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Controlled Pertraction of Plutonium(III) Under Reducing Conditions From Acidic Feeds Using TODGA as the Carrier Extractant

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Transport of Pu^{3+} across PTFE flat sheet supported liquid membranes (SLM) using N,N,N′,N′-tetraoctyl-3-oxapentanediamide (TODGA) in n-dodecane as the carrier extractant was investigated. The feed solution was usually 3.0 M HNO_3 while the receiver phase contained 0.1 M HNO_3. In order to model the transport data, the two-phase liquid-liquid extraction experiments are also reported. A series of reducing agents viz. hydrazinium nitrate (HN), phenyl hydrazine (PH), hydroxyl ammonium nitrate (HAN), and ascorbic acid (AA) were evaluated to maintain plutonium in the +3 state in the feed, out of which phenyl hydrazine was found to be the most effective. Effectiveness of various strippants for quantitative and rapid transport of Pu was also evaluated. Additionally, the effects of feed acidity, carrier concentration, membrane thickness, effect of Pu carrier concentration, etc. were investigated. Membrane diffusion co-efficients were calculated and found to be 1.47×10^{-6} cm²/s for Pu(III). The stability of the SLM, investigated as a function of contact time, was found to be reasonably good even after 20 days of continuous operation.

Keywords actinide partitioning; liquid membrane; plutonium (III); TODGA; waste management

INTRODUCTION

"Actinide partitioning" is emerging as the strategy for the removal of minor actinides from high level waste (HLW) prior to the burial of the latter in the form of vitrified blocks (1–2). Several phosphorus based reagents such as CMPO (carbamoyl methyl phosphine oxide), TRPO (tri-n-alkyl phosphine oxide), and DIDPA (diisodecylphosphoric acid) are found to be promising for separation of actinides from fission products and structural materials (3–6). However, due to the possibility of generation of large volumes of secondary wastes with these reagents, "green" reagents such as malonamides and diglycolamides have been found to be better alternatives. Malonamides such as DMDBTDMA (N,N′-dimethyl-N,N′-dibutyltetradecylmalonamide) and DMDOHEMA (N,N′-dimethyl-N,N′-dioctyl-hexylethoxymalonamide) have been extensively studied by French researchers and their collaborators (7–9) while diglycolamides such as TODGA (N,N,N′,N′-tetraoctyldiglycolamide) have been used by Japanese researchers (10–12). We have also carried out a series of studies using TODGA, and found it to be one of the most promising reagents for "actinide partitioning," due to its exceptional ability to extract trivalent actinides from nitric acid medium (13,14).

Though solvent extraction separation methods have been widely used, alternative separation methods with reduced ligand inventory are being sought from the environmental point of view. In this context, extraction chromatography (XC) and liquid membrane (LM) based methods are becoming increasingly popular (15–19). XC based methods are suitable for systems with low metal ion concentration. The major disadvantages of XC include kinetic and capacity limitations, and leaching out of the reagent which restricts its long-term reusability. On the other hand, liquid membrane based separation methods, particularly those involving supported liquid membranes (SLM), were found to be quite promising. We have been investigating the transport behavior of several actinide ions using SLM containing TODGA as the carrier from acidic solutions as well as from synthetic HLW (20–22). Though the amount of Pu in HLW is much lower as compared to the minor actinides, due to its strategic nature, it is required to recover it quantitatively. It is well known that the most stable ionic species of plutonium is Pu^{4+} (23). However, in view of significantly higher transport rates of trivalent actinide ions as compared to the tetravalent actinides ions (24), it was required to convert plutonium to the +3 oxidation state and investigate its transport behavior.

The present work deals with the transport behavior of Pu^{3+} from HNO_3 feed solutions under varying experimental conditions. Solvent extraction studies were carried

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out to optimize the conditions for extraction as well as stripping while the transport studies were carried out at varying experimental conditions such as, feed nitric acid concentration, TODGA concentration, effect of the nature of the strippant, plutonium concentration, etc. An attempt was made to predict the mechanism of transport and the diffusion coefficient for the permeating species was calculated.

EXPERIMENTAL

Materials

N,N,N′,N′-tetraoctyl diglycolamide (TODGA) was synthesized by a previously reported procedure and was characterized by NMR, IR, and elemental analysis (13). Pu tracer (mainly ^{239}Pu) was purified using an ion-exchange method described elsewhere (25). Alpha spectrometry was used to check the purity of the tracer before making stock solution in dilute nitric acid concentration. Pu(III) was prepared by reducing Pu to its +3 state using different reducing agents such as ascorbic acid, hydroxyl amine (in the nitrate form), phenyl hydrazine, and hydrazine hydrate (in the nitrate form). Conversion of Pu to the +3 state was ascertained by UV-visible spectrophotometry. PTFE (pore size: 0.2 micron, thickness: 60 micron; porosity: 51%) membranes procured from Sartorius, Germany were used throughout the present study. All the other reagents were of AR grade and were used without further purification. Assaying of Pu was done by alpha-liquid scintillation counting using Ultima Gold AB (Perkin Elmer) scintillation cocktail. The material balance in these studies was found to be within ±5%.

Methods

Solvent Extraction Studies

Solutions of the desired concentration of TODGA prepared in *n*-dodecane were agitated with an equal volume of the aqueous phase spiked with the requisite quantity of Pu tracer, (mainly ^{239}Pu) previously adjusted to the oxidation state of + 3, 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 followed by counting using a liquid scintillation counter as mentioned above. The distribution coefficient (D_{Pu}) is defined as the ratio of concentration of metal ion in the organic phase to that in the aqueous phase.

Transport Studies

SLM studies were carried out in 30 mL glass transport cells where the feed and the strip solutions were stirred at an optimum speed of 200 rpm as reported by us earlier (26). The microporous PTFE membranes (0.2 micron pore size) were soaked in the carrier solution (usually 0.1 M TODGA in *n*-dodecane) for at least 10 minutes prior to use (20). Subsequently, the submerged membrane was removed from the solution and wiped carefully with a tissue paper to remove the excess carrier solution on both the sides. Usually, the feed compartment contained 3.0 M HNO_3 while the receiver phase solution was 0.1 M nitric acid. Aliquots were removed from the feed as well as the receiver compartments at regular intervals and the assay of Pu was done as mentioned above. The transport studies were carried out at ambient temperatures (24 ± 1°C). The material balance in these studies was found to be within ±5%.

Transport Equations

Assuming that the diffusion in the feed and the receiver phases are relatively fast and does not affect the metal ion pertraction rate, the transport process in the supported liquid membranes mainly involves three steps, viz. extraction at the feed-membrane interface, diffusion inside the membrane, and stripping at the membrane-receiver interface. The transport experiments were carried out under the conditions that the distribution coefficient (D_{Pu}) is much larger at the feed-membrane interface as compared to the membrane-receiver interface. Under steady state condition, by ignoring the concentration of the metal ion in the receiver phase, one can get the flux (J) from the following equation (27):

$$J = P_f C_f \tag{1}$$

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

$$J = -(1/Q) \cdot dV_f C_f/dt \tag{2}$$

Where V_f is the feed volume and Q is the exposed area of the membrane. Combining Eqs. (1) and (2), and integrating one obtains,

$$\ln\{(V_{f,0}C_{f,0})/(V_{f,t}C_{f,t})\} = Q \cdot P \cdot t/V_f \tag{3}$$

Where $V_{f,0}$, $C_{f,0}$, $V_{f,t}$ and $C_{f,t}$ represent the volume and concentration of feed at starting time and after time ‘t’, respectively. If the volume of the feed does not change significantly during the experiment, then one gets the expression

$$\ln(C_{f,t}/C_{f,0}) = -(Q/V_f)P \cdot t \tag{4}$$

Q is expressed as the product of the geometrical surface area (A) and the porosity (ϵ). The permeability coefficient (P) values were calculated using Eq. (4). The geometric surface area of the membrane was 4.94 cm^2 while the effective surface area was 2.51 cm^2. The cumulative percent transport (% T) at a given time is determined by the following equation,

$$\%T = 100 \cdot (C_{f,0} - C_{f,t})/C_{f,0} \quad (5)$$

The data treatment that follows generally includes plots of %T vs time as well as the calculations of permeability coefficient in some cases. Pu fluxes are also calculated in some cases as indicated above. The material balance in these studies was found to be within ±5%.

RESULTS AND DISCUSSION

Solvent Extraction Studies

Effect of Nature of the Reducing Agent on Pu(III) Extraction

Pu has the unique property of simultaneously existing in +3, +4, +5, and +6 oxidation states at the same time (23). Therefore, the chemistry of plutonium is challenging and requires special care such as finding appropriate conditions for stabilization of a particular oxidation state. It is important to note here that the extraction of trivalent actinides is much higher than the tetra- and hexa-valent actinide ions when TODGA is used as the extractant (12,13). This trend is entirely opposite of the trend observed with other extractants such as CMPO and tetra-alkyl malonamides such as DMDOHEMA or DMDBTDMA. Therefore, Pu can be more efficiently extracted by TODGA if present in the +3 state.

Various reducing agents like ascorbic acid (AA), hydroxyl ammonium nitrate (HAN), phenyl hydrazine (PH), and hydrazinium nitrate (HN) were evaluated for the conversion of Pu to Pu^{3+}. As indicated from the solvent extraction data (Table 1), ascorbic acid was the most suited reducing agent as the D_{Pu} value was the highest using this reducing agent (under no condition D_{Pu} value greater than 100 was obtained). It is also evident from Table 1 that the concentration of the reducing agent also played an important role in determining the extent of conversion of Pu to Pu^{3+} (as indicated by the D_{Pu} using 0.1 M TODGA/n-dodecane). This is due to the fact that the reduction of Pu is not stoichiometric due to the role of nitrous acid which plays a role of oxidizing agent (28). With increasing the concentration of the reducing agent, the total reduction of Pu (from predominantly in the +4 state) to Pu^{3+} was possible which caused an increase in the D_{Pu} value with TODGA. The optimum concentration of the reducing agents, in the concentration range of Pu studied, was found to be 0.1 M, as further increase in the reducing agent concentration does not increase the distribution ratio further. Out of the four reducing agents used, phenyl hydrazine (PH) was found to be the most efficient and was used in the subsequent studies. Though AA is found to be marginally inferior to PH as a reductant, and is a more benign chemical that the latter, it was not subsequently used due to its instability in acidic medium. Complete conversion of Pu to its +3 state in the presence of 0.1 M PH was confirmed by spectrophotometry (Fig. 1) where the bands characteristic of Pu^{4+} are suppressed to a large extent and those belonging to Pu^{3+} appeared prominently. Earlier reports also indicate facile reduction of Pu^{4+} to Pu^{3+} using hydrazine as the reducing agent (28,29).

TABLE 1
Solvent extraction data of Pu^{3+} using 0.1 M TODGA in n-dodecane in the presence of various reducing agents

Reducing agent	D_{Pu} at varying reducing agent concentration 0.01 M	0.1 M
Ascorbic acid	78 ± 1.1	95 ± 0.8
Hydroxyl ammonium nitrate	64 ± 0.2	93 ± 0.3
Hydrazinium nitrate	75 ± 0.7	91 ± 1.0
Phenyl hydrazine	79 ± 0.5	96 ± 0.5

On the basis of the literature report on trivalent actinide extraction using TODGA (12,13), the extraction equilibrium involving Pu^{3+} can be conveniently written as:

$$Pu^{3+} + 3NO_3^- + nTODGA \rightleftharpoons Pu(NO_3)_3 \cdot nTODGA \quad (6)$$

The value of n was determined by measuring the distribution coefficients as a function of TODGA concentration at 3 M HNO_3 and the log D vs log [TODGA] plot gave a slope value close to 4 (Fig. 2). To our knowledge, there is no data available in the literature on the extraction behavior of Pu^{3+} using TODGA as the extractant. However, analogous extracted species was reported for Am^{3+} in an earlier report (13).

Transport Studies

The transport studies were carried out using Pu which was previously reduced to the +3 state. However, in order to rule out the possibility of change in the oxidation state during the experiment, the reducing agent was also used in the feed and sometimes in the membrane phase (*vide infra*). Usually, 0.1 M HNO_3 was used as the strippant in the receiver phase in order to rule out the possibility of hydrolysis.

Effect of Reducing Agent on Pu(III) Transport

As is evident from the solvent extraction studies, the choice of a reducing agent should also play an important role in the transport of Pu^{3+}. Various reducing agents

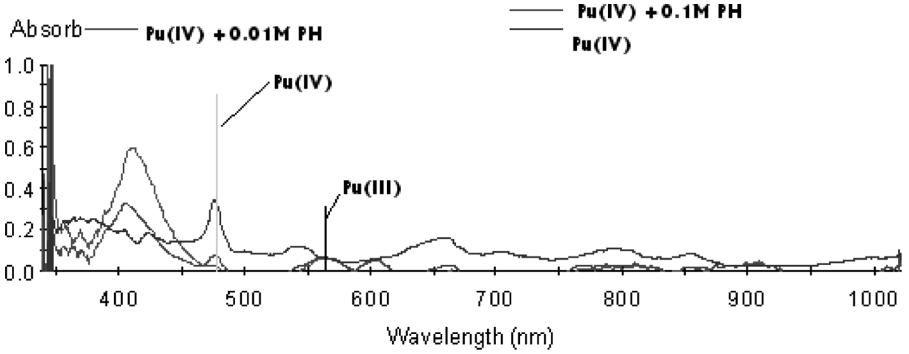

FIG. 1. UV-Visible spectra of Pu in the absence of reducing agent (green line), in the presence of 0.01 M phenyl hydrazine (red line) and in the presence of 0.1 M phenyl hydrazine (blue line).

(at an effective concentration of 0.1 M) were used to study the transport of Pu^{3+} from 3 M HNO_3 into 0.1 M HNO_3 where 0.1 M TODGA/n-dodecane was chosen as the carrier extractant. Similar to the solvent extraction data presented above, Fig. 3 also indicates that phenyl hydrazine (PH) yielded quantitative transport of Pu(III) after about 180 min which is similar to that observed for Am^{3+} (13). Though Ascorbic acid (AA) gave the highest D value (Table 1), the transport rate was found to be quite slow (~86% transport was observed in 360 min). This was attributed to the poor stability of AA in the nitric acid medium. To improve its stability, *tert*-butyl hydroquinone (TBH), an organic reducing agent (30), was added in the carrier phase and the transport of Pu(III) was followed using AA as the reducing agent. Though the rate increased but still it was found to be slower than PH (Fig. 3). Therefore, 0.1 M PH was chosen as the reducing agent in the subsequent transport studies involving Pu^{3+}. The permeability coefficients for different feed conditions (with different reducing agents) were calculated and are listed in Table 2.

The transport rates of Pu^{3+} was compared with those obtained for Am^{3+} and Th^{4+} (carried out under identical condition of distilled water as the strippant in the receiver phase). It may be noted here that our earlier work on Am transport was carried out using distilled water as the strippant while most of the part the of present study use 0.1 M HNO_3 as the strippant). As shown in Table 3, the transport rates for Pu^{3+} were closer to those observed for Am^{3+} than those of Th^{4+}. This confirms near complete conversion of Pu to the +3 oxidation state. The relatively slow transport in case of Pu^{3+} is due to lower $D_{Pu(III)}$ (94) as compared to $D_{Am(III)}$ (297 (13)) at 0.1 M TODGA for a feed acidity of 3 M HNO_3. As already mentioned, the presence of Pu^{3+}

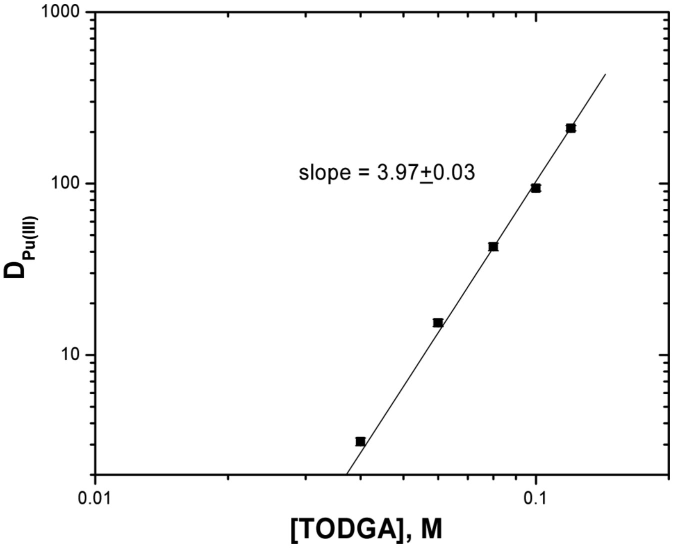

FIG. 2. Dependence of $D_{Pu(III)}$ on TODGA concentration. Aqueous phase acidity: 3 M HNO_3.

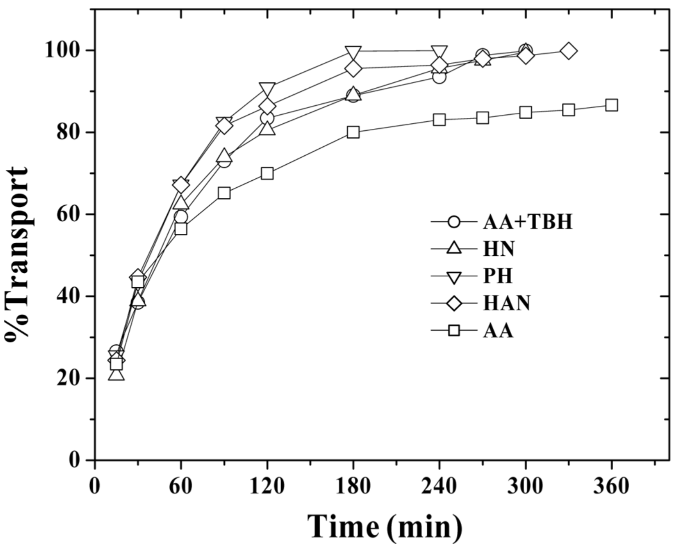

FIG. 3. Effect of nature of strippant on the transport of Pu^{3+}. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M HNO_3.

TABLE 2
Permeability coefficient (P, cm/s) data of Pu^{3+} – TODGA transport system for various strippants and reducing agents

Extraction system		Stripping system	
Reducing agent[a]	$P_{Pu(III)} \times 10^3$	Strippant	$P_{Pu(III)} \times 10^3$
Ascorbic acid	1.34 ± 0.17	0.1 M HNO_3	3.26 ± 0.04
Phenyl hydrazine	3.26 ± 0.04	Distilled water	2.24 ± 0.01
Hydrazinium nitrate	2.05 ± 0.07	0.1 M oxalic acid	1.64 ± 0.02
Hydroxyl ammonium nitrate	2.17 ± 0.11	Buffer mixture	1.78 ± 0.01
Ascorbic acid + *tert*-butyl hydroquinone	1.74 ± 0.10		

Note: [a]strippant: 0.1 M HNO_3; [b]reducing agent: phenyl hydrazine.

in the extracted species was further confirmed by UV-Visible spectrophotometry (Fig. 1).

The Effect of TODGA Concentration

The effect of TODGA concentration on the transport of Pu(III) was studied at different extractant concentration (0.05–0.2 M) using 0.1 M PH as the reducing agent in the feed phase (3 M HNO_3) while 0.1 M HNO_3 was used as the receiver phase. As evident from Fig. 4, the transport rate increased up to 0.1 M and decreased thereafter. For 0.1 M TODGA/*n*-dodecane as the carrier extractant, quantitative transport was observed at about 180 min which was comparable to the transport rate for Am(III) (20). Further increase in TODGA concentration was found to decrease the transport rate which was attributed to an increase in the viscosity of the carrier in the membrane phase. This increased viscosity of the carrier creates a hindrance to the diffusivity of the complex which causes a decrease in the transport rate. The viscosity effect can be explained by the Stokes-Einstein equation

$$D_o = kT/6\pi R\eta \tag{7}$$

Where D_o is the diffusion co-efficient of the extracted complex in the membrane phase, k, the Boltzman constant, T, the absolute temperature, R, the radius of the diffusing species and η, the dynamic viscosity of the carrier solution. The dependence of the permeability coefficient (P) values on viscosity is shown in Table 4.

TABLE 3
Comparison of plutonium transport data with those reported with Am^{3+} and Th^{4+} with TODGA as the carrier extractant. Strippant: Distilled water

	% Metal ion transport		
Time (minutes)	Am^{3+} (present work)	Th^{4+} [31]	Pu (present work)
15	34.5	8.53	27.3
30	57.0	18.1	45.5
60	81.8	31.8	64.2
120	93.6	53.1	83.5
180	99.3	66.6	94.2

The Effect of the Feed Acidity

As indicated by Eq. (6), the extraction of Pu^{3+} is influenced not only by TODGA concentration, but also by the concentration of nitrate ion. We have reported earlier that though increasing the nitrate ion concentration should increase the metal ion extraction at the feed-membrane interface, and nitric acid facilitates higher mass transfer as compared to $NaNO_3$ (20). Therefore, the feed nitric acid concentration was varied and the transport rates of Pu^{3+} were measured. We reported that the transport rate did not follow the same trend for all the actinides using TODGA as carrier with different feed acidity. For Am^{3+} (20) the transport rate was found to increase up to 3 M

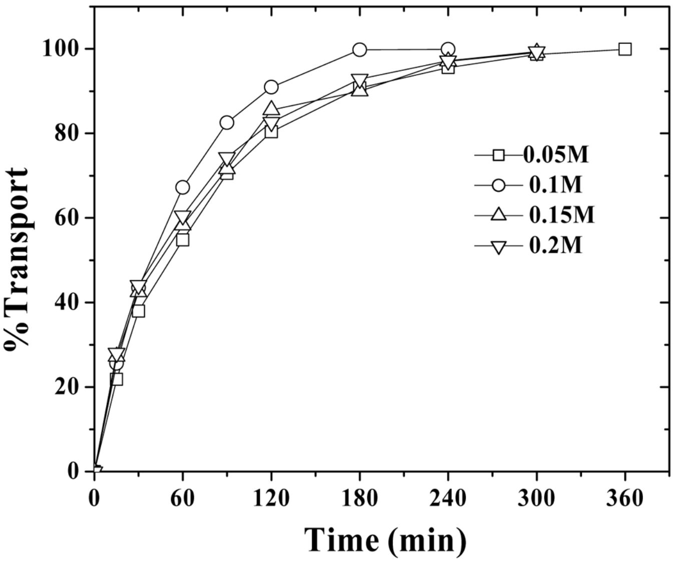

FIG. 4. Effect of TODGA concentration on the transport of Pu^{3+}. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M HNO_3.

TABLE 4
Permeability coefficient (P, cm/s) data of Pu^{3+} – TODGA transport system at varying TODGA and nitric acid concentrations

$[HNO_3]$, M	$P_{Pu(III)} \times 10^{3,a}$	[TODGA], M	$P_{Pu(III)} \times 10^{3,b}$	Viscosity (mPa/S)
0.5	0.61 ± 0.07	0.05	2.44 ± 0.08	1.539
1.0	1.06 ± 0.12	0.10	3.26 ± 0.04	1.641
3.0	3.26 ± 0.04	0.15	2.40 ± 0.15	1.860
6.0	1.19 ± 0.04 $(1.38 \pm 0.06)^c$	0.20	2.54 ± 0.08	2.012

Note: [a][TODGA] = 0.1 M; [b]$[HNO_3]$ = 1.0 M; [c]Values in parenthesis indicates data generated in the presence of *tert*-butyl hydroquinone.

HNO_3 and then decreased thereafter. On the other hand, U transport increased with increasing feed acidity up to 3 M and remained constant thereafter up to 6 M (31). The transport of Pu^{3+} with different feed acidities using 0.1 M PH as the reducing agent was monitored as a function of time. The results (Fig. 5) indicated that the transport rate of Pu^{3+} increased from 0.5 M HNO_3 up to 3 M HNO_3 and then decreased up to 6 M HNO_3 which is similar to our observation with Am^{3+} and Th^{3+}. We also observed near quantitative transport (~99%) for Pu^{3+} at about 180 min for 3 M HNO_3 acidity. The permeability coefficients at various feed acidities are also listed in Table 4.

The receiver phase acidity was found to increase from 0.1 M to 0.4 M HNO_3 after 360 minutes of operation when 6 M nitric acid was used as the feed. It is well known that with increasing nitric acid concentration, the possibility of conversion of Pu^{3+} to Pu^{4+} increases due to the stabilization of the +4 state in higher complexing media provided by 6 M HNO_3 (23). These two effects are likely to decrease the transport rate of Pu from the feed at 6 M HNO_3. To check whether this decrease is due to oxidation of Pu^{3+} to Pu^{4+} at higher acidity, *tert*-butyl hydroquinone (TBH) was added to the organic phase to maintain Pu in the +3 state and the transport rate was followed for 6 M HNO_3. The trend was observed to be the same in the presence and in the absence of TBH which conclusively proved that the decrease in transport rate was due to increase in strip phase acidity and not due to oxidation of Pu^{3+} to Pu^{4+}.

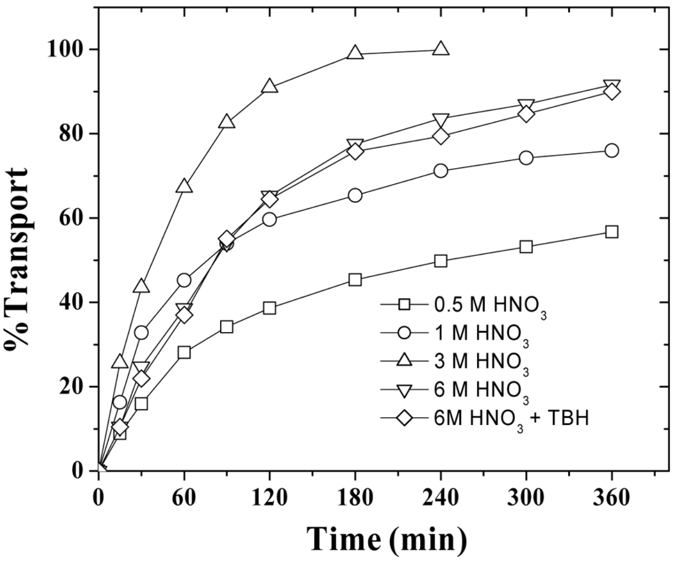

FIG. 5. Effect of feed phase acid concentration on the transport of Pu^{3+}. Receiver phase: 0.1 M HNO_3; Carrier extractant: 0.1 M TODGA.

Effect of Nature of the Strippant

In SLM transport studies, effective transport means efficient extraction, rapid diffusion of the extracted complex, and efficient stripping are the key steps. Therefore, the distribution co-efficient of the metal ion in the receiver compartment should be as low as possible to achieve efficient stripping. For this purpose, the strippant should be of low acidity (as per Eq. (6)) or should consist of metal complexing solution. Transport of Pu(III) was studied using various strippants such as 0.1 M HNO_3, distilled water, 0.1 M oxalic acid, and a buffer mixture (consisting of 0.4 M hydrazine hydrate, 0.4 M formic acid and 0.1 M citric acid) from 3 M HNO_3 which contained 0.1 M phenyl hydrazine as the reducing agent and the transport and permeability data are presented in Fig. 6 and Table 2, respectively. Among these strippants 0.1 M HNO_3 gave near quantitative transport after about 180 min which was about the same time taken for the quantitative transport of Am^{3+} in an earlier report by us (20).

Mechanism of Transport

The probable mechanism for Pu^{3+} transport from the feed compartment across the SLM systems containing TODGA/*n*-dodecane as the carrier to the receiver phase can be suggested as follows:

Step I: Pu^{3+} ions get extracted at the feed–membrane interface with the free TODGA molecules present in the liquid membrane phase in the form of the extractable species: $Pu(NO_3)_3 \cdot 4\,L_{(org.)}$.

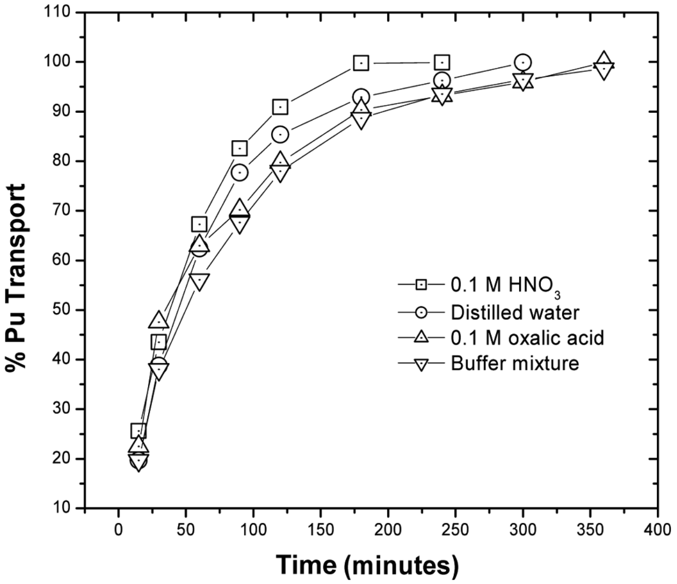

FIG. 6. Effect of nature of strippant on the transport of Pu^{3+}. Feed phase: 3.0 M HNO_3; Carrier extractant: 0.1 M TODGA.

Step II: The extractable species $Pu(NO_3)_3 \cdot 4\,L_{(org.)}$ migrates to the membrane–receiver interface due to a negative concentration gradient.

Step III: The Pu^{3+} ion gets stripped into the strip phase due to very low D_{Pu} value.

Step IV: After stripping of the complex, the TODGA molecules become free and migrate to the feed – membrane interface to complete the cycle.

The acid transport observed at higher feed acidities indicated that a co-transport process involving nitric acid is also taking place in the similar line mentioned above. The transport mechanism is schematically presented in Fig. 7. It is presumed that the extraction and stripping rates are much faster than the diffusion of the metal ion (31,32). It was, however, required to calculate the diffusion parameters to conclusively prove that the mechanism is diffusion controlled.

Calculation of Diffusion Parameters

In case of supported liquid membranes, the transport of a metal ion is usually diffusion controlled. As a result, the transport rate is dependent on the diffusion path length which is proportional to the membrane thickness. With increasing membrane thickness, the diffusion path length and as a result, the diffusional resistance increases which causes a decrease in the transport rate.

To have a clear understanding of the effect of membrane thickness on the transport of Pu(III) transport studies were carried out with varying membrane thickness which was obtained by laminating the required number of membranes. Feed phase was 3 M HNO_3 with 0.1 M PH as the holding reductant, 0.1 M HNO_3 was used as strippant and 0.1 M TODGA/n-dodecane was used as a carrier during these experiments. Membrane pore size was kept at 0.2 µm and the stirring rate was kept at ~500 rpm to minimize the thickness of the aqueous diffusion layer. Expectedly, as shown in Fig. 8, the transport rate decreased continuously from 60 µm to 300 µm.

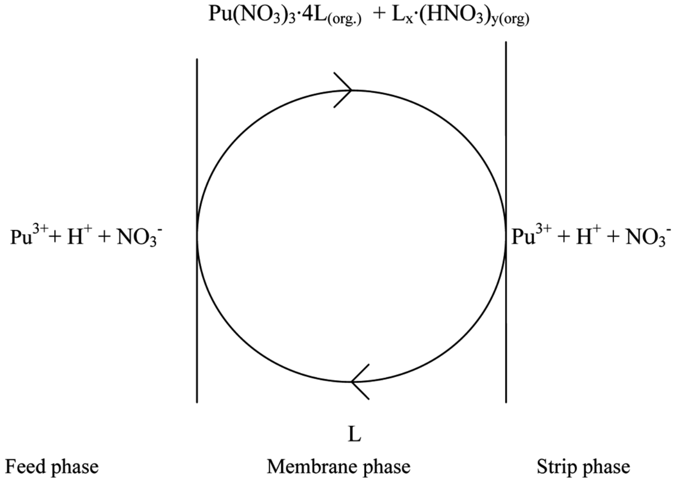

FIG. 7. Schematic representation of the transport mechanism.

As reported by Danesi (33), the permeability coefficients can also be calculated from the distribution ratio measurements, $D_{Pu(III)}$ as per the following equation;

$$P = \frac{D_{Pu(III)}}{[D_{Pu(III)}(d_a/D_a) + (d_o\tau/D_o)]} \tag{8}$$

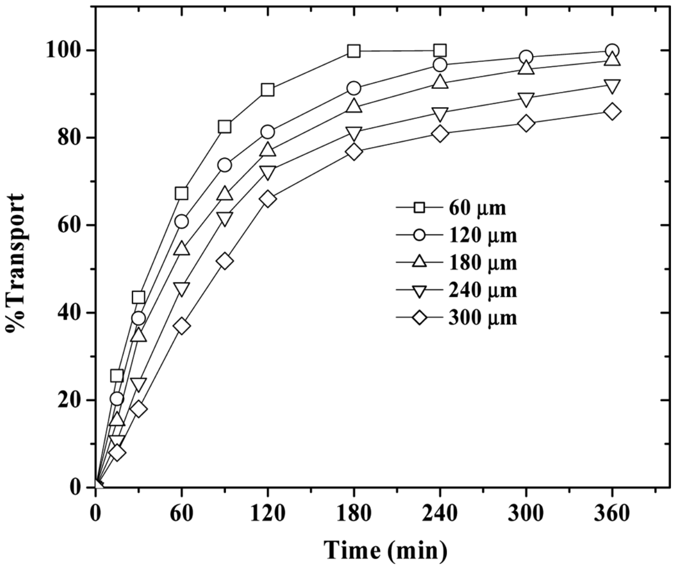

FIG. 8. Effect of membrane thickness on the transport of Pu^{3+}. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M HNO_3; Carrier extractant: 0.1 M TODGA.

where $D_{Pu(III)}$, D_a, and D_o are the distribution ratio, aqueous diffusion coefficient and membrane diffusion coefficients of Pu(III), respectively while d_a, d_o, and τ are the aqueous diffusion layer thickness, membrane thickness, and tortuosity factor, respectively. Assuming that the rate determining step is the diffusion of the bulky Pu(III)-TODGA complex across the membrane, the first term in the denominator of Eq. (8) can be ignored. Thus, P can be represented as:

$$P = \frac{D_{Pu(III)} D_o}{d_o \tau} \quad (9)$$

The tortuosity factor obtained for the 0.2 (m membranes is 2.15 (34). Therefore, from the P values calculated from Eq. (3), the diffusion coefficient, D_o, can be calculated. The plot of P vs 1/thickness gave a straight line (Fig. 9) and from the slope we found the value of D_o as $1.47 \times 10^{-6}\,cm^2/s$ which was in the same order as reported for Am^{3+} ($1.51 \times 10^{-6}\,cm^2/s$, (15)). So, from this study of varying membrane thickness, it was conclusively proved that the transport of Pu(III) across a SLM containing 0.1 M TODGA/*n*-dodecane as carrier is diffusion controlled.

Effect of Pu(III) Concentration in the Feed

Increasing concentration of Pu(III) would increase the flux of Pu as indicated by the transport equation. But due to the limitation of the amount of the carrier in the membrane phase the transport rate as well as the permeability coefficient was found to decrease with increasing metal concentration in the feed phase. The effect of increasing Pu(III) concentration on the transport as well as flux of Pu(III) was investigated in the concentration range of 5–50 mg/L. In the PUREX process, the Pu loss in the HLW is tolerated up to this concentration. It was found that the transport rate decreased with increasing Pu concentration which is expected due to limited carrier concentration. Therefore, when the flux was plotted against the Pu concentration (Fig. 10) it was found to increase and then tended to saturate. We found ~90% transport in around 360 min even for 48 mg/L Pu. Therefore, effective transport Pu can be achieved even for about 50 mg/L concentration when the oxidation state can be adjusted to +3. The values of permeability coefficients for different Pu concentrations are listed in Table 5.

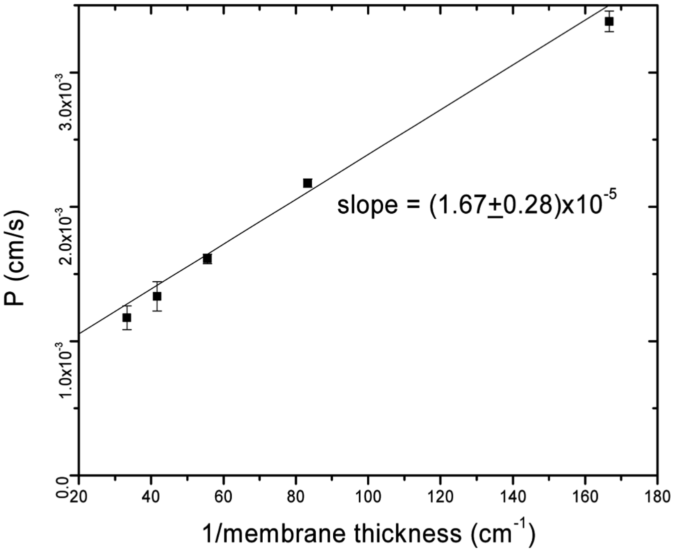

FIG. 9. Plot of 1/P *vs* membrane thickness for calculation of diffusion coefficient for complexes of Pu^{3+} ion. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M HNO_3; Carrier: 0.1 M TODGA.

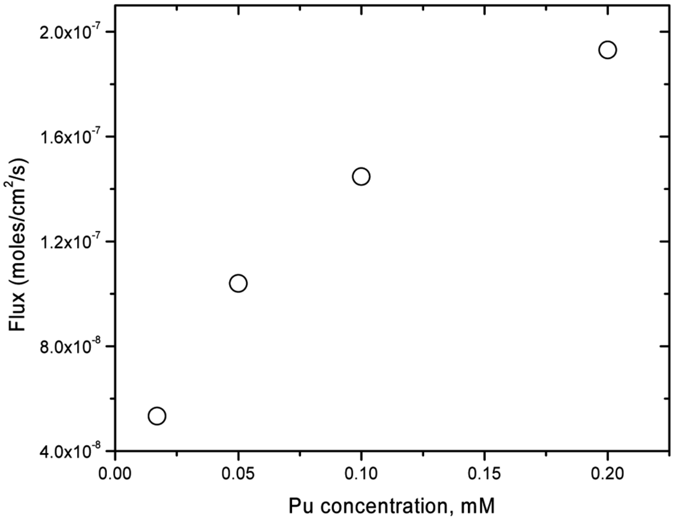

FIG. 10. Effect of Pu concentration on Pu^{3+} flux. Feed phase: 3.0 M HNO_3; Receiver phase: 0.1 M HNO_3; Carrier: 0.1 M TODGA.

It may be pointed out here that for the practical application of the supported liquid membrane technique for the remediation of HLW, which can contain mg amount of Pu, the transport rate should be enhanced significantly compared to what is reported in the present paper. This is possible if the surface area of the SLM can be increased significantly. For this purpose, hollow fiber supported liquid membrane based separation methods can be used which is reported to enhance the transport rate quite significantly (22).

Membrane Stability

The stability of the SLM is one of the major limitations of this separation technique. Kemperman et al. (35) reported various factors that affected the stability of the liquid membrane. We, on the other hand, reported that the stability is mainly dependent on the diluent properties and was found to be reasonably good in cases where

TABLE 5
Permeability coefficients as a function of the Pu concentration in the feed

Pu concentration (g/L)	$P \times 10^3$ (cm/s)	Flux (moles/cm^2/s)
Tracer	3.26 ± 0.04	–
4 mg/L	3.18 ± 0.07	5.33×10^{-8}
12 mg/L	2.08 ± 0.06	1.04×10^{-7}
24 mg/L	1.44 ± 0.02	1.45×10^{-7}
48 mg/L	0.96 ± 0.03	1.93×10^{-7}

n-dodecane was used as the diluent (32). To corroborate, the membrane stability was investigated by continuously operating the same transport system using 0.2 micron PTFE filters for 20 days. Feed and strip solutions used in this studies were 3 M HNO_3 (containing 0.1 M PH as the holding reductant) and 0.1 M HNO_3, respectively. The data (Fig. 11) indicated slight deterioration of the membrane over the entire period of time which is probably due to partial oxidation of Pu(III) to Pu(IV). However, the mean value of P was 3.1×10^{-3} cm/s which indicated no significant decrease in the transport rates. These observations thus led us to the conclusion that the loss of liquid membrane phase (carrier and/or solvent) out of the membrane phase was insignificant under the experimental conditions. This makes a strong case for long-term reusability of the SLM containing TODGA for the recovery of Pu (preferably in the +3 oxidation state) from acidic waste solutions including HLW.

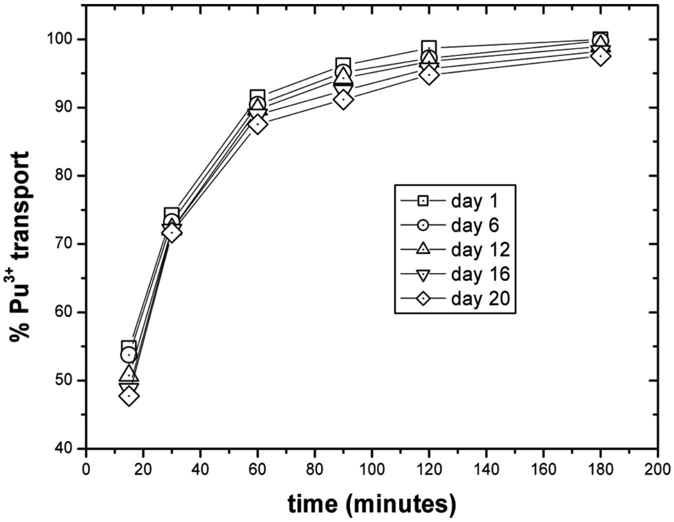

FIG. 11. Successive transport experiments for the stability evaluation of the SLM; Feed phase: 3.0 M HNO_3; Membrane: 0.2 μm PTFE; carrier, 0.1 M TODGA in *n*-dodecane; Receiver phase: 0.1 M HNO_3.

CONCLUSIONS

In conclusion, TODGA loaded PTFE flat sheets were found to be effective for the transport of Pu^{3+} where phenyl hydrazine was used as the reductant and 0.1 M HNO_3 as the strippant. The species being extracted and diffusing inside the membrane were found to be $Pu(NO_3)_3 \cdot 4TODGA$ from solvent extraction experiments. The transport of the complex increased with increasing TODGA concentration up to 0.1 M and decreased thereafter which was attributed to slow diffusion of the complex due to increased carrier viscosity. The transport of the complex increased with increasing feed nitric acid concentration up to 3 M HNO_3 and decreased thereafter which was attributed to inefficient stripping in the receiver compartment due to significant co-transport of nitric acid. Increasing Pu concentration increased the overall flux, which tend to saturate at higher Pu concentrations. The membrane stability was reasonably good for 0.2 micron filters which resulted in highest P values. The results were promising for the possible application of the SLM technique for the recovery of Pu from acidic nuclear waste solutions including HLW.

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ABBREVIATIONS

AA	Ascorbic acid
CMPO	Octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide
DIDPA	diisodecyl phosphoric acid
DIAMEX	Diamide extraction
DMDBTDMA	N,N′-Dimethyl-N,N′-dibutyl tetradecyl-1,3-malonamide
DMDOHEMA	N,N′-Dimethyl-N,N′-dioctylhexylethoxymalonamide
HAN	Hydroxyl ammonium nitrate
HLW	High Level Waste
HN	Hydrazinium nitrate
PH	Phenyl hydrazine
PTFE	Poly Tetra Fluoro Ethylene
PUREX	Plutonium Uranium Reduction Extraction
SLM	Supported Liquid Membrane
TODGA	Tetraoctyldiglycolamide
TRPO	Trialkyl phosphine oxide
TRUEX	Trans Uranium Element Extraction

SYMBOLS

$C_{f,t}$	Concentration of metal ion in aqueous feed at time t
$C_{f,0}$	Initial metal ion concentration (at $t = 0$)

D_a	Aqueous diffusion coefficient
D_o	Membrane diffusion coefficient
D_{Pu}	Distribution coefficient of Pu
d_a	Thickness of aqueous diffusion layer
d_o	Membrane thickness
k	Boltzmann constant
Q	Effective surface area of membrane
A	Geometrical surface area of membrane
V	Time average aqueous feed volume
$V_{f,0}$	Volume of feed at the start of the experiment
$V_{f,t}$	Volume of feed at time 't'

Greek Letters

ϵ	Porosity of the membrane
τ	Tortuosity of the membrane
η	Dynamic viscosity

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