrocarbon solvents [11]. A detailed study on the effect of organic diluents was carried out by Kolarik et al. [14], where several aliphatic and aromatic

non-polar diluents were used in combination with a polar diluent, i.e. 2-ethyl-hexanol, which was used as the modifier. In the present work, *n*-dodecane along with polar modifier diluents viz. 1-decanol, 1-octanol, nitrobenzene and NPOE were used to make 0.04 M *n*-Pr-BTP solution. The polar to non-polar diluent volume ratio was maintained as 3:7 with the exception of nitrobenzene, which is miscible with dodecane with a volume ratio of 2:3 (dodecane:nitrobenzene) only. The distribution ratios of both  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  was found to be increasing in the following order of the diluent mixtures, *n*-dodecane/NPOE < *n*-dodecane/1-decanol < *n*-dodecane/1-octanol < *n*-dodecane/nitrobenzene.  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  values were found to be marginally higher in case of *n*-dodecane/1-octanol mixture as compared to that in case of *n*-dodecane/1-decanol system. Higher  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  values were also observed by Kolarik et al. [14] in case of TPH/1-butanol mixture as compared to TPH/1-octanol mixture. Smaller the carbon chain length of the alcohol, higher the polarity of the organic phase and higher is the metal ion extraction. This suggests that the extractable species for  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  by the *n*-Pr-BTP is polar in nature due to the presence of the nitrate ions in the outer sphere (ion-pair complex). In case of *n*-dodecane/nitrobenzene mixture, the polarity of nitrobenzene is much higher as compared to the alcoholic solvents,

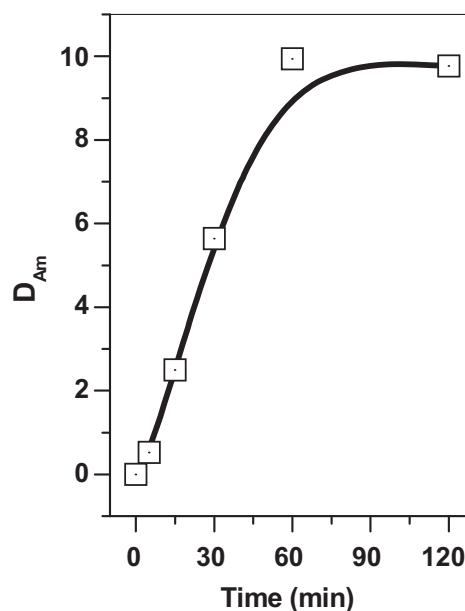


Fig. 1. Extraction of  $\text{Am}^{3+}$  at different time of equilibration; org. phase: 0.04M *n*-Pr-BTP in *n*-dodecane/1-octanol (7:3) mixture; aq. phase: pH 2 containing 1 M  $\text{NaNO}_3$ .

**Table 1**

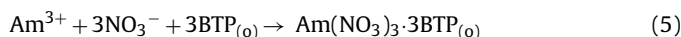
Effect of organic diluents on the extraction of Am(III) and Eu(III); org. phase: 0.04 M *n*-Pr-BTP in different diluent mixture; aq. phase: pH 2 containing 1 M NaNO<sub>3</sub>.

Org. phase	$D_{Am}$	$D_{Eu}$	S.F.
<i>n</i> -Dodecane:octanol (7:3)	26.71 ± 1.77	0.33 ± 0.02	82
<i>n</i> -Dodecane:decanol (7:3)	22.4 ± 4.9	0.26 ± 0.01	85
<i>n</i> -Dodecane:NPOE (7:3)	0.34 ± 0.01	0.02 ± 0.002	18.5
<i>n</i> -Dodecane:nitrobenzene (2:3)	43.8 ± 4.5	1.03 ± 0.01	42

moreover nitrobenzene is present in larger proportion,  $D_{Am}$  and  $D_{Eu}$  values are therefore expected to be still higher in this case and it was observed experimentally also (Table 1).

### 3.1.3. Effect of *n*-Pr-BTP concentration

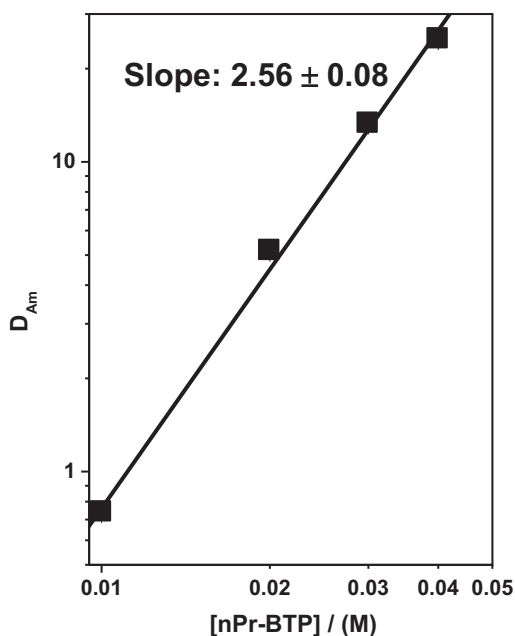
Literature [26,27] shows that the complex species using BTP derivatives usually contain three molecules of the N-donor extractant. Accordingly, the extraction equilibrium involving Am<sup>3+</sup> can be presented as:



where the species in the organic phase are indicated with subscript '(o)' while those in the aqueous phase are without any subscript. Effect of the *n*-Pr-BTP concentration in *n*-dodecane/1-octanol phase was studied on the  $D_{Am}$  value using 1 M HNO<sub>3</sub> as the aqueous phase. A slope value of ~2.6 was observed in the logarithmic plot of  $D_{Am}$  vs *n*-Pr-BTP concentration (Fig. 2) contrary to the expected dependence of 3 [27]. Similar to our result, lower slope value was also reported in the literature, which was explained on the basis of the aggregation of the *n*-Pr-BTP molecules in the organic phase [26].

### 3.1.4. Effect of NaNO<sub>3</sub> concentration in the aqueous phase

Though BTP derivatives extract trivalent actinides and lanthanides from nitric acid medium, it was of interest to understand the extraction behaviour in the absence of hydrogen ions, which may be forming cationic species such as BTP. H<sup>+</sup> thereby decreasing the free extractant concentration. NaNO<sub>3</sub> concentration variation study was therefore carried out using an aqueous phase of pH 2 containing varying amounts of NaNO<sub>3</sub>. As indicated in Eq. (5) above, increasing the nitrate ion concentration should favour the metal ion



**Fig. 2.** Effect of *n*-Pr-BTP concentration on the distribution ratio of Am<sup>3+</sup>; Org. Phase: *n*-Pr-BTP in dodecane/octanol (7:3) mixture; aq. phase: pH 2 containing 1 M NaNO<sub>3</sub>.

**Table 2**

Effect of NaNO<sub>3</sub> concentration on Am(III) and Eu(III) extraction org. phase: 0.04 M *n*-Pr-BTP in *n*-dodecane/*n*-octanol (7:3); aq. phase: pH 2 with varying concentration of NaNO<sub>3</sub>.

[NaNO <sub>3</sub> ]/(M)	$D_{Am}$	$D_{Eu}$	S.F.
0	0.020 ± 0.002	0.0010 ± 0.0001	13.7
0.5	8.74 ± 0.38	0.11 ± 0.01	80
1.0	26.71 ± 1.77	0.33 ± 0.02	82
1.5	58.8 ± 0.2	0.73 ± 0.01	80
2.0	96 ± 4	1.14 ± 0.07	84

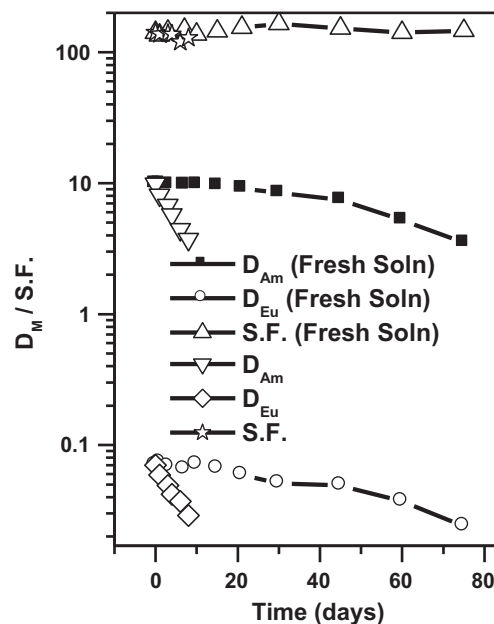
extraction. Both the  $D_{Am}$  and  $D_{Eu}$  values were also found to increase with increasing NaNO<sub>3</sub> concentration in the aqueous phase resulting in no change in the S.F. values (Table 2). Hoshi et al. [16], have also shown a increase in the distribution coefficient of Am<sup>3+</sup>, Nd<sup>3+</sup> and Ce<sup>3+</sup> with increasing nitrate concentration up to 2 M NaNO<sub>3</sub>.

### 3.1.5. Stability of *n*-Pr-BTP

Stability of *n*-Pr-BTP was studied by measuring the  $D_{Am}$  value over a period of time (Fig. 3) and it was observed that the  $D_{Am}$  value decreases with time. The experiments were carried out in two modes. In the first case, the solid BTP was stored and intermittently taken to prepare a solution in the diluent mixture mentioned above and the distribution studies were carried out with both Am<sup>3+</sup> and Eu<sup>3+</sup>. In the second case, the solution itself was stored over a period of time and was used intermittently at varying time intervals. The decrease in  $D_{Am}$  value is higher when *n*-Pr-BTP was stored in the solution form in *n*-dodecane/*n*-1-octanol mixture as compared to the case when *n*-Pr-BTP was stored as such in the solid form. The presence of labile  $\alpha$ -benzyl hydrogen atom is mainly responsible for the poor chemical stability of the *n*-Pr-BTP molecules [28] and the degradation of *n*-Pr-BTP molecules is, therefore, much faster when it is stored in solution form.

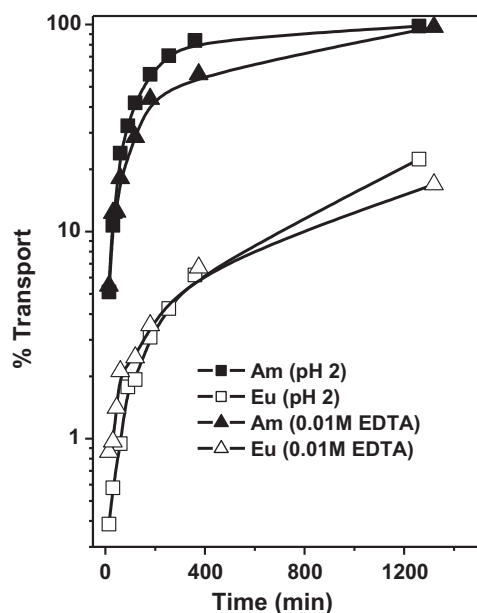
### 3.2. Supported liquid membrane studies

From the solvent extraction studies, significant extraction of Am<sup>3+</sup> was observed with a S.F. value of >100 at 1 M HNO<sub>3</sub>. SLM studies at this acidity, however, show no transport of Am<sup>3+</sup> even



**Fig. 3.** Variation of distribution coefficient of Am<sup>3+</sup> and Eu<sup>3+</sup> and their separation factor with time; org. phase: 0.03 M *n*-Pr-BTP in *n*-dodecane/1-octanol (7:3) mixture; aq. phase: pH 2 containing 1 M NaNO<sub>3</sub>.





**Fig. 4.** Role of stripping agent on the transport of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$ ; feed: pH 2 containing 1 M  $\text{NaNO}_3$ ; membrane: 0.03 M *n*-Pr-BTP in *n*-dodecane/1-octanol (7:3) mixture.

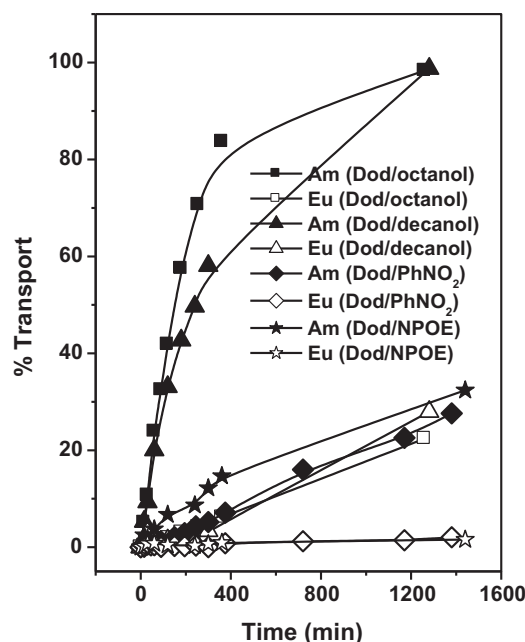
after 24 h, which might be due to the protonation of the *n*-Pr-BTP molecules. Unlike the solvent extraction studies, the SLM studies involve large volumes of aqueous phase as compared to the organic phase, which can result in the protonation of major fraction of the extractant. Apparently, the protonated form of BTP ( $\text{BTPH}^+ \cdot \text{NO}_3^-$  or analogous complex) comes out of the membrane phase leading to negligible  $\text{Am}^{3+}$  transport. The leaching of the carrier was confirmed by the red coloration of the feed and receiver phases when small amount of  $\text{Fe}^{3+}$  was spiked in the respective aqueous phases. Subsequent studies on the transport behaviour of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  through the SLM containing *n*-Pr-BTP were, therefore, carried out after adjusting the feed solution to pH 2 containing varying amounts of  $\text{NaNO}_3$ .

### 3.2.1. Effect of stripping agents

From the nitrate ion concentration variation study, it was observed that the presence of nitrate ion facilitates the metal ion extraction. Consequently, very low  $D_{\text{Am}}$  value was observed at pH 2 in absence of  $\text{NaNO}_3$  and justifying its subsequent use in the receiver phase solution in the SLM studies. 0.01 M EDTA was also evaluated for the stripping and compared with the transport data with pH 2 solution as the strippant. No improvement in the transport profile was observed using EDTA as the strippant (Fig. 4). In the subsequent SLM studies, pH 2 solution was chosen as the strippant while EDTA solution was not preferred.

### 3.2.2. Effect of organic diluents

Transport studies were carried out in mixtures of two diluents where one component was *n*-dodecane and the other was a polar diluent like 1-octanol, 1-decanol, nitrobenzene or NPOE (2-nitrophenyl octyl ether) in the same composition as used in the solvent extraction studies. Out of all the solvent system studied, most favourable transport was observed when *n*-dodecane/1-octanol mixture was used (Fig. 5). *n*-Dodecane/1-decanol system, however, showed marginally slower transport of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  initially which was ascribed to the lower distribution ratio values in *n*-dodecane/1-decanol mixture (Table 1) and higher viscosity of 1-decanol (11.05 mPas [29]) as compared to 1-octanol (7.24 mPas [29]). However, overnight transport data for both the systems were comparable (Fig. 5). Though in the case of



**Fig. 5.** Effect of organic diluents on the transport of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$ ; feed: pH 2 containing 1 M  $\text{NaNO}_3$ ; membrane: 0.03 M *n*-Pr-BTP in different diluent mixture; strip: pH 2 solution.

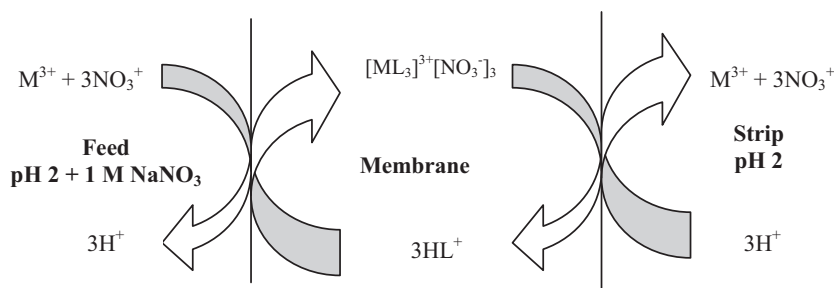
*n*-dodecane/nitrobenzene system the  $D_{\text{Am}}$  value was higher as compared to other solvent systems and viscosity of nitrobenzene is also not so high, transport was found to be very slow, which could be due to leaching out of the carrier solution from the membrane pores. We have reported inefficient transport behaviour with nitrobenzene as the diluent and the use of higher proportion (60% v/v) of nitrobenzene in the diluent mixture may result resulting in poor membrane stability due to its appreciable aqueous solubility [30]. This may be one of the reasons for inefficient cation transport using nitrobenzene as the diluent [31]. In the *n*-dodecane/NPOE mixture, however, the slower transport is expected due to low  $D_{\text{M}}$  values as well as low diffusivity as a consequence of higher viscosity of the diluent mixture [32]. For subsequent transport experiments, the *n*-dodecane/1-octanol mixture, which shows highest transport rate, was chosen as the organic solvent for the liquid membrane.

### 3.2.3. Effect of $\text{NaNO}_3$ concentration in the aqueous phase

From the solvent extraction studies,  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  values were found to be increasing with increasing the concentration of  $\text{NaNO}_3$  in the aqueous phase. A systematic study was, therefore, carried out in order to investigate the transport behaviour of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  with increasing the  $\text{NaNO}_3$  concentration and as expected the permeability coefficient values for both  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  increased (Fig. 6). The increase in  $P_{\text{Eu}}$  value was less significant up to 1 M  $\text{NaNO}_3$  and increased significantly beyond 1 M  $\text{NaNO}_3$ , whereas, significant enhancement in  $P_{\text{Am}}$  value was observed even up to 1 M  $\text{NaNO}_3$ . The separation factor ( $P_{\text{Am}}/P_{\text{Eu}}$ ) value was, therefore, found to be highest at 1 M  $\text{NaNO}_3$ . Decrease in the S.F. values with increasing  $\text{NaNO}_3$  concentration from 1 to 2 M was also seen during our extraction chromatography studies [17].

### 3.2.4. Effect of carrier concentration

The  $P_{\text{Am}}$  value was found to increase with increasing the carrier (*n*-Pr-BTP) concentration (Fig. 7), which can be explained on the basis of increase in the  $D_{\text{Am}}$  value with increasing *n*-Pr-BTP concentration (Fig. 2). The permeability coefficient is dependent on the distribution ratio of  $\text{Am}^{3+}$  in the feed–membrane interface and the diffusion coefficient of the metal–carrier complex in the liquid

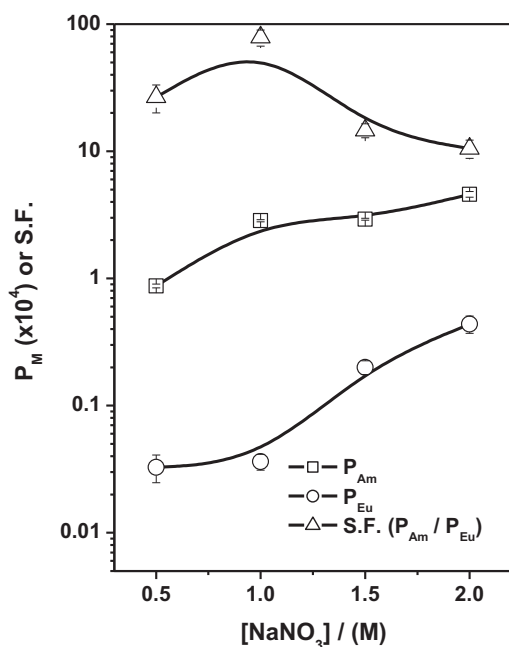


**Scheme 2.** Transport mechanism of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  through the SLM of  $n$ -Pr-BTP.

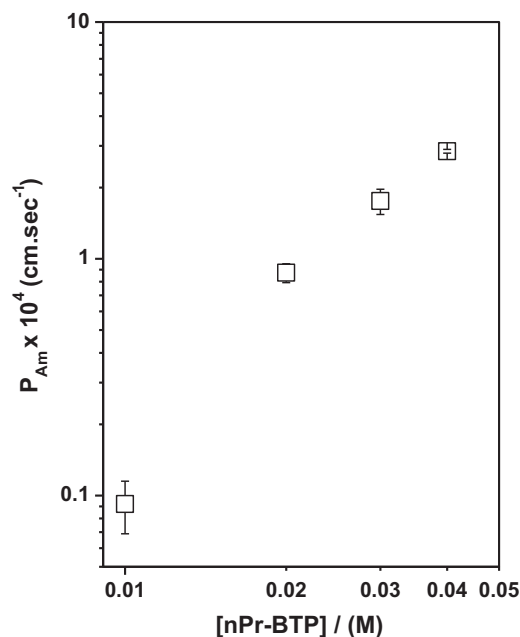
membrane phase. The diffusion coefficient can be considered to be constant irrespective of the carrier concentration studied in the present work as the increase in viscosity of the organic phase with increasing the carrier concentration is insignificant at such a low concentration (0.01–0.04 M) and the metal–carrier complex is also remained unchanged throughout this concentration range. Hence higher  $D_{\text{Am}}$  value is expected to positively influence the  $P_{\text{Am}}$  value. The increase in  $P_{\text{Am}}$  value, however, is more significant at the lower carrier concentration and  $P_{\text{Am}}$  value increases with lower slope at higher carrier concentration, which might be due to the aggregation of  $n$ -Pr-BTP with increasing concentration. Similar observation was also made in the solvent extraction studies (*vide supra*). Based on these studies a mechanism (Scheme 2) can be proposed for the selective transport of  $\text{Am}^{3+}$  over  $\text{Eu}^{3+}$ , where formation of the complex  $[\text{ML}_3]^{3+} \cdot [\text{NO}_3^-]_3$  (L is  $n$ -Pr-BTP) is more favoured in case of  $\text{Am}^{3+}$  as compared to  $\text{Eu}^{3+}$  and this reflects in the selectivity of the membrane for  $\text{Am}^{3+}$  over  $\text{Eu}^{3+}$ .

### 3.2.5. Effect of membrane pore size

Pore size of the PTFE flat sheet has significant role in controlling the transport behaviour of the metal ions. The  $P_{\text{Am}}$  value was found to increase with increasing membrane pore size from 0.2 to 0.45  $\mu\text{m}$  and then decrease up to 5.0  $\mu\text{m}$  (Fig. 8). We have reported that increasing the membrane pore size usually results in a decrease



**Fig. 6.** Effect of  $\text{NaNO}_3$  concentration in the feed solution on the transport and separation behaviour of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$ ; feed: pH 2 with varying concentration of  $\text{NaNO}_3$ ; membrane: 0.04 M  $n$ -Pr-BTP in  $n$ -dodecane/1-octanol (7:3) mixture; strip: pH 2 solution.



**Fig. 7.** Effect of  $n$ -Pr-BTP concentration on the transport behaviour of  $\text{Am}^{3+}$ ; feed: pH 2 containing 1 M  $\text{NaNO}_3$ ; membrane:  $n$ -Pr-BTP in  $n$ -dodecane/1-octanol (7:3) mixture; strip: pH 2 solution.

**Table 3**

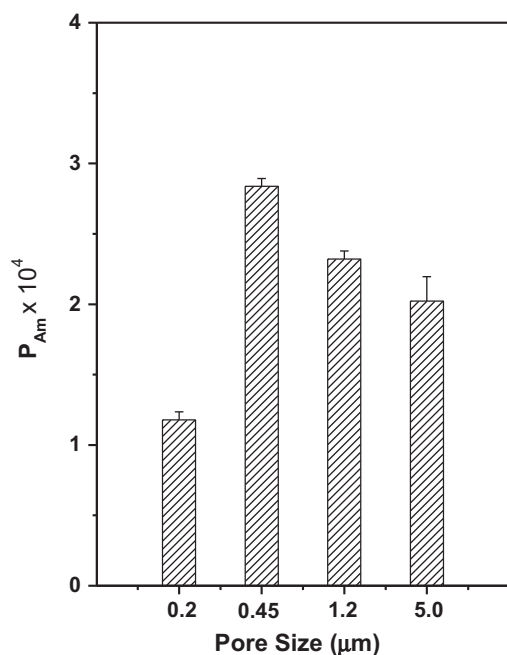
Effect of operational time of the  $n$ -Pr-BTP SLM on the transport of  $\text{Am}^{3+}$ ; feed: pH 2 solution containing 1 M  $\text{NaNO}_3$ ; strip: pH 2 solution; liq. membrane: 0.03 M  $n$ -Pr-BTP in dodecane/octanol (7:3) mixture.

Time (day)	$P_{\text{Am}} \times 10^4 \text{ (cm s}^{-1}\text{)}$
0	$1.75 \pm 0.21$
1	$0.17 \pm 0.02$

in the  $P$ -values, which was attributed to lower capillary forces and higher leachability of the carrier solvent with membranes of higher pore size [33]. Similar observation is made in the present work. However, the increase in the  $P$ -value from 0.2 to 0.45  $\mu\text{m}$  can only be explained on the basis of favourable transport of a bulky complex species at 0.45  $\mu\text{m}$  which is hindered when membranes of 0.2  $\mu\text{m}$  pore size are used. Similar observation was reported when  $\text{UO}_2^{2+}$  ion transport was investigated using Aliquat 336 as the carrier extractant [34].

### 3.2.6. Stability of the membrane

The stability of the supported liquid membrane of  $n$ -Pr-BTP in  $n$ -dodecane/1-octanol (7:3) mixture was studied by measuring the  $P_{\text{Am}}$  value with time.  $P_{\text{Am}}$  value was found to decrease from  $(1.75 \pm 0.21) \times 10^{-4}$  to  $(0.17 \pm 0.02) \times 10^{-4} \text{ cm s}^{-1}$  even in 1 day (Table 3). This poor stability is attributed to two reasons viz., (i) leaching out of the organic phase from the pores of the PTFE support



**Fig. 8.** Effect of the pore size of the PTFE flat sheet on Am<sup>3+</sup> transport; feed: pH 2 solution containing 1 M NaNO<sub>3</sub>; membrane: 0.04 M *n*-Pr-BTP in *n*-dodecane/1-octanol (7:3) mixture; strip: pH 2 solution.

as water has significant miscibility with the 1-octanol and (ii) poor stability of the carrier molecules as described in earlier section the *n*-Pr-BTP molecules degrades with time resulting in decrease in  $D_{Am}$  value (Fig. 3), which ultimately reduces the  $P_{Am}$  value.

#### 4. Conclusions

From the solvent extraction studies highest distribution ratio of Am<sup>3+</sup> was observed by *n*-Pr-BTP in dodecane/nitrobenzene mixture. The SLM study, however, shows promising result in dodecane/octanol mixture, where ~85% transport of Am<sup>3+</sup> was observed in 6 h, which was accompanied by ~6% of Eu<sup>3+</sup>, using 1 M NaNO<sub>3</sub> at pH 2 as feed and pH 2 solution as the strippant. The distribution ratio and permeability coefficient values were found to be increasing with the ligand as well as aqueous NaNO<sub>3</sub> concentration. Poor stability of the carrier molecules and water miscibility of the organic phase has been reflected in the poor membrane stability suggesting the membranes need to be regenerated with fresh carrier solutions for more efficient separation.

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