# Studies on the selective Am$^{3+}$ transport, irradiation stability and surface morphology of polymer inclusion membranes containing Cyanex-301 as carrier extractant

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## ARTICLE INFO

## ABSTRACT

Transport behaviour of Am$^{3+}$ across cellulose triacetate (CTA) based polymer inclusion membranes (PIM) containing Cyanex-301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) as the carrier extractant and tri-n-butyl phosphate (TBP) or 2-nitrophenyloctylether (NPOE) as the plasticizer was investigated from different feed and strip conditions. The TBP plasticized membrane resulted back transport of Am when alpha-hydroxy iso-butyric acid was used as the complexing agent in the strip phase while no such effect was seen when ethylene diamine tetraacetic acid (EDTA) was used as the complexant. Effect of varying Cyanex-301 concentration and bipyridyl (bipy) concentration on Am transport was also investigated. Long term reusability of the membrane was studied by measuring the permeability coefficient ($P$) after exposing the PIMs to a maximum gamma ray dose of ∼200 kGy. The surface morphology of the membranes was analyzed by atomic force microscopy and the roughness parameter was correlated to transport efficiency.

## 1. Introduction

Radioactive wastes are amongst the most hazardous wastes and their remediation by suitable separation techniques is one of the most challenging areas of contemporary research. High level radioactive wastes containing 10–100 Ci levels of activity are proposed to be managed by 'actinide partitioning' followed by the transmutation of long lived actinides and fission products by transmutation in high flux reactors or accelerator driven sub-critical systems. However, the transmutation of actinides can be affected by the presence of co-extracted lanthanides which act as neutron poisons. Therefore, it is required to separate the trivalent lanthanides from the actinides, particularly the trivalent minor actinides. Separation of the minor actinides (mostly Am$^{3+}$ and Cm$^{3+}$) from the trivalent lanthanides is a difficult task in the separation chemistry due to their similar charge and ionic radii. Only difference is the different spatial distributions of their respective valence f-orbitals. The 5f orbitals of the actinides possess higher spatial distribution as compared to that of the 4f orbitals of the lanthanides. The actinides therefore form stronger covalent bond with the soft donor ligands. A very high separation factor (5900) has been reported for Am$^{3+}$ over Eu$^{3+}$ in the solvent extraction study using Cyanex-

301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid; Fig. 1) as the extractant [1]. The main drawback of Cyanex-301 is its poor extractability at lower pH (pH < 3). In order to enhance the extraction, studies were performed in the presence of several oxygen donor auxiliary ligands along with Cyanex-301 [2], and the separation factor values increased several folds in case of the ternary extraction systems. Our studies, carried out in the presence of some nitrogen donor synergists, indicated that the separation factor values increased further to about 40,000 [3].

Though high separation factors are important, it was also required to develop a separation technique to carry out effective separation of the trivalent actinides from the trivalent lanthanides. Though solvent extraction based separation methods are routinely used in the nuclear industry, recent studies using supported liquid membrane technique have shown promise. The liquid membrane based separation methods are important from the point of view of low VOC inventory and much reduced extractant inventory making them suitable 'green' alternatives. The separation of the trivalent actinides and lanthanides by Cyanex-301 using membrane based techniques is rare in the literature [4,5]. From our earlier studies, flat sheet supported liquid membrane (FSSLM) of Cyanex-301 was found to be promising for the separation of trivalent actinides from a bulk of lanthanides [5]. However, the major drawback of the supported liquid membrane method is the poor membrane stability due to the leaching of the organic extractant with time to the feed or strip phases [6,7]. On the other hand, in the polymer

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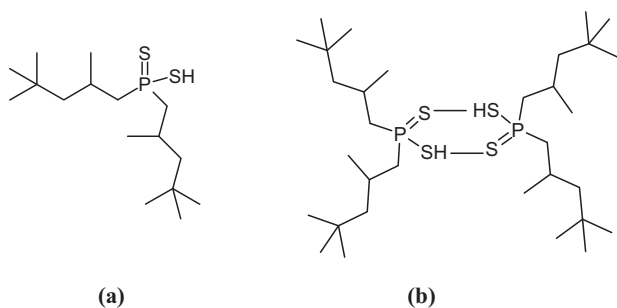E-mail address: mpatra@barc.gov.in (P.K. Mohapatra).

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**Fig. 1.** Structural formula of the (a) monomeric form and (b) dimeric forms of Cyanex-301.

inclusion membrane (PIM), extractant is held in a polymer matrix using a suitable plasticizer and leaching of the extractant from the membrane matrix can be insignificant, resulting in improvement in membrane stability [8]. Cellulose triacetate (CTA) based polymer inclusion membrane of Cyanex-301 has been investigated for the transport studies of various metal ions [9], where SLM yielded higher flux of the metal ions transported as compared to PIM. Similar observations were made by Paugam and Buffle [10] in their transport studies involving $Cu^{2+}$ ion transport using lauric acid as the carrier extractant and TEHP as plasticizer. A recent study comparing the stability of SLM and PIM concluded that PIM has significantly higher stability as compared to the SLM [11]. This makes a strong case for a systematic study on the evaluation of PIM containing Cyanex-301 for selective transport of $Am^{3+}$. In view of the possible use of the present work in radioactive waste management, it was also required to investigate the effect of irradiation dose on the transport efficiency of the membranes.

Transport and separation studies of $Am^{3+}$ and $Eu^{3+}$ were, therefore, carried out employing the cellulose triacetate (CTA) polymer inclusion membrane of Cyanex-301. Performances of two different plasticizers, viz. tri-n-butyl phosphate (TBP) and 2-nitro-phenyl octyl ether (NPOE) were evaluated and difference in the surface morphology of PIMs prepared using these two plasticizers were studied by atomic force microscopy (AFM). Effect of strippant and ligand concentration in the membrane on the transport behaviour of $Am^{3+}$ was also investigated in the present work. A systematic study was also carried out to understand the effect of gamma radiation dose on the transport behaviour of $Am^{3+}$ and $Eu^{3+}$ through the CTA-PIM of Cyanex-301. The change in membrane structure was also studied using the scanning electron microscopy (SEM). This work is a first ever report on the PIM containing Cyanex-301 used for the separation of trivalent lanthanide and actinides.

## 2. Experimental

### 2.1. Materials

Cyanex-301 was obtained from Cytec Canada Inc. as a gift sample. After purification by the reported method [1,3], the purity (>99%) of the product was checked by $^{31}P$ NMR, GC–MS and elemental analysis. 2,2′-Bipyridyl (BDH), CTA (alpha biochem), 2-nitrophenyloctyl ether (Fluka), tri-n-butyl phosphate (Aldrich), ethylene diamine-N,N,N′,N′-tetra-acetic acid (BDH) and alpha-hydroxy iso-butyric acid (Lancaster) were of the highest available purity (>99%) and used as obtained. All the other reagents were of AR grade. Solutions were made using deionized water. $^{241}Am$ was purified and the purity was checked by alpha spectrometry. $^{152,154}Eu$ was procured from Board of Radiation and Isotope Technology (BRIT), Mumbai, India and its radiochemical purity was

checked by gamma spectrometry using HPGe detector coupled to a multi-channel analyzer.

### 2.2. Membrane preparation

The PIMs were prepared using previously reported literature methods [8,12,13]. A mixture of cellulose triacetate (CTA), extractant (Cyanex-301 or synergistic mixture of Cyanex-301/2,2′-bipyridyl) and a plasticizer (tri-n-butyl phosphate (TBP) or 2-nitrophenyl octyl ether (NPOE) in the present studies) in chloroform, which was then allowed to dry slowly after pealing off on a Petri dish, to form a thin film of plasticized CTA containing the extractant. The compositions of the two different types of PIMs used with TBP and NPOE as plasticizer are listed in Table 1.

### 2.3. Transport studies

Transport studies were carried out using a two-compartment Pyrex glass cell as reported earlier [14]. Volumes of the feed and the receiver compartments were 20 mL each and the exposed membrane area was 4.94 $cm^2$. The feed solution for these studies contained 1 M $NaNO_3$ along with 0.02 M sulphanilic acid (buffer) and the pH was adjusted to 3.4. Alpha-hydroxy-isobutyric acid, 1 M $HNO_3$ and disodium salt of ethylene diamine tetra acetic acid at pH 3.4 were used as the strippants. Equal volumes of the source (spiked with $^{241}Am$ tracer) and receiver phase were transferred into the respective compartments and were stirred at 200 rpm by synchronous motors. Typically, the concentration of Am and Eu in the transport studies was of the order of $1 \times 10^{-7}$ M and $1 \times 10^{-5}$ M, respectively. The samples from both the compartments were assayed in duplicate (one from the feed and the other from the receiver side) and counted in an HPGe counter coupled to a multi-channel analyzer. The mass balance in all data points was within ±5% and any notable deviation from mass balance meant that the data point was not considered for permeability coefficient calculations. In order to carry out the effect of gamma radiation on the transport behaviour, the PIM was irradiated by a $^{60}Co$-gamma source with a dose rate of 2 kGy/h.

### 2.4. Membrane characterization

#### 2.4.1. Scanning electron microscopy

The sample was prepared for the SEM studies by mounting the PIM on a carbon tape on top of a stub and both sides of the dry membrane were coated with gold using Polaron E5100 sputter coater. The analysis of the gold coated samples was done using JSM 840 Scanning Electron Microscope (SEM) from JEOL company, Japan with 1000–5000 time magnification of the membrane surface.

#### 2.4.2. Atomic force microscopy

Surface morphology of the polymer inclusion membranes was characterized by atomic force microscopy (AFM). AFM measurements were carried out in contact mode using a scanning probe microscope (SPM-Solver P47, NT-MDT, Russia). Rectangular cantilevers of silicon nitride having force constant of 3 N/m were employed for measurement. The membrane surfaces were compared by means of roughness parameters, such as maximum height ($R_{max}$), mean height ($R_{mean}$), mean roughness ($R_a$) and root mean square (rms) of the Z data ($R_q$) [15].

## 3. Results and discussion

### 3.1. Transport studies with TBP plasticized PIM of Cyanex-301

No transport was observed through the CTA-PIM of Cyanex-301 using 2-nitrophenyl octyl ether (NPOE) as plasticizer using a feed

**Table 1**
Composition of TBP and NPOE plasticized PIM of Cyanex-301 in wt%.

| Membrane | Composition in wt% | | | | |
|---|---|---|---|---|---|
| | CTA | Cyanex-301 | Bipy | TBP | NPOE |
| Membrane with TBP | 21.2–40.3 | 10.0–52.6 | – | 26.2–49.7 | – |
| Membrane with NPOE | 17.5–20.9 | 19.6–23.5 | 1.3–17.5 | – | 45.4–54.3 |

containing 1 M NaNO$_3$ along with 0.02 M sulphanilic acid at pH 3.4 and spiked with [241]Am tracer and receiver compartment containing either 1 M HNO$_3$, alpha-hydroxy-isobutyric acid (AHIBA) or EDTA. This might be due to the poor extraction power of Cyanex-301 in that condition. TBP, a well known plasticizer, was reported to be an efficient synergist for the extraction of Am$^{3+}$ from the solvent extraction studies [2]. It was, therefore, used as an alternative plasticizer in the CTA based polymer inclusion membranes containing Cyanex-301 and significant amount of Am$^{3+}$ transport was noticed as discussed below.

### 3.1.1. Effect of stripping agents

As Cyanex-301 is an acidic chelating agent it is required to maintain the feed phase at low acidity so that the extraction of the metal ion is facilitated. Moreover, in order to strip the metal ions from the membrane phase the receiver phase should contain either higher concentration of acid (as compared to feed) or a solution containing a ligand with high complexing ability towards the metal ion transported. Our studies with 1 M HNO$_3$ in the receiver compartment have indicated inefficient Am$^{3+}$ transport and were ascribed to an unusual back transport phenomena [16]. It was required therefore to carry out transport studies using some complexing agents. Alpha-hydroxy-isobutyric (AHIBA) acid is a well known complexing agent for the lanthanides and actinides, which is used as a common eluting agent used in the intra group chromatographic separation of the lanthanides and actinides [17,18] was not suitable because of back transport Am$^{3+}$ because of AHIBA permeation through the PIM of Cyanex-301 [16]. In view of this, the stripping agent was chosen judiciously, so that it does not permeate through the TBP plasticized CTA-PIM of Cyanex-301 as a neutral or cationic species. In order to facilitate quantitative Am$^{3+}$ transport, experiments were thus carried out using EDTA as the stripping agent. This reagent is present as anion in the form of sodium salt at the pH range studied and the TBP plasticized CTA-PIM of Cyanex-301 is impermeable to the anionic species [16]. The feed solution was identical to the case where AHIBA was used as the strippant and quantitative Am transport was achieved in about 1.5 h with about 20% transport of Eu$^{3+}$ resulting in a decontamination factor of 5 (Fig. 2).

### 3.1.2. Effect of Cyanex-301 concentration

Transport of Am$^{3+}$ increased significantly with increasing Cyanex-301 concentration in the TBP plasticized PIM (Fig. 3). The transport of metal ions across the membrane is measured in terms of their permeability coefficient (P) that can be obtained using the following equation:

$$\ln \frac{[M]_t}{[M]_o} = -\left(\frac{Q}{V}\right) Pt \tag{1}$$

where $[M]_t$ and $[M]_o$ are the concentration of metal ion in aqueous feed at time $t$ (in s) and initial metal ion concentration (at $t = 0$), respectively, $Q$ (in cm$^2$) is the effective membrane area $A\varepsilon$ where $A$ (in cm$^2$) is the geometrical surface area and $\varepsilon$ is the porosity, $V$ is the aqueous feed volume (in mL). In PIMs the effective membrane area is taken as the geometrical surface area [8]. The flux

(J) (in mmol cm$^{-2}$ s$^{-1}$) for each metal ion is calculated as per the expression:

$$P = \frac{J}{C} \tag{2}$$

$P_{Am}$ value was calculated using Eq. (1) and was found to increased from $1.38 \times 10^{-4}$ to $8.24 \times 10^{-4}$ cm s$^{-1}$ when Cyanex-301 concentration was increased from 10 wt% to 35 wt%. This gave a slope of 1.4 in the log $P$ vs log(Cyanex-301) plot (Fig. 3). From the solvent extraction studies, however, $D_{Am}$ value increased with Cyanex-301 concentration with a slope of 3. Lower slope in case of the membrane study may be attributed to formation of aggregates as indicated in Fig. 1. Closer look Fig. 1 suggests that no percolation threshold Cyanex-301 concentration was required for Am$^{3+}$ transport in sharp contrast to literature reports with PIM systems [19], and the profile is more related with a transport diffusive mechanism than with a fixed-site jumping [20]. On the other hand, the plateau observed at higher Cyanex-301 concentration cannot be explained on the basis of diffusion mechanism and may be attributed to the fixed-site jumping mechanism similar to a literature report where LIX-84-I was used as the carrier extractant and TBEP, the plasticizer [19]. Similar observation was also reported for Cd$^{2+}$ transport through the CTA-PIM containing di-2-ethyl hexylphosphoric acid (D2EHPA), where Cd$^{2+}$ flux was found to be even decreased when D2EHPA concentration was increased beyond 50 wt% [21]. This could be attributed to viscosity effects.



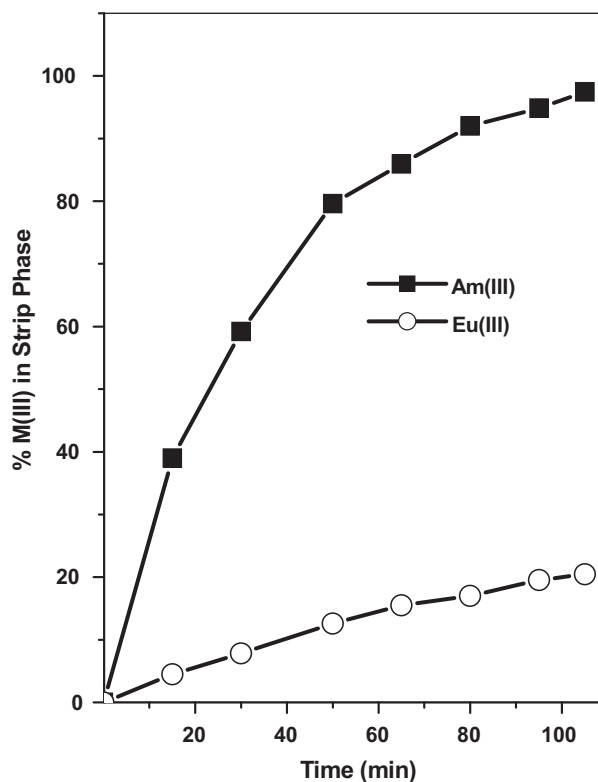**Fig. 2.** Transport of Am$^{3+}$ and Eu$^{3+}$ through the TBP plasticized CTA-PIM of Cyanex-301 employing 0.01 M EDTA at pH 3.5 as the strippant.
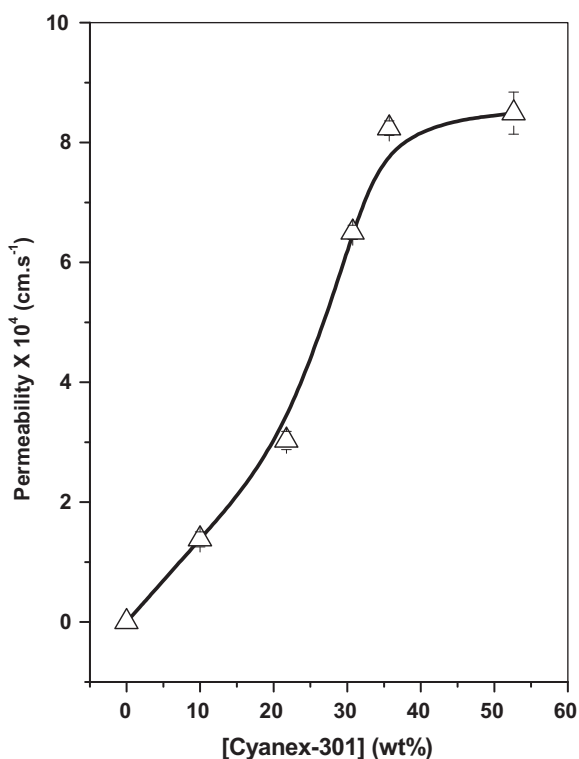
**Fig. 3.** Effect of Cyanex-301 concentration on the transport of Am$^{3+}$ through the TBP plasticized CTA-PIM of Cyanex-301. Feed: Am$^{3+}$ tracer in 0.02 M sulphanilic acid containing 1 M NaNO$_3$ at pH 3.4. Strip: 0.01 M EDTA at pH 3.4.

As it has been pointed out by Cussler et al. [22], the solute flux across chained carrier membrane varies with the concentration of the solute in a manner similar to the normal mobile carrier membranes, making it difficult to distinguish between these two types of mechanisms, viz. carrier–solute diffusion and fixed-site jumping responsible for the transport process. It has also been postulated that the PIMs can be regarded as borderline between the conventional flat sheet supported liquid membranes and fixed site carrier membranes and it is expected that both the carrier diffusion and jumping between the 'fixed' carriers may be taking place simultaneously within the PIM [22]. As seen in Fig. 3, an increase in Cyanex-301 concentration beyond 35 wt% resulted in a plateau which may be due to viscosity effects similar to those observed in case of supported liquid membranes or in case of PIM [21].

### 3.1.3. Stability of the membrane and effect of gamma radiation on transport behaviour

Long term stability with respect to both chemical and radiation is an important parameter of the membrane to be used for nuclear waste management. Effect of gamma radiation on the transport behaviour of PIM of Cyanex-301 is interesting to study because of gamma emitting nature of $^{241}$Am and most of the lanthanide isotopes present in the nuclear waste. A systematic study was, therefore, carried out in order to evaluate the TBP plasticized CTA PIM of Cyanex-301 as far as the chemical and radiation stability is concerned. The transport profile of Am$^{3+}$ was generated at different time intervals up to 10 days using unirradiated and irradiated PIM of Cyanex-301. It was observed from Table 2, that with the unirradiated PIM, the transport of Am$^{3+}$ decreased from $8.24 \times 10^{-4}$ to $5.13 \times 10^{-4}$ even after 10 days without much deterioration in the selectivity over Eu$^{3+}$. In the first experiment (day 1), not much difference was observed in the $P_{Am}$ and selectivity using the unirradiated and irradiated PIM. This suggests that the membrane structure or morphology was not affected much by the gamma radiation, which was also supported by the scanning electron microscopy (Fig. 4), where no change is observed in the PIM structure after irradiation with 194.4 kGy gamma radiation after 5000 times magnification. Similar smooth SEM picture was also

**Table 2**
Effect of gamma radiation on the transport behaviour of Am(III) and Eu(III) through cellulose triacetate PIM of Cyanex-301 (PIM: 35.5 wt% Cy-301 + TBP + CTA).

| Unirradiated | | | Irradiated (194.4 kGy) | | |
|---|---|---|---|---|---|
| Time (days) | $P_{Am}$ | S.F. | Time (days) | $P_{Am}$ | S.F. |
| 1 | $(8.2 \pm 0.4) \times 10^{-4}$ | 10.9 | 1 | $(6.5 \pm 0.2) \times 10^{-4}$ | 8.9 |
| 4 | $(6.6 \pm 0.1) \times 10^{-4}$ | 10.24 | 3 | $(1.5 \pm 0.4) \times 10^{-4}$ | 3.7 |
| 6 | $(5.4 \pm 0.3) \times 10^{-4}$ | 8.77 | 6 | $(1.5 \pm 0.1) \times 10^{-4}$ | 3.1 |
| 10 | $(5.1 \pm 0.1) \times 10^{-4}$ | 8.64 | 10 | $(1.1 \pm 0.3) \times 10^{-4}$ | 2.7 |

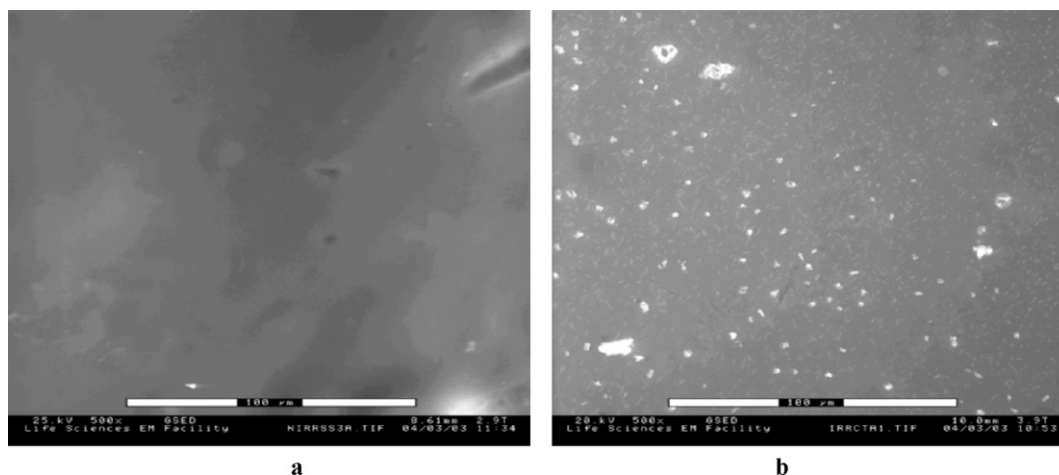*Note*: S.F. is defined as $P_{Am}/P_{Eu}$.



**Fig. 4.** SEM pictures of TBP plasticized PIM of Cyanex-301 with 5000 times magnification; (a) unirradiated and (b) irradiated with γ radiation (194.4 kGy).
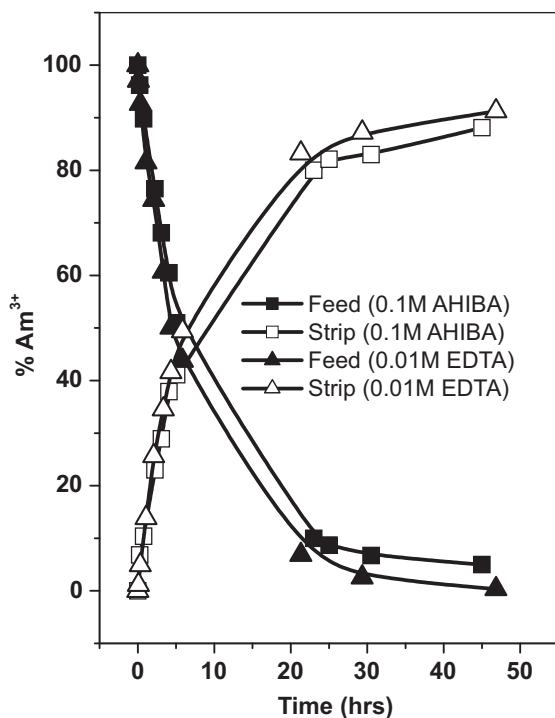
**Fig. 5.** Transport behaviour of $Am^{3+}$ through the NPOE plasticized CTA-PIM of Cyanex-301 (23.5 wt%) and bipy (2.63 wt%) using 0.1 M AHIBA and 0.01 M EDTA as the strippant. Feed: 0.02 M sulphanilic acid at pH 3.4 containing 1 M $NaNO_3$.

reported for the surface of NPOE plasticized CTA-PIM containing cryptands and crown ethers as carriers, where no trace of pore or fibre was seen [23]. Membrane stability, however, deteriorated significantly which was seen clearly from the significant decrease in
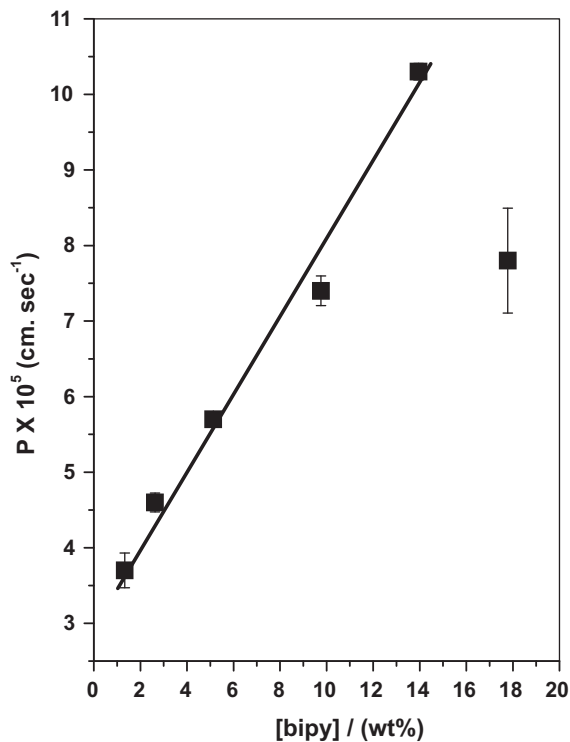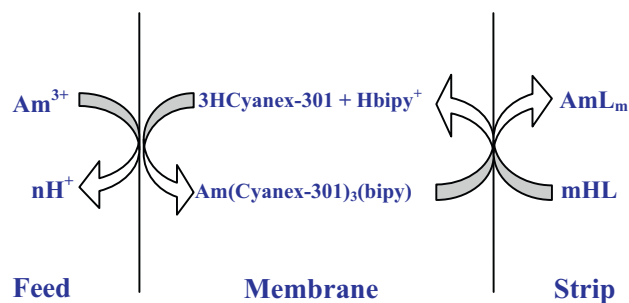


**Fig. 6.** Effect of bipy concentration on the transport of $Am^{3+}$ through the NPOE plasticized CTA-PIM of Cyanex-301 and bipy mixture. Feed: 0.02 M sulphanilic acid at pH 3.4 containing 1 M $NaNO_3$. Strip: 0.01 M EDTA at pH 3.4.



**Scheme 1.** Proposed mechanism for the transport of $Am^{3+}$ through the NPOE plasticized PIM of Cyanex-301 and bipy: HL is the strippant, viz. EDTA, AHIBA or $HNO_3$.

$P_{Am}$ and separation factor value. This deterioration in membrane stability after irradiation could be due to the degradation of the membrane components at the molecular level which is not seen by SEM.

### 3.2. Transport studies with NPOE plasticized PIM of Cyanex-301 and 2,2′-bipyridyl

#### 3.2.1. Effect of stripping agent

In the TBP plasticized PIMs containing Cyanex-301, back transport of $Am^{3+}$ was observed when AHIBA was used as the strippant making the transport system inefficient for actual application [16]. On the other hand, no back transport was seen when EDTA was used as the stripping agent. The back transport phenomenon was explained on the basis of interaction of TBP and AHIBA through H-bonding interactions [16]. Therefore, it was of interest to study the transport behaviour of $Am^{3+}$ through the PIM of Cyanex-301, where TBP is absent. NPOE, a well known plasticizer for CTA, has been used by us in PIMs made for the transport of $Sr^{2+}$ using crown ether as the carrier extractant [13]. $Am^{3+}$ transport was, therefore, studied through the NPOE plasticized PIM of Cyanex-301. In case of TBP plasticized PIM of Cyanex-301, TBP can act both as plasticizer and synergist and no additional synergist is, therefore, required to achieve measurable transport rate. As the use of Cyanex-301 alone did not lead to any transport of the metal ion in case of NPOE plasticized PIM of Cyanex-301, a mixture of Cyanex-301 + bipy (synergist) was used as the carrier extractant and AHIBA and EDTA were evaluated as the stripping agent. Expectedly, no back transport of $Am^{3+}$ was observed here with any of these stripping agents (Fig. 5). However, though ∼90% of the total $Am^{3+}$ was transported in 45 h in case of both the stripping agents, it was much slower as compared to that with TBP plasticized PIM containing Cyanex-301. This could be attributed to higher viscosity of NPOE as compared to TBP as similar observation has also been reported in the literature [24].

**Table 3**
Roughness parameters for the surfaces of two cellulose tri-acetate PIM of Cyanex-301 plasticized with two different plasticizers.

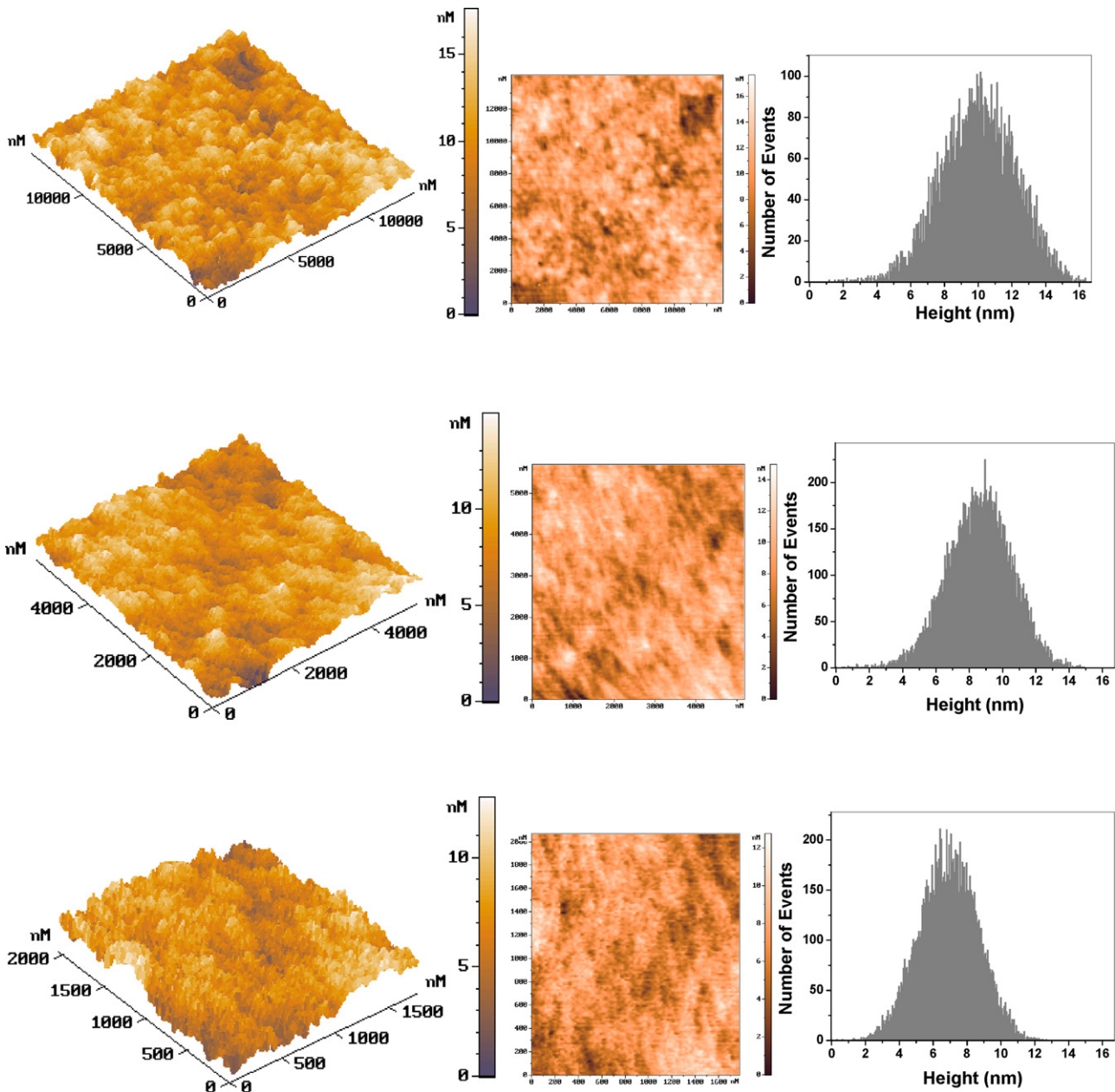| TBP plasticized CTA-PIM of Cyanex-301 | | | |
|---|---|---|---|
| Scan area ($\mu m^2$) | $14 \times 13$ | $5.6 \times 5.1$ | $2.6 \times 1.7$ |
| $R_{max}$ (nm) | 16.35 | 14.91 | 12.69 |
| $R_{mean}$ (nm) | 10.01 | 8.60 | 6.90 |
| $R_a$ (nm) | 1.78 | 1.55 | 1.39 |
| $R_q$ (nm) | 2.22 | 1.95 | 1.73 |
| NPOE plasticized CTA-PIM of Cyanex-301 | | | |
| Scan area ($\mu m^2$) | $13 \times 12$ | $5.7 \times 5.7$ | $2 \times 2$ |
| $R_{max}$ (nm) | 79.92 | 55.59 | 40.09 |
| $R_{mean}$ (nm) | 45.02 | 23.65 | 18.21 |
| $R_a$ (nm) | 6.84 | 6.22 | 5.39 |
| $R_q$ (nm) | 8.87 | 7.71 | 6.64 |

**Fig. 7.** 3D and 2D view of atomic force micrographs of polymer inclusion membranes of Cyanex-301 plasticized with TBP at different scan sizes (nm$^2$).

### 3.2.2. Effect of 2,2′-bipyridyl (bipy) concentration

As Cyanex-301 alone was not capable of Am$^{3+}$ transport and a mixture of Cyanex-301 and bipy when used as carrier resulted in Am$^{3+}$ transport, it was required to understand the role of bipy on Am$^{3+}$ transport. The presence of bipy alone as the carrier did not lead to any transport of Am$^{3+}$. However, in the presence of Cyanex-301, the permeability coefficient of Am$^{3+}$ linearly increased from $3.7 \times 10^{-5}$ to $10.3 \times 10^{-5}$ cm s$^{-1}$ with increasing the bipy concentration in the membrane from 1.3 wt% to 13.9 wt% resulting in a slope of 0.45 and further increase in bipy concentration to 17.8 wt% resulted in a decrease in the transport rate as reflected in as decreased $P_{Am}$ value of $7.8 \times 10^{-5}$ cm s$^{-1}$ (Fig. 6). From our earlier solvent extraction studies, $D_{Am}$ was found to increase with increasing bipy concentration with a slope of close to 1, resulting in formation of Am(Cyanex-301)$_3$(bipy) as the extractable species [3]. Due to higher polarity of the membrane system (NPOE as the plasticizer) vis-à-vis the solvent extraction system where relatively non-polar toluene was used as the diluent, possibility of extraction of acid is also higher. This could lower the dependence of bipy concentration from 1 to about 0.5. Based on these observations a mechanism (Scheme 1) can be proposed for Am$^{3+}$ transport using the mixture of Cyanex-301 and bipy.

### 3.3. Characterization of membrane morphology by atomic force microscopy

Surface morphology of the TBP and NPOE plasticized PIM of Cyanex-301 was studied using AFM. The roughness parameters are smaller in the TBP plasticized membrane as compared to the NPOE plasticized one (Table 3). This indicates that in case of TBP plasticized membrane, the height difference between the highest and lowest points in the surface ($R_{max}$) and standard deviation in $z$-
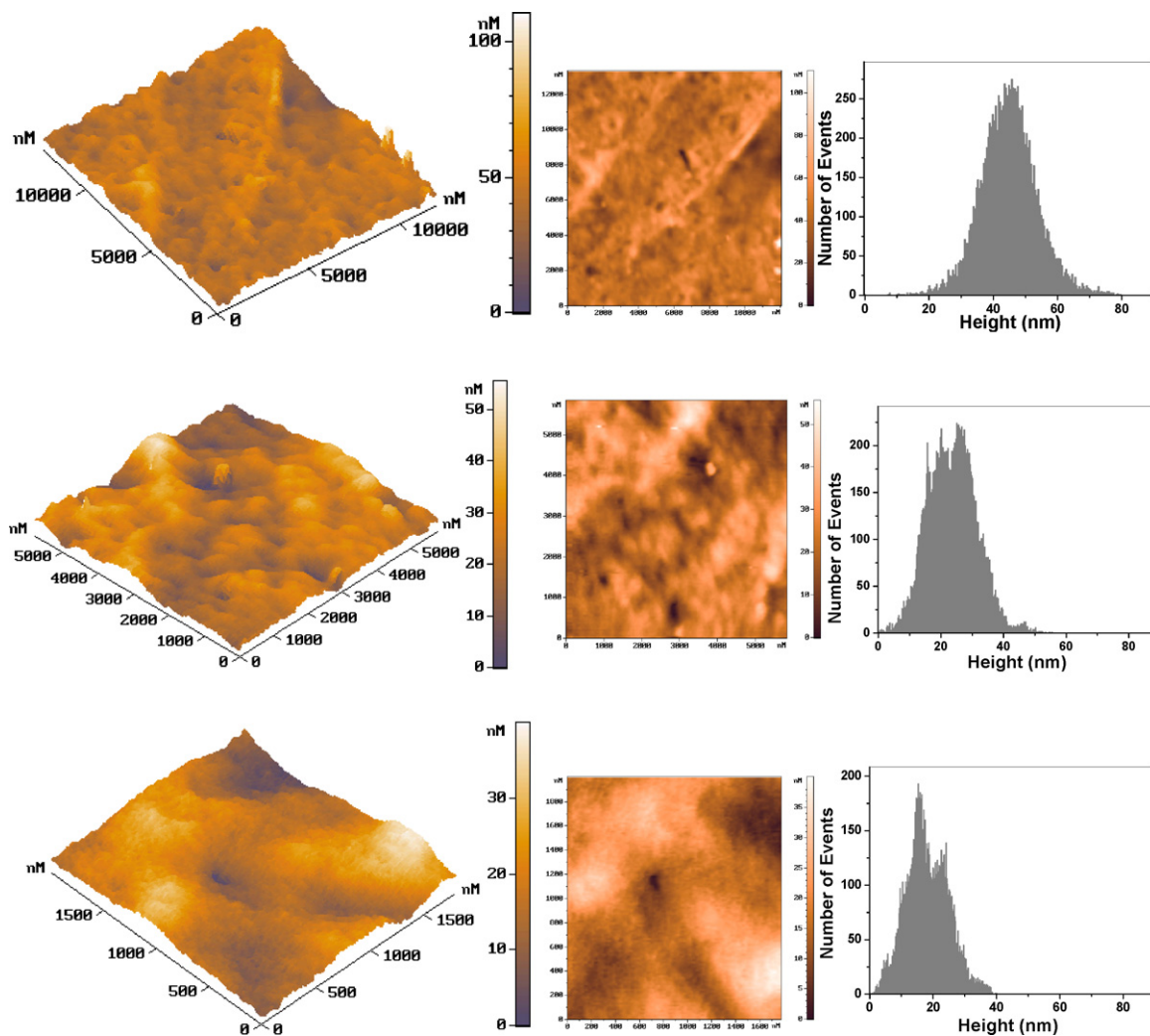
**Fig. 8.** 3D and 2D view of atomic force micrographs of polymer inclusion membranes of Cyanex-301 plasticized with NPOE at different scan sizes (nm$^2$).

values are less and hence forms smooth surface. This can arise from higher degree of homogeneity in the TBP plasticized membrane because of higher plasticizer–polymer and plasticizer–extractant interaction. Miguel et al. have also reported similar observation where higher degree of homogeneity was observed from the transmission infrared mapping microscopy (TIMM) in the CTA-PIM of Cyanex-272 plasticized with tri-2-ethylhexylphosphate (TEHP), which is a higher homologue of TBP as compared to that plasticized with NPOE [25]. The homogeneous surface with ultrasmall crests and troughs are further evident from the fact that TBP plasticized membrane shows less decrease in roughness parameters with decrease in the scanning area, while the decrease in the roughness parameters is higher in the NPOE plasticized membrane when the scan area of the membrane surface reduced. In the NPOE plasticized membrane the surface is, therefore, much rougher in broader dimension and with decrease in the dimension of the scanning area, the roughness decreases significantly. This is clearly evident from the shift of the peak position in the height distribution analysis plot towards height in case of NPOE plasticized membrane as compared to that in case of TBP plasticized one (Figs. 7 and 8). Thus the observed enhancement in the permeation rate of TBP plasticized membrane can be attributed to the improved homogeneity in the polymer matrix beside the lower viscosity of TBP as compared to NPOE.

## 4. Conclusions

Back transport of Am$^{3+}$ was observed through the TBP plasticized PIM of Cyanex-301, when AHIBA was used as the strippant and this back transport could be avoided using EDTA as the strippant and quantitative transport of Am$^{3+}$ could be achieved in 1.5 h with ∼20% Eu$^{3+}$ transport resulting a *df* value of 5. The back transport was not seen also employing the CTA-PIM of Cyanex-301 and bipy where NPOE was used as plasticizer with any of these two stripping agents, but Am$^{3+}$ transport was found to be much slower in case of NPOE plasticized PIM as compared to the TBP plasticized one. Clear difference in surface morphology was observed in the PIMs prepared using these two plasticizers. It appears that homogeneous distribution of plasticizer leads to smooth membrane surface and enhanced permeation. From the transport studies at varying carrier concentration it was clear that mobile carrier diffusion mechanism is operated for the transport of Am$^{3+}$. TBP plasticized PIM of Cyanex-301 was most suitable for the separation study of Am$^{3+}$ and Eu$^{3+}$ using 0.01 M EDTA as the stripping agent. Chemical and radiation stability of the TBP plasticized PIM was, therefore, studied which tells that the effect of radiation does not reflect in the membrane structure or morphology as shown from the transport data and SEM.

## Acknowledgement

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