Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Selective Recovery of Am(III) over Eu(III) by Hollow Fiber Supported Liquid Membrane Using Cyanex 301 in the Presence of Synergists as the Carrier

A. Bhattacharyya[a]; S. A. Ansari[a]; P. Kandwal[a]; P. K. Mohapatra[a]; V. K. Manchanda[a]
[a] Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India

Online publication date: 18 January 2011

To cite this Article Bhattacharyya, A. , Ansari, S. A. , Kandwal, P. , Mohapatra, P. K. and Manchanda, V. K.(2011) 'Selective Recovery of Am(III) over Eu(III) by Hollow Fiber Supported Liquid Membrane Using Cyanex 301 in the Presence of Synergists as the Carrier', Separation Science and Technology, 46: 2, 205 — 214
To link to this Article: DOI: 10.1080/01496395.2010.509079
URL: http://dx.doi.org/10.1080/01496395.2010.509079

Separation Science and Technology, 46: 205–214, 2011

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.509079

Taylor & Francis
Taylor & Francis Group

Selective Recovery of Am(III) over Eu(III) by Hollow Fiber Supported Liquid Membrane Using Cyanex 301 in the Presence of Synergists as the Carrier

A. Bhattacharyya, S. A. Ansari, P. Kandwal, P. K. Mohapatra, and V. K. Manchanda

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India

Lanthanide/actinide separation was investigated on 0.5 L scale (both feed and receiver phase volumes) with Cyanex-301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) as the carrier using the Hollow Fiber Supported Liquid Membrane (HFSLM) technique under varying feed pH conditions. At pH 3.4, the quantitative transport of Am(III) was achieved within 15 minutes with 0.5 M Cyanex 301 as the carrier with separation factor of >100 over Eu(III). The transport rate of Am(III) decreased significantly with increasing feed acidity, and was independent of the feed nitrate concentration. The effect of neutral auxiliary donor ligands as synergists, viz. tri-*n*-butyl phosphate (TBP), N,N,-dihexyl octanamide (DHOA) and 2,2′-bipyridyl (Bipy) on the selective recovery of Am(III) over lanthanides was also investigated. The presence of synergists led to the possibility of Am(III) recovery at lower pH values with improved separation factors (SF). It was particularly beneficial as the use of buffer for feed pH adjustment could be avoided. In the presence of synergists, >85% transport of Am(III) was achieved in 30 minutes of operation at pH 2.0. The SF value at pH 2.0 for different synergists followed the order: bipyridyl (350) >DHOA (50) >TBP (8). The transport rate of Am(III) by HFSLM system was found to be satisfactory for 25 hours of continuous operation. However, the SF values deteriorated significantly with the time of operation.

Keywords cyanex 301; hollow fiber supported liquid membrane; lanthanide actinide separation; synergism

INTRODUCTION

The raffinate after the PUREX process generally contains un-extracted U, Pu, and bulk of minor actinides such as Am, Np, Cm and a host of fission products like Tc, Pd, Zr, Cs, Sr, and rare earth elements as well as structural elements like Fe, Cr, etc. At present, the most accepted approach for the management of HLW is to vitrify it in the glass matrix followed by disposal in deep geological repositories (1,2). Since the half lives of minor actinides concerned range between a few hundreds to millions of years, the surveillance of vitrified waste blocks for such a long period is disadvantageous from economic as well as environmental safety considerations. Therefore, a strategy of P&T (Partitioning of long-lived radionuclides followed by transmutation) is being considered as a viable alternative by several countries around the world (3,4). In the P&T process, however, the separation of trivalent actinides from trivalent lanthanides is essential to avoid difficulties for subsequent transmutation (5). The lanthanides do not form solid solutions in metal alloys or in mixed oxide, and as a result, segregates into separate phases. Since transplutonium actinides tend to concentrate in these phases, this leads to an unacceptable non-uniform heat distribution in the fuel matrix during their burning. Another important reason is the high neutron absorption cross sections of some rare earth nuclides, which cause neutron poisoning.

The group separation of lanthanides and actinides is still one of the most challenging chemical processes due to the similarity in their chemical properties. However, the trivalent actinides are considered soft metal ions as compared to trivalent lanthanides due to their more diffused *f*-orbitals. Extractants containing soft donor atoms (N or S) have shown selectivity for trivalent actinides due to greater complex stability (metal-ligand covalent bonding) (6). Amongst various soft donor ligands studied, purified Cyanex-301 (bis(2,4,4-trimethyl pentyl) dithiophosphinic acid) has been claimed to display a very high separation factor (SF) between Am(III) and Eu(III) in aqueous medium at pH 3.2 (7). Since, Cyanex 301 becomes an effective extractant only at pH 3.2 or higher, it was of interest in the present work to use neutral auxiliary ligands as synergists in order to improve the extraction at lower pH regions. It was found that by the addition of tri-*n*-butyl phosphate (TBP) to a solution containing Cyanex 301 facilitate Am(III) extraction from feed solutions at lower pH values (8–9). However, the SF between Am(III) and Eu(III) ($SF = D_{Am}/D_{Eu}$) decreased with the addition of TBP. The effect was more pronounced when TOPO

Received 7 April 2010; accepted 14 July 2010.
Address correspondence to V. K. Manchanda, Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India. Fax: 91-22-25505151. E-mail: vkm@barc.gov.in

(tri-*n*-octyl phosphine oxide) was used as the synergist where practically no selectivity was seen (10). On the other hand, the use of N-donor synergists such as 2,2′-bipyridyl (Bipy) and 1,10-phenanthroline along with Cyanex 301 increased the SF values to >40,000 (11).

Usually, the large-scale solvent extraction processes are performed using centrifugal contactors, mixer-settlers or pulsed columns. However, such processes involve handling of the large volumes of VOC's (Volatile Organic Compounds). The growing concerns for the environment and cost necessitate the use of alternative techniques with low extractant/solvent burden. Techniques such as supported liquid membrane (SLM) appear to be a promising alternative to the solvent extraction as the extractant inventory can be cut down drastically (12,13). Moreover, using high surface to volume ratio in hollow fiber supported liquid member (HFSLM), the throughput can be increased manifold as compared to the simple flat sheet supported liquid membrane (FSSLM) (13,14). Several reports on HFSLM technology for possible application in "actinide partitioning" or for "lanthanide actinide separation" are available (14–18). Geist et al. (18) used the hollow fiber membrane technique for lab-scale separation of actinides from lanthanides using 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (BTP) and bis-chlorodiphenyl dithiophosphinic acid as the extractants. We, on the other hand, reported the use of HFSLM technique for lanthanide – actinide separations using Cyanex-301 as the extractant (15).

In the present work, HFSLM technique has been used for the separation of Am(III) over Eu(III) using a binary mixture of Cyenex-301 and neutral donor ligands for the first time. The feed solution containing 1 g/L Eu (spiked with ^{154}Eu) and tracer concentration of ^{241}Am. The composition is relevant for subsequent lanthanide/actinide separation after actinide partitioning step as the concentration of lanthanides are manifold times higher than the trivalent actinides. Am(III) and Eu(III) have been taken as the surrogates of trivalent actinides and trivalent lanthanides, respectively. In order to improve the metal permeation at a lower pH range, the present work deals with the use of a variety of synergistic mixtures as the carrier, especially for their potential application in lanthanide-actinide separation in liters scale.

EXPERIMENTAL

Materials

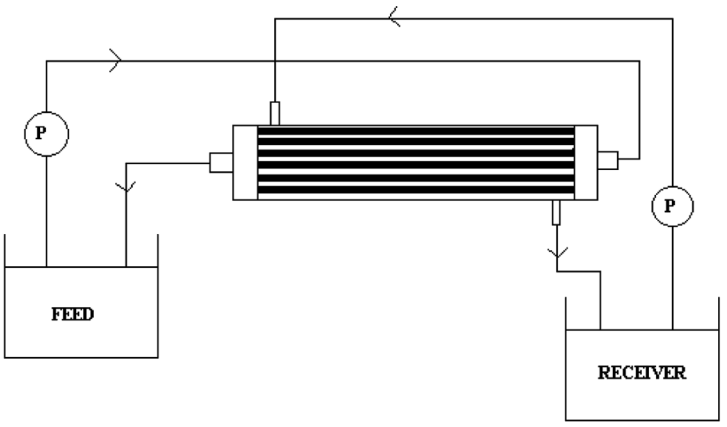
Bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex-301) obtained from Cytec Canada Inc., was purified by a reported method (7). The purity of the product was checked by ^{31}P-NMR (Phosphorus-31 Nuclear Magnetic Resonance), FT-IR (Fourier Transform Infra Red) spectroscopy and elemental analysis. In the ^{13}P-NMR spectrum, the signal was singlet at 67.07 ppm, which was assigned to the pentavalent phosphorous. The appearance of characteristic vibrational frequency at 2430 cm^{-1} and at 756 cm^{-1} in FT-IR spectrum demonstrated the presence of P-S-H (thiophosphinic acid group) and P=S groups of dithiophosphinic acid, respectively. Sulphanilic acid was procured from Sisco Research Laboratory (SRL), Mumbai and was used as received. Bipyridyl was obtained from Sigma-Aldrich and used as received. Tri-*n*-butyl phosphate (TBP) received from Heavy Water Board, India was used after washing with alkali (Na_2CO_3) to remove any acidic impurities. On the other hand, *N,N*-dihexyl octanamide (DHOA) was synthesized indigenously by following the procedure described elsewhere (19). Europium oxide (>99.99%) was obtained from Alpha Biochem. Suprapur nitric acid (Merck) was used for preparing the solutions. All other reagents were of AR grade. The radiotracers ^{241}Am and ^{154}Eu were used from the laboratory stock after ensuring their purities by gamma spectrometry.

Hollow Fiber Supported Liquid Membrane Studies

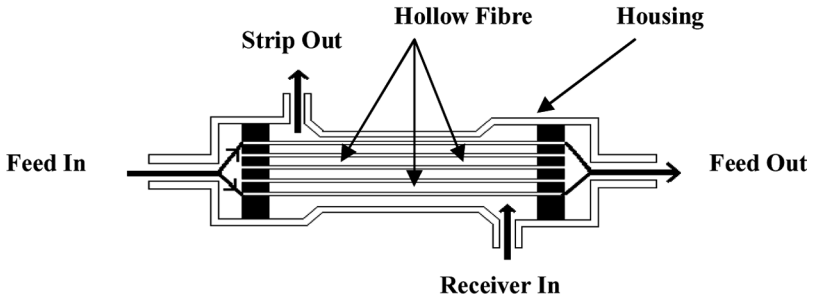
A commercial Liqui-Cel Extra flow X 50 hollow fiber module (Alting France) measuring $2.5'' \times 8''$ with about 10,000 polypropylene lumens was used in the present work. The specifications of the module are given in Table 1. The HFSLM was prepared by pumping about 500 mL ligand solution through the lumen side of module at a pressure of 20 kPa in recirculation mode. To ensure the complete soaking of the membrane pores, the ligand solution was circulated for ~15 minutes when the solution started percolating from lumen side to the shell side. The excess of the ligand solution was washed out completely with sufficient distilled water, prior to the introduction of the feed and strip solutions. For all the experiments, the feed solution was passed through the lumen side while the receiver solution was passed through the shell side of the module operated in recirculation mode. Both the feed and the receiver phases were contacted inside the hollow fiber module in counter-current flow for the effective transport of metal

TABLE 1
Specifications of hollow fiber membrane contactor (Liqui-Cel® X50 : 2.5×8 Membrane Contactor)

Fiber material	Polypropylene
Number of Fibers	9950
Fiber internal diameter (μm)	240
Fiber outer diameter (μm)	300
Fiber wall thickness (μm)	30
Effective pore size (μm)	0.03
Porosity (%)	40
Tortuosity	2.5
Effective Fiber length (cm)	15
Effective surface area (m^2)	1.4



(a)



(b)

FIG. 1. Schematic representation of hollow fiber module used in the present work; (a) HFSLM unit with direction of liquid flow; (b) HF Module.

ions. The flow rates of the feed and receiver solutions were maintained constant at 200 mL/min with the help of gear pumps equipped with precise flow controllers. A schematic diagram of the hollow fiber unit used in the present work is shown in Fig. 1. The volume of the feed and receiver solutions were usually 500 mL each, except stated otherwise. Disodium salt of ethylenediamine tetraacetic acid (EDTA) solution (0.01 M) was employed as a strippant throughout the study. The permeation of the metal ion was calculated by estimating the feed as well as the receiver samples at regular interval. Assay of ^{241}Am and ^{154}Eu were carried out using high purity germanium (HPGe) detector interphased to a multichannel analyzer.

Theoretical Background

The extraction of Am(III) and Eu(III) with Cyanex 301 (HA) in the presence as well in the absence of nitrate ions followed the following equilibrium reaction (11),

$$Am^{3+}_{(aq.)} + 3HA_{(org.)} \backslash\!=\!=\backslash [Am(A)_3]_{(org.)} + 3H^{+}_{(aq.)}$$
(In the presence and absence of nitrate) (1)

$$Eu^{3+}_{(aq.)} + 3HA_{(org.)} \backslash\!=\!=\backslash [Eu(A)_3]_{(org.)} + 3H^{+}_{(aq.)}$$
(In the absence of nitrate) (2)

$$Eu^{3+}_{(aq.)} + 2HA_{(org.)} + NO^{-}_{3} \backslash\!=\!=\backslash [Eu(A)_2(NO_3)]_{(org.)} + 2H^{+}_{(aq.)}$$
(In the presence of nitrate) (3)

Here, the subscripts (aq) and (org) represent the aqueous and the organic phases, respectively. It can be seen from equilibrium reactions (1–3) that the extraction of trivalent actinides and lanthanides depends on the aqueous feed acidity as protons are released during the metal-ligand complexation (7,11). Cyanex 301 is a weak acid (pKa = 2.6) and is an effective extractant only at pH > 3. Similarly, the decomplexation reaction between Am(III) and Cyanex 301 (HA) can be written as,

$$[Am(A)_3]_{(org.)} + [H_2EDTA^{2-}]_{(aq.)} + [H^{+}]_{(aq.)} \backslash\!=\!=\backslash 3[HA]_{(org.)} + [Am \cdot EDTA]^{2-}_{(aq.)} \quad (4)$$

Considering linear concentration gradients, fast interfacial reactions, distribution coefficients of the metal ions between the membrane phase and the receiver phase are much lower than that between the feed phase and membrane phase, the final equation for the permeability of the metal ion could be obtained as described earlier (20–22),

$$\ln\left(\frac{C_t}{C_o}\right) = -\frac{A \cdot P}{V}\left(\frac{\phi}{\phi + 1}\right) \cdot t \quad (5)$$

where, P is the permeability coefficient of metal ions, C_t and C_o are the respective concentrations of the metal ions in the feed solution at an elapsed time t (min) and at zero time, and V is the total volume of the feed solution (mL). The parameter A represents the total effective surface area of the hollow fiber (cm^2), which is calculated as follows,

$$A = 2\pi r_i LN \in \quad (6)$$

where, r_i is the internal radius of the fiber (cm), L is the length of the fiber (cm), N is the number of fibers and $\in$ is the membrane porosity. The parameter, ϕ for a module containing N number of fibers is expressed as follows,

$$\phi = Q_T/Pr_iLN\pi \in \quad (7)$$

where, Q_T is the total flow rate of the feed solution (mL/min). The specifications of the hollow fiber module employed in the present study are given in Table 1. By plotting $\ln(C_t/C_o)$ as a function of t a straight line is expected, and the P value for the given system can be obtained from the fitted slope with the help of Eqs. (6) and (7). The transport profiles in the HFSLM were calculated theoretically using the membrane permeability coefficients and were compared with the experimentally determined data points. The percentage transport (%T) of the metal ions was calculated as follows,

$$\%T = 100x\left[\frac{(C_{f,o} - C_{f,t})}{C_{f,o}}\right] \quad (8)$$

where, $C_{f,o}$ is the concentration of the metal ion in the feed solution at the start of the experiment and $C_{f,t}$ is the concentration of metal ions in feed at time t.

RESULTS AND DISCUSSION

Transport Studies with Cyanex 301

The separation studies of tracer concentration of Am(III) were carried out from the bulk of lanthanides with 0.5 M Cyanex 301 dissolved in *n*-dodecane. The aqueous feed solution was 1 g/L Eu spiked with ^{154}Eu and tracer concentration of ^{241}Am along with 1 M $NaNO_3$ at required pH value (buffered with 0.02 M sulphanillic acid). Here, Eu has been used as a surrogate for all the lanthanides. The above lanthanide concentration is expected to be generated from the strip solution of the actinide partitioning cycle of the high level waste of the PHWR (pressurized heavy water reactor) with a burn up of 6500 MWD/tonne (23). Figure 2 shows the transport profile of Am and Eu. It was found that the quantitative transport of Am(III) was possible in 10 minutes of operation at aqueous phase pH of 3.4. On the other hand, Eu transport was <0.01% showing SF values >100. However, the present composition of the aqueous phase would be difficult to maintain while dealing with a large scale of radioactive solution. It was of interest,

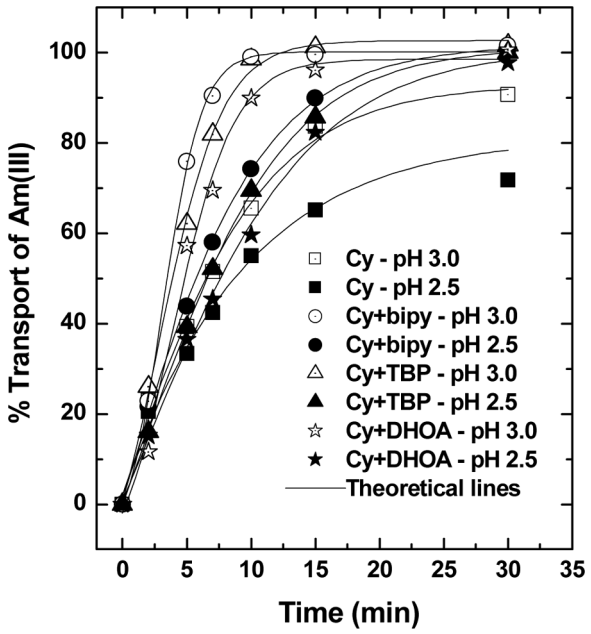


FIG. 2. Transport of Am(III) and Eu(III) by Cyanex 301-HFSLM; Carrier: 0.5 M Cyanex 301 dissolved in *n*-dodecane; Feed: 1 g/L Eu + 0.02 M sulphanillic acid +1 M $NaNO_3$ at pH 3.4 spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min; Temperature: 25°C.

therefore, to optimize the condition where the system can be used at a lower pH condition for example, pH 2 – 2.5. Figure 3 shows the effect of aqueous feed acidity (pH) on the transport of Am(III) by Cyanex 301-HFSLM system. It was found that the transport of Am(III) decreased significantly with decreasing the pH of the aqueous phase. The transport of Am(III) decreased from >99% at pH 3.4 to ~70% at pH 2.5 in 30 minutes of operation. As represented by equilibrium reaction (1), the extraction equilibrium for Am(III) by Cyanex 301 strongly depends on the aqueous feed acidity. The presence of protons in the feed at low pH (2.5) would not favor the complexation of Am(III) with Cyanex 301, resulting in decreased transport of Am(III). The study at further lower pH was, therefore, not performed due to a significantly reduced transport rate. The SF values of Am(III) with respect to Eu(III) also decreased from 100 at pH 3.4 to 6 at pH 2.5. These observations are in line with the solvent extraction studies which revealed a decrease in the SF between Am(III) and lanthanides at reduced pH (24).

Effect of Feed Nitrate Concentration

The effect of feed nitrate concentration on the separation of Am(III) and Eu(III) was investigated at pH 3.0 and the results are shown in Table 2. It was found that the transport of Am(III) was independent of the nitrate ions concentration. As shown in equilibrium reactions (2,3), the extraction equilibrium of Eu(III) changes in the

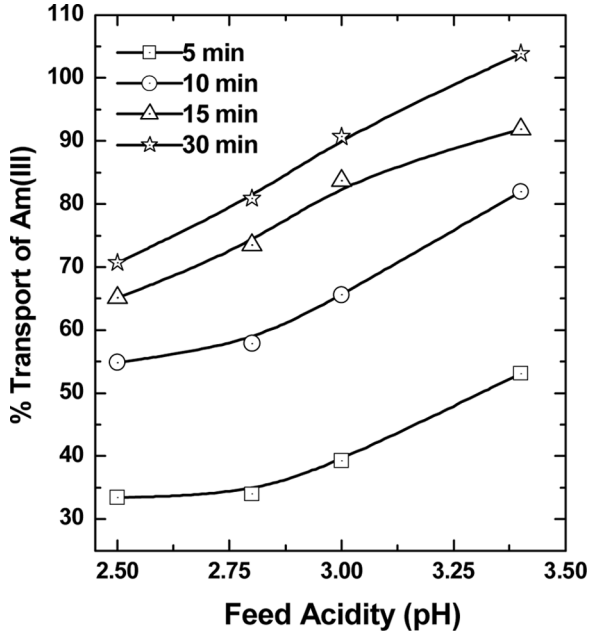


FIG. 3. Effect of feed acidity on the transport of Am(III) by Cyanex 301-HFSLM; Carrier: 0.5 M Cyanex 301 in *n*-dodecane; Feed: 1 g/L Eu + 0.02 M sulphanillic acid +1 M $NaNO_3$ spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C.

presence of nitrate ions. In the presence of nitrate ions Eu(III) requires two molecules of Cyanex 301 for extraction as compared to three in the absence of nitrate (11). Therefore, the presence of sufficient nitrate ions leads to the formation of Eu(III) complex with two Cyanex-301 molecules and results in the lower lipophilicity of the extractable complex. As a consequence, the transport rate of Eu(III) decreases in the presence of nitrate which increases the SF values. On other hand, the extracted species of Am(III) are independent of nitrate ion concentration, which justifies the unchanged transport rate of Am(III). In the present work, 1 M $NaNO_3$ was employed as this concentration is expected in the aqueous product containing lanthanides and actinides generated in the "actinide partitioning" cycle after neutralization of the strip solution (16).

TABLE 2
Effect of nitrate ion on the permeation of Am(III) by Cyanex 301-HFSLM; Carrier: 0.5 M Cyanex 301 in *n*-dodecane; Feed: 1g/L Eu + 0.02 M sulphanillic acid at pH 3.0 spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C

[$NaNO_3$], M	$P \times 10^2$ (cm/min)	% Transport of Am(III) in 30 min	D.F. values
0.5 M	1.09 ± 0.07	91.2	65
1 M	1.19 ± 0.03	95.1	60
2 M	1.22 ± 0.07	92.8	52

Pre-Concentration of Am(III)

Due to sufficiently higher transport rate of Am(III) where quantitative recovery was possible within 45 min at pH 3.0, experiments were conducted at increased feed to receiver phase volume ratio so that the actinide fraction could be concentrated. In this context, the feed volume was varied from 0.5 L to 2 L while the receiver phase was kept constant at 0.5 L. Whereas the quantitative transport of Am(III) was possible within 1 hr at 1:1 feed to receiver phase volume ratio with SF value of 50, about 40% transport of Am(III) could be achieved in the same operation time for a feed to receiver phase ratio of 4 with SF value decreasing to 35. The transport was not quantitative even after 5 hrs of operation and only about 80% transport was observed. At the same time the SF values decreased with the time of operation from 35 after one hr to <10 after 5 hrs. Initially, the Am(III) transport was faster as compared to Eu(III). However, after some time the transport of Am(III) attained saturation, whereas, the transport of Eu(III) continued with the time of operation. This resulted in decreased SF value with increasing time of operation. The

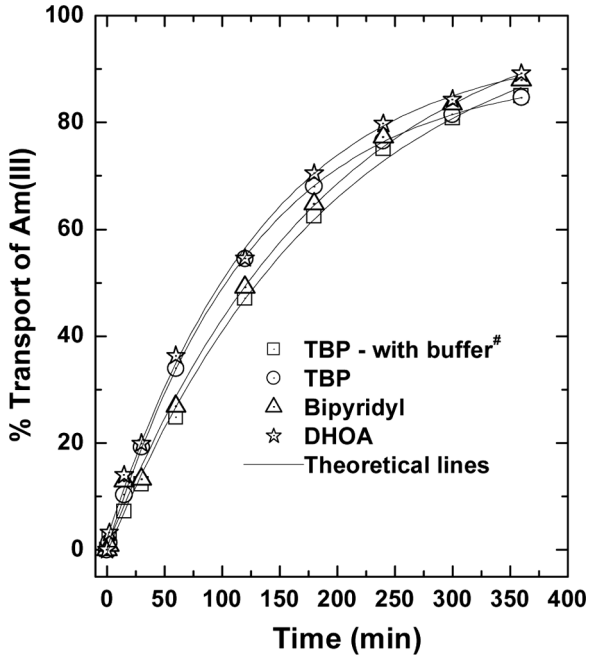


FIG. 4. Transport of Am(III) by Cyanex 301-HFSLM in the presence of synergists; Carrier: 0.5 M Cyanex 301 + 0.25 M TBP or 0.25 M DHOA or 0.03 M bipyridyl in *n*-dodecane; Feed: 1 g/L Eu + 0.02 M sulphanillic acid +1 M $NaNO_3$ spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C.

TABLE 3
Effect of feed acidity on permeability coefficient (P) of Am(III) in HFSLM; Carrier: 0.5 M Cyanex 301, 0.5 M Cyanex 301 + 0.25 M TBP, 0.5 M Cyanex 301 + 0.03 M Bipyridyl and 0.5 M Cyanex 301 + 0.25 M DHOA; Diluent: *n*-dodecane; Feed: 1 g/L Eu + 0.02 M sulphanillic acid + 1 M $NaNO_3$ spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C

	$P \times 10^3$ (cm/min)			
pH	Cyanex 301	Cyanex 301 + TBP	Cyanex 301 + Bipyridyl	Cyanex 301 + DHOA
3.0	11.9 ± 0.03	30.4 ± 3.45	33.9 ± 1.22	26.2 ± 2.83
2.5	7.52 ± 0.04	13.9 ± 0.26	15.6 ± 1.03	12.8 ± 1.07
2.0	–	0.64 ± 0.02	–	–
2.0[a]	–	0.65 ± 0.01	0.67 ± 0.02	0.75 ± 0.03

[a]Sulphanillic acid buffer was not added in the feed.

pre-concentration factor (PF) was defined as, $PF = C_{st}/C_{fo}$, where C_{st} is the concentration of Am(III) in the strip solution at an elapsed time t and C_{fo} is the Am(III) concentration in the feed solution at zero time. The PF values at feed to receiver phase volume ratio of 4 were: 1.7 and 3.2 after 1 hr and 5 hrs of operation, respectively.

Transport Studies with Synergistic Extraction Systems

The transport studies of Am(III) by Cyanex 301 shown in the previous section suggested that recovery of Am(III) strongly depended on the aqueous feed acidity. However, solvent extraction studies revealed that the addition of synergists to Cyanex 301 not only increased the SF values, but was also effective for feed solutions at lower pH values (9,11). Development of lanthanide/actinide separation process at lower pH (~pH 2) would be more acceptable as the difficulty in the feed adjustment with the buffer could be avoided. In this context, 0.25 M TBP (tri-n-butyl phosphate), 0.25 M DHOA (N,N-dihexyl octanamide), and 0.03 M Bipyridyl (2,2′-bipyridyl) have been investigated as synergists along with 0.5 M Cyanex 301 in *n*-dodecane. The extraction mechanism of Am(III) and Eu(III) by Cyanex 301 in the presence of synergists has been described earlier (9,11). It has been verified that synergists used in the present work, viz. TBP, DHOA, and Bipyridyl do not extract trivalent actinide and lanthanides at the conditions used in the present work. However, their presence along with Cyanex 301 enhances the extraction of Am(III).

The transport profiles of Am(III) by Cyanex 301 along with the different synergists are shown in Fig. 4. The transport data of Am(III) with pure Cyanex 301 has also been included in the figure for comparison purpose. The feed solution was 1 g/L Eu + 1 M $NaNO_3$ (spiked with ^{154}Eu and ^{241}Am) at pH 3.0 and 2.5 adjusted with 0.02 M sulphanillic acid. It was observed that the transport of Am(III) increased significantly in the presence of synergists. The transport profiles were also predicted using the membrane permeability coefficient (P) values and were compared with the experimentally determined data points. As shown in Fig. 4, good agreements between the calculated and

TABLE 4
Effect of feed acidity on the transport (T) and separation factor (SF) of Am(III) with respect to Eu(III) by HFSLM; Carrier: 0.5 M Cyanex 301, 0.5 M Cyanex 301 + 0.25 M TBP, 0.5 M Cyanex 301 + 0.03 M Bipyridyl and 0.5 M Cyanex 301 + 0.25 M DHOA; Diluent: *n*-dodecane; Feed: 1 g/L Eu + 0.02 M sulphanillic acid + 1 M $NaNO_3$ spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C

	Cyanex 301		Cyanex 301 + TBP		Cyanex 301 + Bipyridyl		Cyanex 301 + DHOA	
pH	%T (in 30 min)	SF	%T (in 30 min)	SF	%T (in 30 min)	SF	%T (in 30 min)	SF
3.0	91.7	60	99.9	225	99.9	350	99.9	300
2.5	70.7	6	99.9	150	99.9	325	97.8	250
2.0[a]	–	–	85.0	10	–	–	–	–
2.0[a,b]	–	–	84.7	8	88.0	350	89.2	50

[a]Transport data after 6 hrs.
[b]Without buffer in the feed.

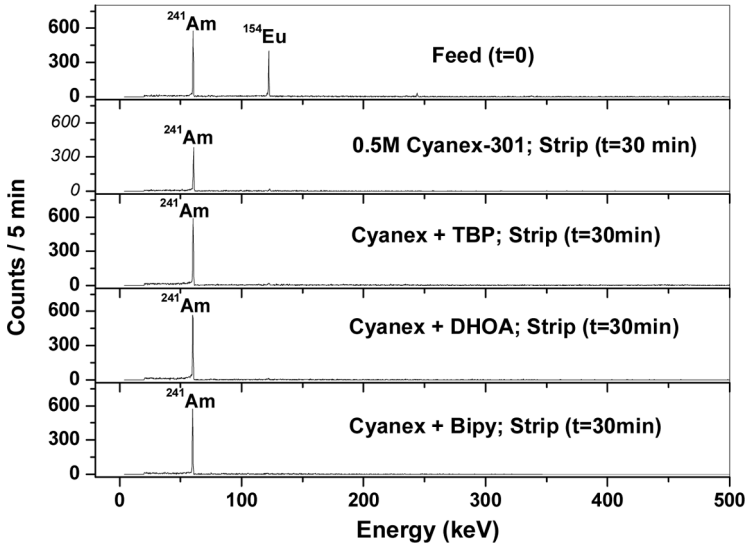


FIG. 5. High resolution gamma spectrum of ^{241}Am and ^{154}Eu in the feed and receiver phase solutions. Carrier: 0.5 M Cyanex 301 alone and in the presence of 0.25 M TBP or 0.25 M DHOA or 0.03 M bipyridyl in *n*-dodecane; Feed: 1 g/L Eu + 0.02 M sulphanillic acid +1 M $NaNO_3$ at pH 2.5 spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C.

experimental data points were obtained. The P value of Am(III) increased about two times in the presence of synergists as compared to the pure Cyanex 301 carrier (Table 3). The transport data and SF values for Am(III) are summarized in Table 4. At pH 2.5, ~70% Am was transported in 30 minutes with pure Cyanex 301 carrier, which increased to >99% in the presence of any of the synergists. An interesting observation was the co-transport of Eu(III) along with the Am(III) which affect the SF values. In case of pure Cyanex 301, the SF value decreased from 60 at pH 3.0 to 6 at pH 2.5. In the presence of synergists, however, the SF values were sufficient (>150) even at pH 2.5 for any process application. The high resolution gamma spectra of ^{241}Am and ^{154}Eu from the feed at the start of the experiment and in the product is shown in Fig. 5. The spectra clearly indicated the absence of any trace of Eu(III) in the product.

The transport of Am(III) was also investigated at pH 2.0 and the results are shown in Fig. 6. At first, the transport was carried out in the presence as well as in the absence of sulphanillic acid buffer with Cyanex 301 + TBP mixture. As indicated in Table 4, the transport data was not affected by the absence of sulphanillic acid buffer. Further transport experiments at pH 2.0 were, therefore, carried out without buffer. This is relevant from the process application point of view where the absence of buffer will require easier feed adjustment. The transport of Am(III) was between 85–90% with all the three synergists in 6 hours of operation. However, the SF values were significantly different for these synergists. The SF value after 6 hours followed the order: bipyridyl (350) >DHOA (50) >TBP (8). Interestingly, the SF values for bipyridyl was significantly large even after 6 hours when 88% transport of Am(III) could be achieved at feed acidity of 0.01 M HNO_3. It has been reported that synergists containing N donor atom increases the selectivity of Am(III) over Eu(III) in addition to increasing the D value of Am(III)

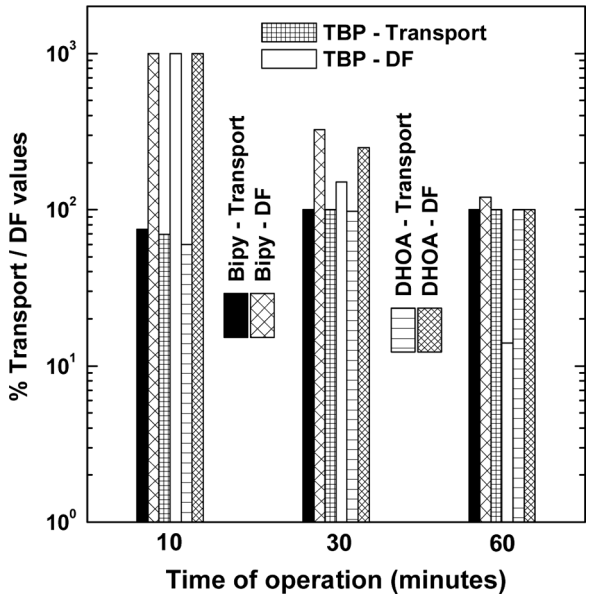


FIG. 6. Transport of Am(III) by Cyanex 301-HFSLM; Carrier: 0.5 M Cyanex 301 + 0.25 M TBP or 0.25 M DHOA or 0.03 M bipyridyl in *n*-dodecane; Feed: 1 g/L Eu + 1 M $NaNO_3$ at 0.01 M HNO_3 spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C. #: pH was adjusted with 0.02 M sulphanillic acid.

TABLE 5
Transport of Am(III) and separation factor (SF) values as a function of time in HFSLM system; Carrier: 0.5 M Cyanex 301 + 0.25 M TBP or 0.25 M DHOA or 0.03 M bipyridyl in *n*-dodecane; Feed: 1 g/L Eu + 0.02 M sulphanillic acid +1 M $NaNO_3$ at pH 2.5 spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min; Temperature: 25°C

	Transport of Am(III)			SF values		
Carrier used	10 min	30 min	60 min	10 min	30 min	60 min
Cyanex + Bipyridyl	73.4	>99.9	>99.9	1010	330	125
Cyanex + DHOA	58.8	>99.9	>99.9	1100	250	100
Cyanex + TBP	68.2	>99.9	>99.9	1000	150	14

(11). On the other hand, the presence of O donor synergists increases the D values of both, Am(III) and Eu(III) (9). Higher SF value in bipyridyl was associated to the soft 'N' donor site of bipyridyl which increased the selectivity of Am(III) over Eu(III). Whereas, in case of synergists like TBP and DHOA, the donor atom is 'O' which increases the D_{Am} values but selectivity for Am(III) does not increase. It was found that the SF value decreased with the time of operation (Table 5). For any given system, the transport of Am(III) increased with time and attained saturation value after certain time. On the other hand, the transport of Eu(III) showed a linear dependence with time causing a decrease in the SF value. From the present studies, bipyridyl seems to be a favourable synergist which can be used even at lower pH regions for selective recovery of Am(III) over lanthanides with reasonably good SF values.

Stability of the Liquid Membrane

The long-term stability of the HFSLM is an important issue from its application point of view. For such a stability test, the module was impregnated once with the carrier solution (0.5 M Cyanex 301) and the system was allowed to run continuously for 100 hrs with feed and strip solutions. The stability of the HFSLM was monitored by measuring the transport data of Am(III) and Eu(III) at regular time intervals. The feed solution was 1 g/L Eu + 0.02 M sulphanillic acid +1 M $NaNO_3$ at pH 3.0 spiked with ^{241}Am and ^{154}Eu tracers. From the transport data shown in Table 6, the Am(III) transport was 91.7% (in 10 minutes) at the start of the experiment, which decreased to 77.5% (in 10 minutes) after 100 hours of continuous operation. Though the %T data did not change significantly after 25 h, the SF value reduced to half. In line with this deterioration of the separation efficiency, the SF value decreased significantly to 4 after 100 h of continuous operation. Instability of the membrane can be described as two types, viz. the chemical stability of the carrier molecule and the physical stability of the liquid membrane which is related to the loss of carrier molecules from the pores of the membrane support. Pearson (25) has given the probable causes for the loss of carrier from the membrane support as:

(a) loss of extractant by solubility in adjacent aqueous solution,
(b) progressive wettabilty of the support pores induced by lowering of the organic-water interfacial tension which results from the surface active nature of the carrier molecules, and
(c) the differential pressures existing between the inside and outside of the HFSLM caused by pumping of the solutions.

Danesi (14,22) reported that the loss of carrier from the pores is more significant when carrier molecules are a very strong surfactant such as alkylaryl sulphonic acids and long chain quaternary ammonium salts. Cyanex 301 being a weaker surface active carrier and dodecane being a diluent, one may expect good physical stability of the membrane. The significant decrease in the SF value observed in the present work reflects the chemical instability of the carrier (Cyanex-301). It is well known that in the presence of acid, Cyanex 301 undergoes hydrolysis and is converted into Cyanex 302 and Cyanex 272. These derivatives of

TABLE 6
Successive Am(III) transport experiments to evaluate the stability of Cyanex 301-HFSLM; Carrier: 0.5 M Cyanex 301 in *n*-dodecane; Feed: 1g/L Eu + 0.02 M sulphanillic acid +1 M $NaNO_3$ at pH 3.0 spiked with ^{241}Am and ^{154}Eu tracers (500 mL); Receiver phase: 0.01 M EDTA (500 mL); Flow rate: 200 mL/min.; Temperature: 25°C

Time lapse (Hrs)	$P \times 10^3$ (cm/min)	% Transport in 10 min	S.F. values
0.0	11.9	91.7	60
25	8.43	89.5	30
50	6.80	83.6	15
75	5.12	79.2	9
100	4.35	77.5	4

Cyanex show strong extraction of lanthanides along with Am(III). Hill et al. (9), have shown that the presence of even a trace amount of other derivatives of Cyanex favor the extraction of Eu(III) over Am(III) by Cyanex 301. It seems that due to the formation of these derivatives of Cyanex, a significant amount of Eu was also transported thereby decreasing the SF value to 4 after 100 hrs of operation.

CONCLUSIONS

Selective recovery of Am(III) from lanthanides was demonstrated at 0.5 L scale with Cyanex-301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) using hollow fiber supported liquid membrane (HFSLM) technique. The transport rate of Am(III) was found to be affected by the feed acidity and was independent of the feed nitrate concentration. The presence of synergists such as tri-*n*-butyl phosphate (TBP), N,N,-dihexyl octanamide (DHOA) and 2,2′-bipyridyl (Bipy) revealed superior transport rate at low feed pH with a reasonably high separation factor (SF). The SF value decreased with the times of operation which was associated with continuous increase in Eu(III) transport with saturation in Am(III) transport after a certain time. In the presence of synergists, >85% transport of Am(III) was achieved in 6 hours of operation at pH 2.0 even in the absence of buffer. The SF value after 6 hours for different synergists at pH 2.0 followed the order: Bipy (350) >DHOA (50) >TBP (8). The HFSLM system was found to be deteriorating with time observed for 100 hours of continuous operation due to hydrolysis of the carrier molecule.

ABBREVIATIONS

Bipy	2,2′-Bipyridyl
BTP	2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine
DHOA	Di-*n*-hexyl octanamide
EDTA	Ethylenediamine tetraacetic acid
FSSLM	Flat sheet supported liquid membrane
HFSLM	Hollow fiber supported liquid membrane
HLW	High level waste
PUREX	Plutonium uranium reduction extraction
SF	Separation factor
TB	Tri-n-butyl phosphate
TODGA	N,N,N',N'-tetraoctyl diglycolamide
TOPO	Tri-n-octyl phosphine oxide
VOC	Volatile organic compounds

Symbols

A	Internal surface area of membrane
C_o	Initial metal ion concentration (at t = 0)
C_t	Concentration of metal ion in aqueous feed at time t
L	Length of the fiber
N	Number of fibers
P	Overall permeability coefficient
Q_T	Flow rate of the feed solution
V	Time average aqueous feed volume

Greek Letters

$\in$	Porosity of the membrane
ϕ	Transport parameter

REFERENCES

1. Baisden, P.A.; Choppin, G.R. (2007) Nuclear Waste Management and the Nuclear Fuel Cycle. In: *Radiochemistry and Nuclear Chemistry*, Nagyl, S.; ed. Encyclopedia of Life Support Systems (EOLSS), Eolss Publishers: Oxford, UK.
2. Ahearne, J.F. (1997) Special issue: Radioactive wastes. *Physics Today*, 50: 22.
3. Baestle, L.H. (1992) Burning of actinides: A complementary waste management option? *IAEA Bulletin*, 34: 32.
4. Proceedings of the Seventh Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Jeju, South Korea, 14–16 October, 2002.
5. Christiansen, B.; Apostolidis, C.; Carlos, R.; Glatz, J.; Malmbeck, R.; Pagliosa, G.; Romer, K.; Purroy, D.S. (2004) Advanced aqueous reprocessing in P&T strategies: process demonstrations on genuine fuels and targets. *Radiochim. Acta*, 92: 475.
6. Jensen, M.P.; Bond, A.H. (2002) Comparison of covalency in the complexes of trivalent actinide and lanthanide cations. *J. Am. Chem. Soc.*, 124: 9870.
7. Zhu, Y.J.; Chen, J.; Rio, R. (1996) Extraction of Am(III) and Eu(III) from nitrate solution with purified Cyanex-301. *Solv. Extr. Ion Exch.*, 14: 61.
8. Modolo, G.; Odoj, R. (1998) Separation of trivalent actinides from lanthanides by dithiophosphinic acids from nitric acid medium. *J. Alloy & Comp.*, 271–273: 248.
9. Hill, C.; Madic, C.; Baron, P.; Ozawa, M.; Tanaka, Y. (1998) Trivalent minor actinides/lanthanides separation using organophosphinic acids. *J. Alloy & Comp.*, 271–273: 159.
10. Ionova, G.; Ionova, S.; Rabbe, C.; Hill, C.; Madic, C.; Guillaumont, R.; Krupa, J.C. (2001) Mechanism of trivalent actinide/lanthanide separation using bis(2,4,4trimethylpentyl) dithiophosphinic acid (Cyanex 301) and neutral O-bearing co-extractant synergistic mixture. *Solv. Extr. Ion Exch.*, 19: 391.
11. Bhattacharyya, A.; Mohapatra, P.K.; Manchanda, V.K. (2006) Separation of Am(III) and Eu(III) from nitrate medium using binary mixture of Cyanex 301 with N-donor ligands. *Solv. Extr. Ion Exch.*, 24: 1.
12. Hoshi, H.; Tsuyoshi, A.; Akiba, K. (2000) Separation of americium from europium using liquid membrane impregnated with organothiophosphinic acid. *J. Radioanal. Nucl. Chem.*, 243: 621.
13. Bhattacharyya, A.; Mohapatra, P.K.; Manchanda, V.K. (2006) Separation of trivalent actinides and lanthanides using a flat sheet supported liquid membrane containing Cyanex-301 as the carrier. *Sep. Purif. Technol.*, 50: 278.
14. Danesi, P.R. (1985) Separation of metal species by supported liquid membranes. *Sep. Sci. Technol.*, 19: 857.
15. Ansari, S.A.; Bhattacharyya, A.; Raut, D.R.; Mohapatra, P.K.; Manchanda, V.K. (2009) Separation of actinides using hollow fiber supported liquid embranes. *Radiochim. Acta*, 97: 149.
16. Ansari, S.A.; Mohapatra, P.K.; Manchanda, V.K. (2009) Recovery of actinides and lanthanides from high-level waste using hollow-fiber supported liquid membrane with TODGA as the carrier. *Ind. Eng. Chem. Res.*, 48: 8606.

17. Geist, A.; Gompper, K. (2008) Miniature DIAMEX process in a hollow fiber module micro plant process development and optimization. *Radiochim. Acta*, 96: 211.
18. Geist, A.; Weigl, M.; Gompper, K. (2005) Small-scale actinide(III) partitioning processes in miniature hollow fiber modules. *Radiochim. Acta*, 93: 197.
19. Thiollet, G.; Musikas, C. (1989) Synthesis and use of the amide extractants. *Solv. Extr. Ion Exch.*, 7: 813.
20. Danesi, P.R. (1984) Permeation of metal ions through hollow fiber supported liquid membrane: concentration equations for once-through and recycling module arrangement. *Solv. Extr. Ion Exch.*, 2: 115.
21. Amrani, F.Z.; Kumar, A.; Beyer, L.; Sastre, A.M. (1999) Mechanistic study of active transport of silver(I) using sulphur containing novel carriers across liquid membrane. *J. Membr. Sci.*, 152: 263.
22. Danesi, P.R. (1984) A simplified model for the coupled transport of metal ions through hollow-fiber supported liquid membranes. *J. Membr. Sci.*, 20: 231.
23. Ansari, S.A.; Prabhu, D.R.; Gujar, R.B.; Kanekar, A.S.; Rajeswari, B.; Kulkarni, M.J.; Murali, M.S.; Natarajan, V.; Rajeswari, S.; Manivannan, R.; Antony, M.P.; Srinivasan, T.G.; Manchanda, V.K. (2009) Counter-current extraction of uranium and lanthanides from simulated high level waste using N,N,N′N′-tetraoctyl diglycolamide. *Sep. Purif. Technol.*, 66: 118.
24. Wang, X.; Zhu, Y.; Jio, R. (2001) Separation of Am from macro amount of lanthanides by a counter-current multistage extraction with purified Cyanex 301 and TBP. *Solv. Extr. Ion Exch.*, 19: 1007.
25. Pearson, D. (1983) *Ion Exchange Membranes*, Flett, D.S. ed.; Society of Chemical Industry: London, 55–73.