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

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To cite this Article Panja, S. , Mohapatra, P. K. , Tripathi, S. C. and Manchanda, V. K.(2010) 'Transport of Thorium(IV) Across a Supported Liquid Membrane Containing N,N,N',N'-Tetraoctyl-3-oxapentanediamide (TODGA) as the Extractant', Separation Science and Technology, 45: 8, 1112 — 1120

To link to this Article: DOI: 10.1080/01496391003697416

URL: http://dx.doi.org/10.1080/01496391003697416

Separation Science and Technology, 45: 1112–1120, 2010
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003697416

Transport of Thorium(IV) Across a Supported Liquid Membrane Containing N,N,N′,N′-Tetraoctyl-3-oxapentanediamide (TODGA) as the Extractant

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The transport behavior of Th^{4+} was investigated from a feed containing 3.0 M HNO_3 into a receiver phase containing 0.1 M oxalic acid across a PTFE flat sheet supported liquid membrane (SLM) which contained TODGA (N,N,N′,N′-Tetraoctyl-3-oxapentanediamide) in *n*-dodecane as the extractant. Effects of the nature of the strippant, extractant concentration, Th concentration in the feed, and feed acidity on the transport rates were investigated. The transport behavior apparently depended on the rate of extraction of the metal ion at the feed-membrane interface and was not diffusion controlled. Influence of Th concentration on flux was also investigated. Transport mechanism was elucidated and the diffusion coefficient was calculated to be 2.13×10^{-7} cm^2/s. Solvent extraction studies at varying feed acidity and TODGA concentration were also carried out.

Keywords diglycolamide; liquid membrane; nuclear waste management; thorium; transport

INTRODUCTION

Due to the increasing concern for the environment, a two-step strategy of

i) use of green reagents and
ii) reducing the inventory of organic solvents is emerging as the focus for novel separation technologies.

Liquid membrane (LM) based methods have been suggested as a viable alternative to solvent extraction methods. The latter require not only a large inventory of organic solvents but also suffer from drawbacks such as third phase formation and a large volume of secondary wastes (1–3). Though there are numerous applications of membrane technology in effluent treatment, the food processing, and the pharmaceutical industry, its application to the nuclear industry is at its infancy stage (4). LM offers exciting opportunities for the selective metal ion separations particularly relevant at the back end of the nuclear fuel cycle (5–8).

Out of the processes relevant at the back-end of the nuclear fuel cycle, “actinide partitioning” is proposed to play a pivotal role in radioactive waste management. TODGA (N,N,N′,N′-tetraoctyl-3-oxapentanediamide, Fig. 1) appears to be one of the most promising extractants for trivalent actinide ions and has been suggested as a “green” alternative to CMPO (carbamoylmethylphosphine oxide) used in the TRUEX (TRansUranium EXtraction) process (9–12). It is intriguing to observe that TODGA extracts trivalent actinides better than tetravalent/hexavalent actinides which are its unique characteristics (13). We have carried out extensive studies on the solvent extraction, extraction chromatographic, and membrane-based separations of actinides using TODGA as the extractant (12,14–16). Out of all these separation methods, the supported liquid membrane based separation methods were found to be the most promising.

While trivalent actinides such as Am^{3+} and Cm^{3+} are of particular relevance in “actinide partitioning,” it is also required to understand the extraction of Pu and Np which are invariably present in the High Level Waste (HLW) stream. While Pu is mainly present as Pu^{4+}, it can also simultaneously be present in the +3 as well as +6 oxidation states. To understand the behavior of Pu^{4+} (without any possible interference from Pu^{3+} and PuO_2^{2+}) Th^{4+}, in view of its non-variable oxidation state, was used as a model tetravalent actinide ion. Moreover, it is also of interest to recover Th from various effluent streams (including THOREX (THORium EXtraction) process effluents) in nitric acid.

The present work deals with the transport behavior of Th^{4+} from HNO_3 medium under varying experimental conditions such as, nitric acid concentration, TODGA concentration, and Th concentration. PTFE flat sheets impregnated with containing 0.1 M TODGA in n-dodecane have been used as the extractant while 0.1 M oxalic acid has been used as the strippant solution.

Received 7 October 2009; accepted 11 January 2010.

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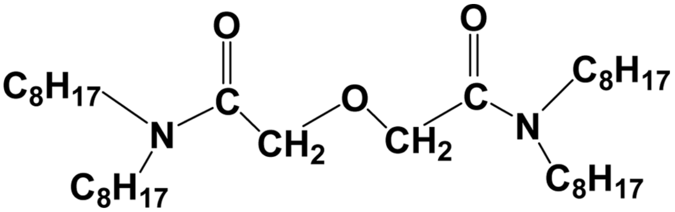


FIG. 1. Structural formula of TODGA.

EXPERIMENTAL

Materials

N,N,N′,N′-tetraoctyl diglycolamide (TODGA) was synthesized by a reported method (11). Characterization of TODGA was done by elemental analysis, NMR, and IR spectroscopy. Oxalic acid (AR Grade) was procured from Merck, Germany and was used as received. PTFE membranes used in the present study were procured from Sartorius, Germany. All the other reagents were of AR grade and were used without further purification.

Th-234 Stock

Th-234 tracer ($t_{1/2} = 24$ days) was used after freshly obtaining the radiotracer from natural uranium by a procedure reported earlier (17). A feed containing 200 g/L natural U in 6 M HCl was contacted with three successive lots of 30% Aliquat 336 in chloroform. The raffinate contained Th-234 activity with traces of U. Decontamination from the residual U was achieved by extracting the Th-234 with 0.5 M HPBI (3-phenyl-4-benzoyl-5-isoxazolone), as reported earlier (17). Studies with Th^{4+} ion carrier were carried out using nitrate salts of natural Th and spiking with the radiotracer. Assaying of Th-234 was done by gamma counting of the 63 and 93 keV peaks using NaI(Tl) scintillation detector. Analysis of Th in case of studies involving the Th carrier solution was done using a spectrophotometric method involving Arsenazo III (17).

Characterization of PTFE Membrane Filters

The membrane thickness was measured by a Mitutoyo Digital micrometer while the porosities of the membranes were measured by an Electroscan 2020 environmental scanning electron microscope (ESEM) as reported earlier (18). The porosity and effective area of the membrane flat sheets (pore sizes 0.2 μm) were determined as 51% and 2.50 cm^2, respectively.

Methods

Solvent Extraction Studies

Solutions of desired concentration of TODGA prepared in *n*-dodecane were agitated with an equal volume of the aqueous phase (containing the requisite quantity of ^{234}Th tracer) in a rotary thermostated water bath for an hour at 25.0 ± 0.1°C. The two phases were then centrifuged and assayed by taking suitable aliquots from both the phases. The distribution ratio (D_{Th}) is defined as the ratio of concentration of metal ion in the organic phase to that in the aqueous phase.

Transport Studies

The SLM studies were carried out using 30 mL glass transport cells with feed/strip solutions (~30 mL each) stirred at 200 rpm (18). A previous report has suggested that 10 minutes of soaking time for PTFE membranes was adequate (15). The microporous membrane filters were thus soaked in the extractant solution (usually 0.1 M TODGA in *n*-dodecane) for 10 minutes prior to use. Subsequently, the submerged membrane was removed from the solution and wiped carefully with a tissue paper to remove the excess fluid on the support.

Usually, the feed compartment contained 3.0 M HNO_3 while the strip solution was 0.1 M oxalic acid for Th^{4+}. Assay of Th-234 in the feed as well as in the receiver side was done by removing 100 μL aliquots at different time intervals to calculate the flux as well as the permeability coefficients. Volume correction was made while calculating the transport parameters (*vide infra*). The transport studies were carried out at ambient temperatures (24 ± 1°C). The material balance in these studies was found to be within ±5%. The dynamic viscosity of TODGA solutions was measured by a viscometer (Anton Par, Austria).

THEORETICAL

Transport Equations

In SLM studies, the transport process is a result of three steps, viz. the extraction at the feed-membrane interface, diffusion inside the membrane, and stripping at the membrane-receiver interface (Fig. 2). The efficiency of the transport depends on all the three stages. Additionally, the diffusion of the metal ions from the bulk of feed to the feed-membrane interface and from the membrane-receiver interface to the bulk of the receiver phase is also important. These, in short, convey that the overall

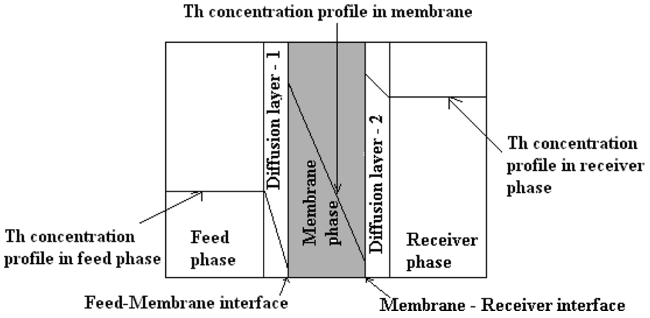


FIG. 2. Transport model for SLM system containing TODGA as the extractant.

transport process not only depend on the kinetic and thermodynamic parameters such as the distribution of the metal ion at the feed – membrane interface represented by the following equilibrium

$$M^{n+} + nNO_3^- + mL_{(o)} \rightleftharpoons M(NO_3)_n \cdot mL_{(o)} \quad (1)$$

where the subscript (o) represent species in the organic or the membrane phase, but also on the diffusional parameters concerning the permeating species. Assuming the extraction and stripping of the metal ion is much faster compared to the diffusion of the complex in the membrane phase (*vide infra*), the transport process will depend on these three diffusion processes which can be given by Fick's first law of diffusion:

$$J_f = D_f\{C_f - C_{fm}\}/d_f \quad (2)$$

where D_f is the diffusion coefficient of the metal ion, d_f is thickness of the aqueous diffusion layer of the feed phase, and C_f and C_{fm} are the concentration of metal ion at the feed and feed-membrane interface, respectively. Similarly, the flux through the membrane is represented by the following equation.

$$J_m = D_o\{C_{mf} - C_{mr}\}/d_o \quad (3)$$

where C_{mf} and C_{mr} are the metal ion concentrations, in the membrane phase at the membrane – feed and membrane – receiver interfaces, respectively. D_o is the diffusion coefficient in the membrane phase and d_m is the membrane thickness. Ignoring the flux equation for the metal ion diffusion at the membrane-receiver interface, the flux, J, can be represented under steady state condition as

$$J = (D_o/d_o)\{C_{mf} - C_{mr}\} = (D_f/d_f)\{C_f - C_{fm}\} \quad (4)$$

where the term $\{C_{mf} - C_{mr}\}$ is nothing but the concentration of the extracted species in the membrane phase. The flux equation can be modified to

$$J = K_d^f C_f/[(d_o/D_o) + K_d^f(d_f/D_f)] = PC_f \quad (5)$$

where P is the permeability coefficient. Since the flux can alternatively be expressed as

$$J = -(V/Q) \cdot dC_f/dt \quad (6)$$

Combining these two Eqs. (7) and (8), and integrating one obtains,

$$\ln(C_{f,t}/C_{f,0}) = -(Q/V)Pt \quad (7)$$

where V, $C_{f,0}$, and $C_{f,t}$ represent the volume and concentration of feed at starting time and after time 't', respectively. Q is the effective surface area defined as $A\varepsilon$ where A is the geometrical surface area and ε is the porosity, V is the time average aqueous feed volume (in mL). It is assumed that the feed and receiver phase volumes do not change significantly during the experiment. The percent transport (%T) as viewed from the feed compartment at a given time is determined by the following equation,

$$\%T = 100 \cdot (C_{f,o} - C_{f,t})/C_{f,o} \quad (8)$$

The data treatment that follows generally includes plots of %T vs time as well as calculations of the permeability coefficient in some cases. Thorium fluxes are also calculated in some cases as indicated below.

RESULTS AND DISCUSSION

Solvent Extraction Studies

The extraction of tetravalent Th from aqueous nitrate medium using TODGA is represented by the following extraction equilibrium:

$$Th^{4+} + 4NO_3^- + nTODGA_{(o)} \overset{K_{ex}}{\rightleftharpoons} Th(NO_3)_4 \cdot nTODGA_{(o)} \quad (9)$$

where, the species with subscript '(o)' represent those in the organic phase while those without any subscript indicate species in the aqueous phase. Solvent extraction studies were carried out as a function of TODGA concentration as well as aqueous HNO_3 concentration. As indicated in Table 1, Th^{4+} extraction increased with TODGA concentration as well as with HNO_3 concentration. The log-log plot of D_{Th} (distribution ratio) vs TODGA concentration (Fig. 3) with a slope of 3.82 ± 0.10 indicated that the extracted species contained about 4 molecules of TODGA resulting in the extraction of species of the type $Th(NO_3)_4 \cdot 4TODGA_{(o)}$, which was in sharp contrast to the results reported by Zhu, et al. (13), who had reported that the extracted species contained about 3 TODGA molecules in the extract. The extraction constant (log K_{ex}), represented as

$$K_{ex} = \frac{[Th(NO_3)_4 \cdot 4TODGA_{(o)}]}{[Th^{4+}][NO_3^-]^4[TODGA]^4} \quad (10)$$

TABLE 1
Distribution data of Th^{4+} – TODGA extraction system

$[HNO_3]$	D_{Th} (0.1 M TODGA)	[TODGA]	D_{Th} (3 M HNO_3)
0.5 M	12	0.03 M	341
1 M	198	0.05 M	675
2 M	5318	0.08 M	9812
3 M	15893	0.10 M	15893
6 M	95672	0.15 M	42892

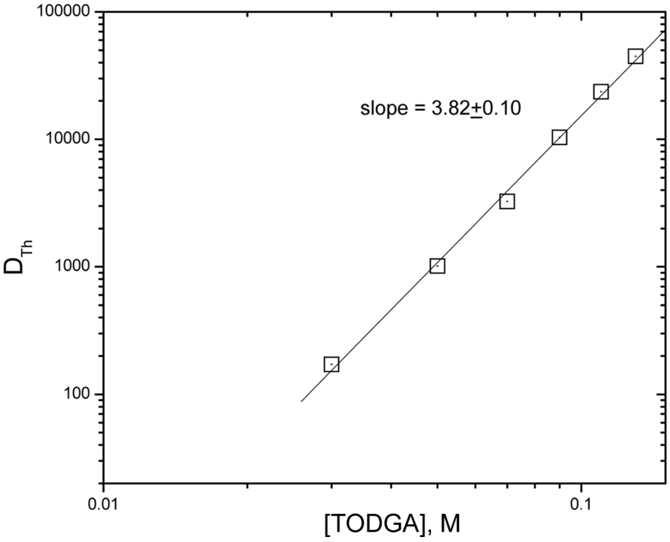


FIG. 3. Dependence of D-Th on TODGA concentration. Aqueous phase acidity: 3 M HNO_3.

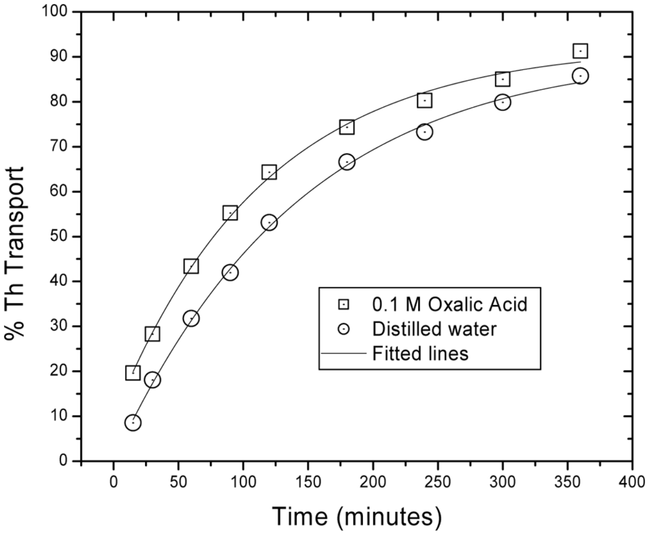


FIG. 4. Transport profiles of Th^{4+} with distilled water and 0.1 M oxalic acid as the strippant. Feed: 3 M HNO_3; Extractant: 0.1 M TODGA.

was calculated to be 7.91 ± 0.16 (after making corrections for the nitrate ion complexation (20)). This is in sharp contrast to the value reported by Sasaki et al. (11) (log $K_{ex} = 5.55 \pm 0.04$) and can be attributed to the difference in the nature of the extracted species as explained above. For the stripping studies, dilute nitric acid was not used as the strippant. On the other hand, distilled water and oxalic acid were evaluated. Solvent extraction studies carried out for the stripping process using distilled water and 0.1 M oxalic acid indicated D_{Th} values to be 2.08 and 0.38, respectively. In view of efficient stripping by oxalic acid, for all subsequent studies, 0.1 M oxalic acid was used as the strippant in the receiver compartment. This is in view of the strong preference of tetravalent actinides for oxalate ions (21). The kinetics of extraction of the extraction and stripping steps were fast enough to consider the transport process controlled by the diffusion kinetics of the extracted species.

Transport Studies

Effect of Nature of Strippant

As the distribution ratio at the membrane-receiver interface should be as low as possible, the strippants used in the receiver compartment should be low in acidity (<0.1 M HNO_3) or should contain a complexing agent. Distilled water and oxalic acid were evaluated as strippants for the effective transport of Th from the membrane phase. The transport data are presented in Fig. 4. It is clearly seen that 0.1 M oxalic acid when used as the strippant, is very effective as the strippant as compared to distilled water. This is evident from the fact that for 60% transport of Th, about 107 minutes is required for 0.1 M oxalic acid as the strippant while >155 minutes was needed if distilled water was used as the strippant (Fig. 4). Higher concentration of oxalic acid was avoided as it could result in the precipitation of Th in the presence of large concentration of carrier thorium concentration in the feed. Our earlier studies on the non-dispersive extraction of Th have indicated similar results (22).

Effect of Feed Nitric Acid Concentration

The transport rates showed an interesting trend with the variation in the feed acid concentration. On the basis of Eq. (9) one would expect an increase in the transport rates with the feed acidity. Though an increase was indeed observed up to 3 M HNO_3, a decrease in the transport rate was observed when 6 M HNO_3 was used as the feed. Figure 5 shows the rate of Th transport from the feed to the receiver side as a function of the feed acidity. For the purpose of comparison, the time required for about 65% Th transport was 125 minutes for 3 M HNO_3, 145 minutes for both 2 M as well as 6 M HNO_3, 225 minutes for 1 M HNO_3, and 350 minutes for 0.5 M HNO_3. The permeability coefficients were calculated using Eq. (7) and are listed in Table 2. This increase in the transport rate was attributed to the increasing tendency of the formation of the nitrate complexes with increase of feed acidity while the decrease is ascribed to the formation of $TODGA \cdot HNO_3$ adduct formation (resulting in the decrease of the free ligand, TODGA). The interaction of TODGA with HNO_3 has been reported by Sasaki et al., in an earlier publication (23). We have earlier observed that some amount of acid was transported from the feed compartment to the receiver compartment, and the effect was pronounced especially at 6 M HNO_3 (15). As reported earlier, the enhanced acid transport at 6 M HNO_3 as the feed acidity reduced the

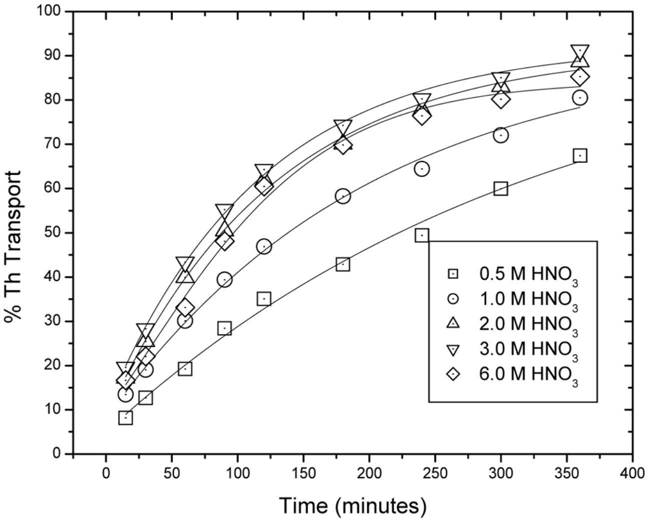


FIG. 5. Effect of feed phase acid concentration on the transport of Th^{4+}. Receiver phase: 0.1 M oxalic acid; Extractant: 0.1 M TODGA.

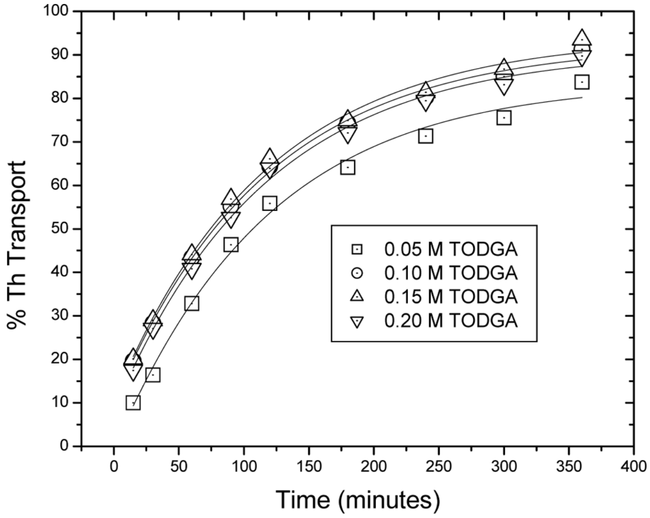


FIG. 6. Effect of TODGA concentration on the transport of Th^{4+}. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M oxalic acid.

stripping efficiency of the receiver phase. A similar observation on the co-transport of HNO_3 was also made in the present case.

Effect of Extractant Concentration

The extractant concentration in the organic phase has a significant effect on the metal ion transport across the membrane. The transport experiments carried out with membranes dipped in dodecane alone (without TODGA) have shown no transport of Th from the feed side to the receiver side. On the other hand, increasing TODGA concentration resulted in increase in Th transport rate (Fig. 6). Similar observation was made during our studies on Am(III) transport, though transport studies were limited to 0.1 M TODGA (15). As the transport rates (on the basis of the %T vs time profiles) appear similar in the TODGA concentration range of 0.1–0.2 M (Fig. 6), the permeability coefficients (P) were calculated to arrive at a trend. The increase in P with increasing TODGA concentration is ascribed to the increase in D_{Th} values at the feed-membrane interface (Table 1). On the other hand, though an increase in the D_{Th} value on increasing TODGA concentration was observed during the solvent extraction studies, the decrease in the P values (Fig. 7) is ascribed to the viscosity effects as per the Stokes-Einstein equation:

$$D_o = kT/6\pi R\eta \tag{11}$$

where D_o is the membrane diffusion coefficient, R, the radius of the diffusing species and η, the dynamic viscosity of the extractant solution, k, is the Boltzmann constant, and T, is the absolute temperature. The viscosity and density data along with the permeability coefficient data are pre-

TABLE 2
Permeability data of Th^{4+} using TODGA as the extractant

$[HNO_3]$, M^a	P (cm/s)	[TODGA], M^b	P (cm/s)
0.5 M	$(4.81 \pm 0.14) \times 10^{-4}$	0.05	$(0.79 \pm 0.04) \times 10^{-3}$
1.0 M	$(7.02 \pm 0.21) \times 10^{-4}$	0.10	$(1.18 \pm 0.05) \times 10^{-3}$
2.0 M	$(9.87 \pm 0.40) \times 10^{-4}$	0.15	$(1.27 \pm 0.08) \times 10^{-3}$
3.0 M	$(1.18 \pm 0.05) \times 10^{-3}$	0.20	$(1.04 \pm 0.05) \times 10^{-3}$
6.0 M	$(8.46 \pm 0.04) \times 10^{-3}$	–	–

Note. ^{a}[TODGA] = 0.1 M; ^{b}3 M HNO_3.

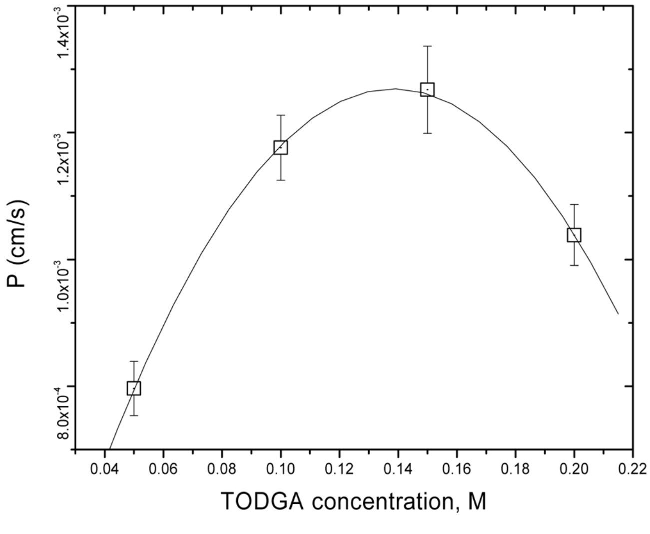


FIG. 7. Effect of TODGA concentration on Th^{4+} permeability coefficients. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M oxalic acid.

TABLE 3
Viscosity and density data for TODGA solutions used in the present studies along with the P (cm/s) values

[TODGA], M	Viscosity (mPa/S)	Density (g/cc)	P (cm/s)
0.05	1.539	0.754	$(7.96 \pm 0.43) \times 10^{-4}$
0.1	1.641	0.758	$(1.18 \pm 0.05) \times 10^{-3}$
0.15	1.860	0.764	$(1.27 \pm 0.07) \times 10^{-3}$
0.2	2.012	0.771	$(1.04 \pm 0.05) \times 10^{-3}$

sented in Table 3. As the %T values were only marginally higher in case of 0.15 M TODGA (56.8% 90 minutes and 93.5% after 360 minutes) as compared to 0.10 M TODGA (55.2% 90 minutes and 91.3% after 360 minutes), in all subsequent studies, 0.1 M TODGA in *n*-dodecane was chosen as the extractant solution.

Effect of Th Carrier Concentration

The transport equations have indicated that the flux would increase with an increase in the metal ion concentration. However, there is a limitation posed by the ligand concentration in the membrane phase. The effect of Th carrier concentration in the feed was investigated using thorium concentration up to 5 g/L. Figure 8 shows the transport rates as a function of feed phase Th concentration. The saturation effect is clearly seen in the Th concentration range of 1–5 g/L and the transport rates slowed down thereafter significantly. Due to loading of the membrane phase with Th-TODGA extracted complex, the P values should effectively decrease as the effective TODGA concentration becomes lower. The effect was reflected in the flux values with increasing concentration of Th. Figure 9 represents the plot of flux vs Th concentration in the feed phase and a steady increase suggests an efficient transport system up to 5 g/L. As reported by Danesi et al. (19), when the carrier is completely converted to the metal-carrier complex, $Th(NO_3)_4 \cdot 4TODGA_{(o)}$, the flux should remain constant with time. However, as this is not true, the flux changes with time as indicated in Fig. 9.

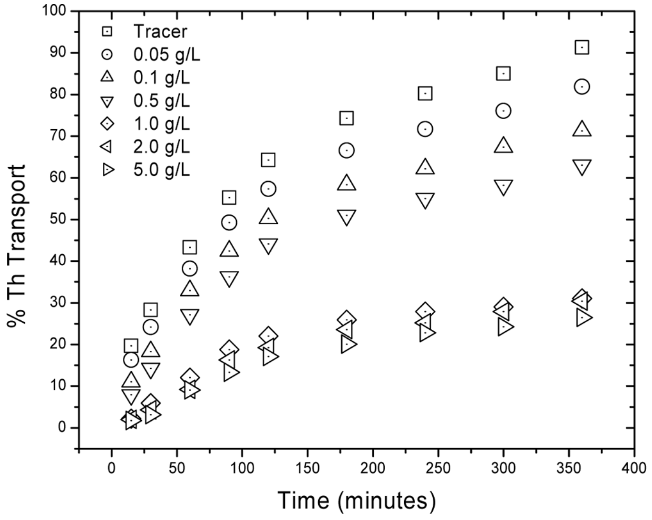


FIG. 8. Effect of the metal ion concentration on the transport of Th^{4+}. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M oxalic acid; Extractant: 0.1 M TODGA.

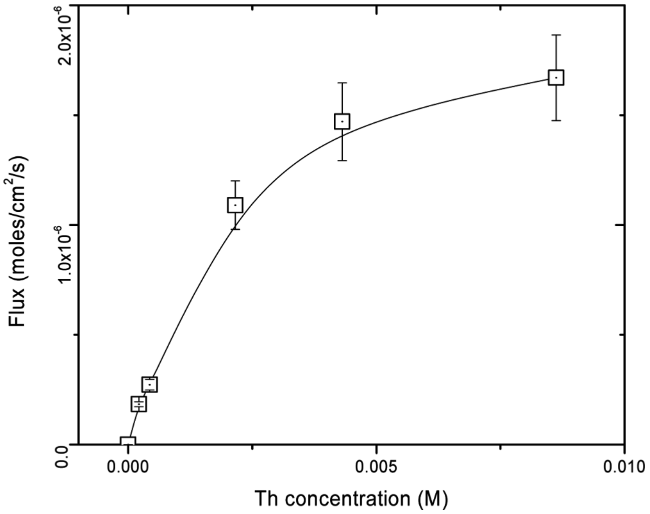


FIG. 9. Effect of the metal ion concentration on Th^{4+} flux. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M oxalic acid; Extractant: 0.1 M TODGA.

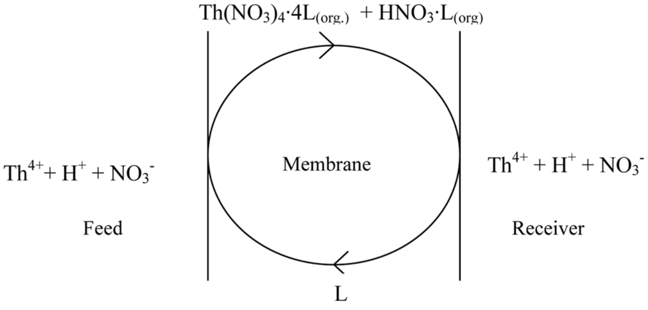
Transport Mechanism

From the above discussion, the transport mechanism can be formulated as a four-step process.

Step-1: Extraction of Th^{4+} by TODGA at the feed-membrane interface.
Step-2: Diffusion of the Th-TODGA complex in the membrane phase from the membrane-feed interface to the membrane-receiver interface.
Step-3: Release of Th^{4+} ion into the receiver phase by the dissociation of the Th-TODGA complex at the membrane-receiver interface.
Step-4: The free TODGA molecules migrate back to the feed–membrane interface.

The co-transport of nitric acid can also be represented by analogous extraction, diffusion and stripping steps. Significant co-transport of nitric acid can affect the transport rates as the effective extractant concentration decreases. Additionally, the stripping efficiency can also be lower. The transport mechanism is schematically shown in Scheme I.

As the extraction and stripping reactions (interfacial resistances) are apparently fast enough as compared to the transport time scale observed in the present case (less than 20 minutes were required as compared to several



SCH. I. Proposed mechanism for Th^{4+} and H^+ transport with TODGA as the carrier extractant.

hours required for quantitative transport), the rate determining step is the diffusion of the complex in the membrane phase (24). In the same line, literature reports have indicated that the chemical reactions taking place at the aqueous feed phase membrane (and membrane-receiving solution) interfaces are fast (25) and it is suggested that rapid chemical reactions can be considered to occur instantaneously relative to the diffusion processes (26). The diffusion coefficient D_o can be calculated as per the empirical Wilke–Chang equation (27) for the bulk diffusion coefficient defined as:

$$D_o = 7.4 \times 10^{-8}(\chi^{0.5}M^{0.5}T)/(\eta V_m^{0.6}) \qquad (12)$$

where M, χ, and η are the molecular weight (M for TODGA and $Th(NO_3)_4 \cdot 4TODGA$ are 580 and 2800, respectively), solvent association parameter and the viscosity of the solvent, respectively, V_m the molar volume of TODGA and T is the temperature. The association parameters for the diluents are taken as unity (27). The molar volume of TODGA was calculated to be $834.06\,cm^3 \cdot mol^{-1}$ (28). Using the dynamic viscosity value for 0.1 M TODGA as 1.641 mPa/S, and assuming that the extracted species contained the diffusion coefficient (D_o) was calculated from Eq. (12) to be $2.13 \times 10^{-7}\,cm^2/s$ which is about much lower than the value reported for Am^{3+} in an identical transport system for a feed containing 1 M HNO_3 (15). This is expected as the diffusion of the Th^{4+}-TODGA complex should be slower as compared to the Am^{3+}-TODGA complex. This is also reflected in the lower transport rates of Th^{4+} as compared to Am^{3+}. Due to the large excess of TODGA (0.1 M) in the SLM as compared to the Th concentration, the transport process may not be dependent on the kinetics of back extraction of the metal ion at the membrane–strip interface and also the diffusion rate of the extractant molecule.

Stability of Membrane

We have earlier reported the stability of supported liquid membranes in a variety of extraction systems (15,18,29,30). From those studies, we have concluded that diluent plays a significant role in the stability of the supported liquid membranes. Diluents such as chloroform and nitrobenzene have indicated poor stability while n-dodecane has displayed much satisfactory stability over a period of 20 days (15). As the present system involves TODGA in n-dodecane as the extractant solution, the stability of this SLM was expected to be no different than that reported by us earlier (15). Stability studies carried out over a period of 15 days have indicated negligible variation in the permeability coefficient in the present case as well.

CONCLUSIONS

In conclusion, TODGA loaded PTFE flat sheets were found to be effective for the transport of Th^{4+}. The transport rates are lower than that of the trivalent actinide ions as reported by us earlier. The results suggest that TODGA can be used for Pu recovery from the high level waste along with Am recovery during the "actinide partitioning" stage with a suitable adjustment of its oxidation state to either +3 or +4 state. However, in case the separation method is applied to solutions containing large Pu concentrations, the flux would decrease. In such cases, the hollow-fiber SLM can be used to enhance the transport rates (31). It is debatable whether the FSSLM method can be actually applied for plant application as an alternative to the solvent extraction technique. For solvent extraction methods, separate scrubbing stages are required for decontamination, which may not be possible with the FSSLM technique. However, it is possible with the HFNDX (hollow fiber non-dispersive extraction) technique which can have the advantage of both the solvent extraction (scrubbing is possible) as well as liquid membrane technique (low ligand inventory) (22). Alternatively, extremely specific ligands can be designed so that very high decontamination is possible in a single extraction and stripping step as in the SLM based methods.

ACKNOWLEDGEMENTS

One of the authors (S.P.) wishes to thank Mr. P. K. Dey, Head, Fuel Reprocessing Division for his keen interest and constant encouragement.

ABBREVIATIONS

CMPO	Carbamoylmethylphosphine oxide
FSSLM	Flat sheet supported liquid membrane
HFNDX	Hollow fiber non-dispersive extraction
HLW	High level waste
PTFE	Polytetrafluoroethylene
SLM	Supported Liquid Membrane
THOREX	Thorium extraction
TODGA	N,N,N′,N′-Tetraoctyl-3-pentane-diamide
TRUEX	Trans Uranium Extraction

SYMBOLS

J_f	Flux in the feed phase
J_m	Flux in the membrane phase
$C_{f,t}$	Concentration of metal ion in aqueous feed at time t
$C_{f,0}$	Initial metal ion concentration (at $t = 0$)
C_{mf}	Metal ion concentration in the membrane phase at the membrane – feed interface
C_{ms}	Metal ion concentration in the membrane phase at the membrane – strip interfaces
D_f	Diffusion coefficient at feed phase
D_o	Diffusion coefficient in the membrane phase
d_f	Thickness of aqueous diffusion layer at feed phase
d_o	Membrane thickness
D_{Th}	Distribution ratio of Th^{4+} ion
Q	Effective surface area
A	Geometrical surface area
V	Time average aqueous feed volume
V_m	Molar volume of the extractant

Greek Letters

ε	Porosity of the membrane
η	viscosity of the solvent
χ	solvent association parameter

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