Desalination and Water Treatment
www.deswater.com

12 (2009) 73–78

1944-3994 / 1944-3986
doi: 10.5004/dwt.2009.961

Transport of americium(III) across SLM containing CMPO as the carrier extractant

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Received 9 March 2009; Accepted in revised form 7 September 2009

ABSTRACT

The transport behaviour of Am^{3+} was investigated from nitric acid as well as from aqueous nitrate media under neutral pH conditions across PTFE flatsheet supports (0.45 micron) containing octyl,phenyl-N,N-di-*iso*-butyl carbamoylmethyl phosphine oxide (CMPO) as the carrier extractant. The effect of CMPO concentration and presence of tri-n-butyl phosphate (TBP) as phase modifier was studied. The results showed strong influence of hydrogen ion on Am(III) transport which was more pronounced in the presence of TBP. Acid transport data along with permeability coefficients for Am(III) transport are also presented.

Keywords: CMPO; Americium; Liquid membrane; Transport

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1. Introduction

'Partitioning and Transmutation' (P&T) is a promising strategy for the remediation of the high level waste (HLW) emanating from the back end of the nuclear fuel cycle [1,2]. The 'Partitioning' step involves the selective extraction of minor actinides such as Am, Cm and Np from the HLW leaving behind most of the fission products and structural materials in the raffinate. Table 1 gives a representative composition of HLW relevant for the waste from the pressurized heavy water reactor (PHWR). Several extractant such as CMPO (carbamoyl methyl phosphine oxide) [3–6], malonamides [7–9], DIDPA (di-iso-decyl phosphoric acid) [10], TRPO (tri-alkyl phosphine oxide) [11] and TODGA (N,N,N',N'-tetraoctyldiglycolamide) [12] have been used for the extraction of minor actinides from HLW. Out of these, CMPO has been used extensively for the extraction of trivalent actinide ions from moderate concentrations of acid suggesting its utility in the recovery of minor actinides (including Am(III) and Cm(III)) from high level waste (HLW). Based on its unique extraction property of 'internal buffering' [3,6,13], flow sheet for solvent extraction (SX) method has been developed for process scale applications. However, due to the large concentration of TBP used (as a phase modifier) along with CMPO, the possibility of generation of large amounts of secondary waste from SX operations is high.

Use of toxic and inflammable solvents causes a great deal of concern towards industrial/personnel safety. Separation methods with low solvent inventory have gained popularity over the past few decades. Amongst them, liquid membrane (LM) based techniques are particularly attractive as they involve much lower inventory of organic extractants and solvents [14–17]. In addition, liquid membrane based separation methods alleviate the short comings of SX based methods such as third phase formation and settling time limitations and have

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Presented at the Symposium on Emerging Trends in Separation Science and Technology (SESTEC-2008)
March 12–14, 2008, University of Delhi, Delhi, India

Table 1
Typical composition of PHWR – SHLW. Acidity: 3.12 M HNO_3

Element	Concentration (g/L)
Fe	0.72
Cr	0.12
Ni	0.11
Na	5.50
K	0.22
Mn	0.43
Cs	0.32
Rb	0.07
Zr	0.77
Pd	0.05
Sr	0.03
Ba	0.06
La	0.18
Ce	0.06
Pr	0.09
Nd	0.12
Sm	0.086
Y	0.06
Cd	0.016
Sn	0.01
Ru	0.16
Mo	0.14

the additional advantage of simultaneous extraction and stripping. There are, of course, several shortcomings of the liquid membrane system such as membrane stability, low throughput, etc. Danesi et al. have carried out studies on the liquid membrane transport of Am from nitrate media using CMPO as the carrier [18,19].

In the present work, SLMs containing a CMPO derivative (octyl,phenyl-N,N-diisobutyl carbamoylmethyl phosphine oxide*)* in the presence and absence of TBP are used for understanding the transport behaviour of Am(III). The effects of carrier concentration and feed nitric acid concentration on Am transport are also investigated.

2. Experimental

2.1. Materials

Octyl,phenyl-N,N-di-*iso*-butyl carbamoylmethyl phosphine oxide (CMPO) was synthesised in laboratory and was purified to yield >99.9% purity [6]. PTFE membranes (0.45 micron pore size) used in the present study were procured from Sartorius, Germany. AR grade TBP (tri-n-butyl phosphate) was used without further purification. Am-241 was purified using a previously reported procedure and assayed by gamma counting using a NaI(Tl) scintillation detector [20].

2.2. Transport studies

PTFE membranes were procured from Sartorius, Germany. A PTFE membrane (47 mm diameter) of pore size 0.45 μm having a nominal thickness of 80 μm and 72% porosity had a typical effective membrane area (*Q*) of 3.14 cm^2. The transport studies were performed in 20 mL glass transport cells with feed/strip solutions stirred at 200 rpm. The stirring rate has been optimized in an earlier report [21]. The PTFE membrane was soaked in the carrier solution (desired concentration of CMPO or its mixture with 1.2 M TBP in *n*-dodecane) for about 10 min prior to use [22]. Subsequently, the submerged membrane was removed from the solution and wiped carefully with a tissue paper to clear it of the excess fluid at the outside of the support. This impregnation technique led to SLMs which were reproducible within 5% with respect to their Am(III) transport behaviour. The feed phase usually contained nitric acid/sodium nitrate solutions while the receiver phase contained distilled water. In some cases, a buffer mixture (0.4 M formic acid, 0.4 M hydrazine hydrate and 0.1 M citric acid) was also used as the receiver phase. Membrane permeabilities were determined by assaying the samples from the feed as well as the strip sides at different time intervals and following a method described below.

For the transport of the metal ions across a supported liquid membrane (SLM), parameter of relevance is the permeability coefficient (*P*) which also depends on the distribution ratio, *D* (defined as the ratio of Am(III) concentration in the organic phase to that in the aqueous phase). Permeability coefficient for the metal ion transport can be calculated by using the following formula:

$$\ln\left(C_{f,t}/C_{f,0}\right) = -(Q/V)\,P\,t \tag{1}$$

where $C_{f,t}$ and $C_{f,0}$ are the concentrations of metal ions in the feed side at a given time interval and at the start of the experiment, respectively, *Q* is the effective membrane area, *V* is the volume of the feed solution in cm^3 and *t* is the permeation time (s). The cumulative percentage transport (% *T*) of the metal ion at a given time is determined by the following equation.

$$\%T = 100 \cdot C_{r,t}/C_0 \tag{2}$$

where $C_{r,t}$ is the concentration of the metal ion in the receiver at time *t*.'

The material balance in the transport studies was usually within ±5%.

3. Results and discussion

Am(III) transport studies were carried out using 0.1 and 0.2 M CMPO in the presence as well as absence of TBP and the data are presented in Fig. 1. It is reported that TBP worked as a phase modifier when used along with CMPO [2,6]. The transport process is a result of the

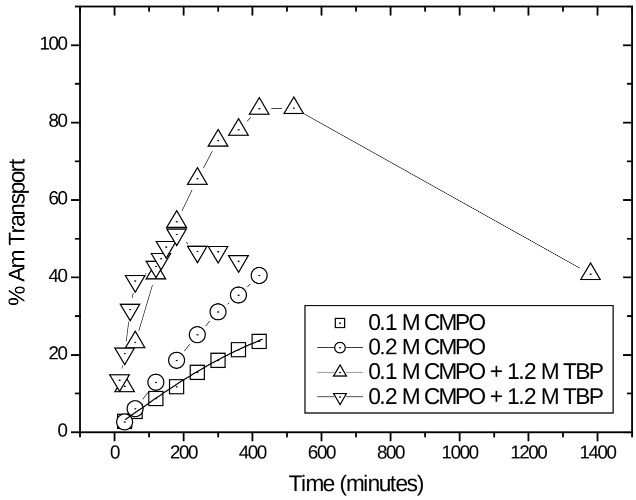

Fig. 1. Transport data of Am(III) using various carrier solutions. Feed: 3 M HNO_3; receiver: buffer mixture.

simultaneous extraction and stripping as represented by the equation:

$$\text{Am}^{3+} + 3\text{NO}_3^- + 3\text{CMPO}_{(\text{org})} \underset{\text{Stripping}}{\overset{\text{Extraction}}{\rightleftharpoons}} \text{Am(NO}_3)_3 \cdot 3\text{CMPO}_{\text{org)}} \quad (3)$$

where the species with the subscript (org) indicate those in the organic phase and those without any subscript indicate species in the aqueous phase. TBP is not part of the extracted species, though (as will be seen below) it extracts a significant amount of nitric acid, thereby impeding the stripping process.

3.1. *Effect of carrier concentration:*

The data presented in Fig. 1 shows that % transport though increased while increasing the CMPO concentration from 0.1 M to 0.2 M (in the absence of TBP), was quite slow. On the other hand, the presence of 1.2 M TBP increased the % transport as well as transport rates for both 0.1 M as well as 0.2 M CMPO. However, quantitative transport was not achieved in any of these cases due to back transport of the metal ions which was a consequence of the reverse transport mechanism (from the receiver phase to the feed phase) with build up of acid in the receiver phase. As indicated in Table 2, acid transport was <5% in 6 h when 3.0 M HNO_3 was used as the feed as compared to the case when 0.5 M HNO_3 was used as the feed (>10% acid transport in 5 h). On the other hand, increasing carrier concentration from 0.1 M CMPO to 0.2 M CMPO indicated much higher acid transport (Table 3) along with a superior rate of Am(III) transport (Fig. 1). In the presence of TBP, the acid transport rate increased in line with the Am(III) transport rate as indicated in Fig. 1. This suggested that the acid transport did not depend on the feed acid concentration alone but also on the carrier extractant concentration. Higher nitric acid transport in the case of CMPO+TBP carrier system as compared to CMPO was ascribed to a parallel co-transport mechanism involving TBP molecules. The acid uptake constant (K_H) is represented as:

$$L_{(\text{o})} + \text{NO}_3^- + \text{H}^+ \overset{K_H}{\rightleftharpoons} L \cdot \text{HNO}_{3(\text{o})} \quad (4)$$

Table 2
Acidity of the feed compartment as a function of time for varying feed acidities. Carrier — 0.1 M CMPO in *n*-dodecane

Time (h)	Feed composition			
	0.5 M HNO_3	1.0 M HNO_3	2.0 M HNO_3	3.0 M HNO_3
0.5	0.48	0.98	1.93	2.95
1	0.46	0.97	1.92	2.92
2	0.45	0.96	1.9	2.89
3	0.44	0.96	1.9	2.86
4	0.44	0.95	1.89	2.85
5	0.44	0.94	1.88	2.83

Table 3
Acidity of the feed side as a function of time at two different CMPO concentration (in the presence as well as absence of TBP)

Time (h)	Carrier composition			
	0.1 M CMPO[a]	0.1 M CMPO + 1.2 M TBP[a]	0.2 M CMPO[b]	0.2 M CMPO + 1.2 M TBP[b]
0.5	2.95	2.94	0.48	0.48
1	2.92	2.88	0.47	0.46
2	2.89	2.76	0.46	0.44
3	2.86	2.67	0.44	0.42
4	2.85	2.55	0.43	0.40
5	2.83	2.4	0.42	0.38
6	2.82	2.37	—	—

[a]Feed 3.0 M HNO_3; [b]Feed 0.5 M HNO_3

where K_H is the acid uptake constant of L (TBP or CMPO). Though the basicity of TBP (K_H = 0.16) is slightly lower as compared to CMPO (K_H = 0.20), the presence of the former in large concentration in the carrier solution caused significantly higher transport of nitric acid from the feed to the receiver compartment. This transport of nitric acid not only caused inefficient stripping in the receiver phase, it also initiated a reverse transport mechanism from the receiver to the feed side. While about 4% acid transport was observed in 5 h when 0.1 M CMPO was used as the carrier, it increased to >20% in the presence of 1.2 M TBP.

3.2. *Effect of feed acidity*

The effect of acid concentration was investigated using 0.1 M CMPO as the carrier extractant and the Am(III) transport data are presented in Fig. 2. It is clearly seen that with increasing acidity, the transport rates decreased. The reason for this is again the transport of significant amount of nitric acid from the feed to the receiver side (Table 2) along with a significant decrease in the free ligand concentration. The permeability coefficients (P) were calculated from Eq. (1) and are listed in Table 4. In line with the data on the Am transport rates with different feed acidity (Fig. 2), the P values decreased with increasing feed acidity.

The effect of feed acidity was more clearly evident from a set of experiments, carried out with $NaNO_3$ in place of HNO_3 taken in the feed solution (Fig. 3). The absence of hydrogen ions caused a remarkable enhancement in Am transport. In all the cases, it appeared that quantitative Am transport was possible. For comparison purpose, about 3 h of operation yielded about 99% and 12% Am transport with 3 M $NaNO_3$ and 3 M HNO_3, respectively. The permeability coefficients for the $NaNO_3$ system were also calculated using Eq. (1) and are also listed in Table 4. The permeability coefficients with $NaNO_3$ as the feed were about one order of magnitude higher as compared to those with HNO_3. As indicated in Fig. 4, the P values with nitric acid as the feed decreased sharply with increasing acidity. On the other hand, a slow increase in the permeability coefficient values was noticed which decreased slightly at a higher nitrate concentration (3 M) when $NaNO_3$ was used as the feed. The decrease in the P value at 3M $NaNO_3$ as the feed is not clearly understood.

Table 4
Permeability data of Am^{3+} using CMPO as the carrier extractant

[HNO_3]	P (cm/s)×10^4	[$NaNO_3$]	P (cm/s)×10^3
0.5 M	8.47±0.51	0.5 M	1.80±0.13
1.0 M	6.40±0.40	1.0 M	3.08±0.12
2.0 M	2.89±0.21	2.0 M	3.50±0.11
3.0 M	1.17±0.44	3.0 M	2.97±0.21

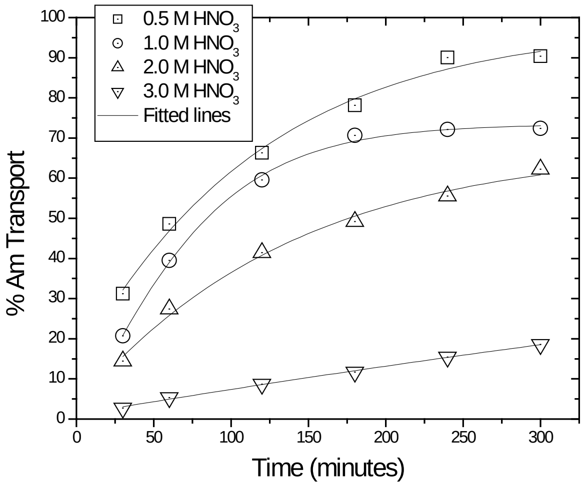

Fig. 2. Influence of feed nitric acid concentration on Am transport. Carrier: 0.1 M CMPO in *n*-dodecane.

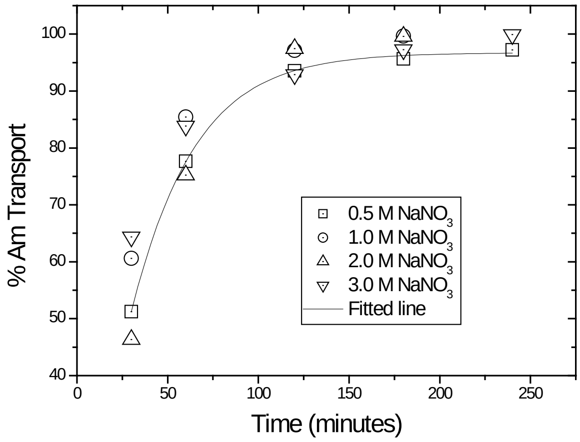

Fig. 3. Influence of $NaNO_3$ concentration on Am(III) transport. Carrier: 0.1 M CMPO in *n*-dodecane.

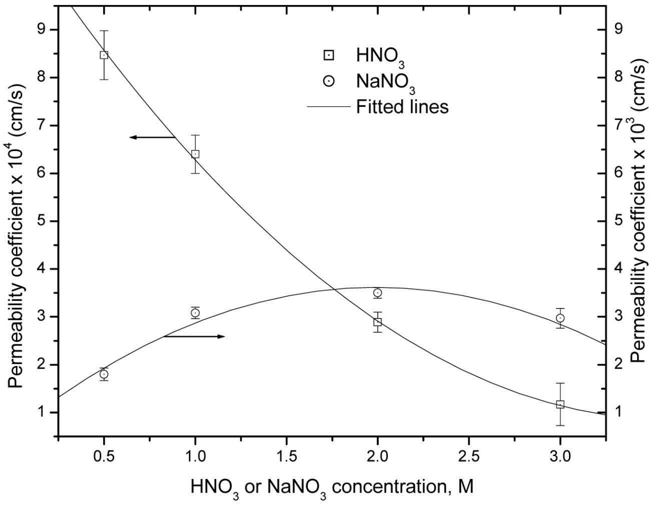

Fig. 4. Effect of feed nitrate concentration on Am(III) permeability. Carrier: 0.1 M CMPO in *n*-dodecane.

Table 5
Permeability data with different carrier extractants. Feed: 3 M HNO_3; receiver: distilled water (DMDBTDMA)/buffer mixture (CMPO)

System	P (cm/s) × 10^4	Remarks
Carrier 0.1 M CMPO	1.17±0.44	Present work
Carrier 0.1 M CMPO[a]	27	Ref. [16]
Carrier 0.1 M TODGA[b]	38	Ref. [20]
Carrier 1 M DMDBTDMA	1.16	Ref. [19]

[a]Feed 2 M $LiNO_3$ (pH 2.0); Receiver 0.5 M HCOOH
[b]Feed 2 M HNO_3; Receiver 0.01 M HNO_3

The permeability coefficients (P) obtained for the present system were compared with those reported by Danesi et al. for a similar system with 2 M $LiNO_3$ as the feed and 0.5 M formic acid as the receiver phase (Table 5). As no acid co-transport was involved in their case, the transport efficiency was nearly one order higher as compared to the present system. The P values obtained with 1 M DMDBTDMA as the carrier extractant were comparable to those obtained in the present system (Table 5) though acid transport was lower to a great extent. On the other hand, 0.1 M TODGA resulted in much higher P value for a feed containing 2 M HNO_3 and 0.01 M distilled water as the receiver [22].

The P values depend on the nature of the extraction system as follows:

- In the CMPO + TBP system: The low permeability coefficient values were due to high TBP concentration and hence high HNO_3 uptake by the liquid membrane. This not only resulted in poor stripping (due to acid transport to the receiver phase) but also affected Am(III) extraction due to lower free extractant concentration.
- In the DMDBTDMA system: Lower P values at higher acidities can again be explained on the basis of high acid uptake (1 M ligand was used in stead of 0.1 M CMPO or TODGA).
- In the TODGA system: Higher P value is ascribed to both efficient extraction as well as stripping at the feed — membrane and membrane — receiver interfaces, respectively.

3.3. Transport mechanism

The transport mechanism involved the three parallel processes as indicated by the extraction equilibria represented by Eqs. (3) and (4) for Am(III) transport by CMPO, hydrogen ion transport by CMPO and by TBP, respectively. The individual steps for each of these are as follows:

- Step I: Extraction of Am(III) by CMPO or H^+ ions by CMPO or TBP at the feed–membrane interface.
- Step II: Diffusion of these extracted species across the membrane phase obeying the Fick's law of diffusion.
- Step III: Stripping of Am(III) and H^+ at the membrane–receiver interface.
- Step IV: Back transport of the free carrier molecules to the feed–membrane interface.

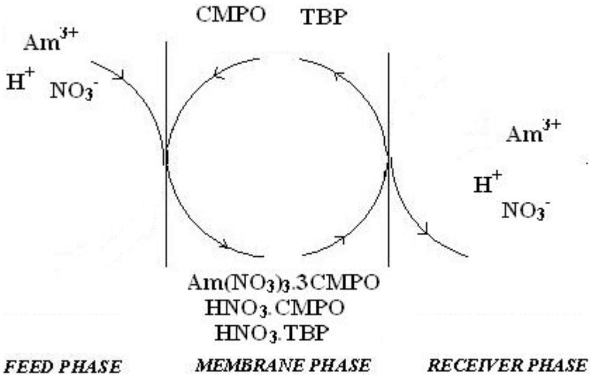

Fig. 5. Schematic representation of the transport mechanism.

The transport mechanism involving the transport of Am(III) by CMPO and co-transport of hydrogen ion by two different pathways using CMPO and TBP as the carrier extractants, is illustrated in Fig. 5.

The results indicated that the transport of Am from nitric acid feed solutions (the HLW contains about 3–4 M HNO_3) is not possible when CMPO alone or its mixture with TBP is used as the carrier. On the other hand, if the acidity in neutralized using NaOH, transport of Am is possible from the resulting feed containing $NaNO_3$.

3.4. Stability of membrane

Kempermann et al. [23] have reviewed the factors affecting the stability of the supported liquid membranes. Among them, the osmotic pressure difference and diluent property are most important. We have seen that the liquid membrane stability used to be reasonably good when n-dodecane was used as the diluent [21,22]. As the present work also used n-dodecane as the diluent, the liquid membrane stability is expected to be good. Regarding stability of the polymer support during its long term use, PTFE is highly chemical and thermal resistant [24]. However, its radiation stability is poor [25] and one needs to use radiation resistant polymers for long term application of the supported liquid membrane.

4. Conclusions

In conclusion, CMPO cannot be used for the quantitative transport of Am from acidic feed solutions. The carrier can be effectively used for Am transport only at low HNO_3 (0.5–1.0 M HNO_3) concentration or in presence of $NaNO_3$. TBP has only a negative influence on the Am transport rate and should not be used along with CMPO as the carrier. CMPO and DMDBTDMA have comparable transport efficiencies though the former has complications due to significant acid transport. On the other hand, TODGA is a far efficient carrier extractant.

Acknowledgements

One of the authors (A.K.D.) wishes to thank Mr. P.K. Dey, Head, Fuel Reprocessing Division, and S.K. Munshi, Plant Superintendent, for their constant encouragement.

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