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Macrocycle-Mediated Selective Transport of Plutonium(IV) Nitrate through Bulk Liquid and Supported Liquid Membranes Using Dicyclohexano-18-crown-6 as Mobile Carrier

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Macrocycle-Mediated Selective Transport of Plutonium(IV) Nitrate through Bulk Liquid and Supported Liquid Membranes Using Dicyclohexano-18-crown-6 as Mobile Carrier*

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Abstract

Macrocycle-facilitated transport of Pu(IV) against its concentration gradient from aqueous nitric acid solutions across an organic bulk liquid membrane (BLM) and a thin-sheet supported liquid membrane (SLM) containing dicyclohexano-18-crown-6 as the mobile carrier and toluene as the membrane solvent was investigated. Extremely dilute and moderately concentrated plutonium nitrate solutions in about 3 mol/dm^3 nitric acid generally constituted the source phase. Plutonium transport appreciably increased with stirring of both the source and recovery phases and also with the carrier concentration in the organic phase up to 0.3 mol/dm^3 DC18C6 and then decreasing with higher concentrations of the carrier. Enhanced acidity of the aqueous source phase beyond 4 mol/dm^3 HNO_3 seriously affected the stripping of the cation. Among the several reagents tested, dilute sodium carbonate (0.5 mol/dm^3) served efficiently as the strippant. Enka Accurel thin flat-sheet polypropylene (PP) films were used as the solid support for SLM. By using both BLM and SLM systems, more than 90% of plutonium could be transported through 0.2 mol/dm^3 DC18C6/toluene into dilute sodium carbonate strippant in about 7–8 h. The lack of any contamination from even appreciable amounts of possible fission product contaminants is a notable feature of this novel separation technique.

*Part of this work was presented at the International Symposium on Radiochemistry and Radiation Chemistry, BARC, Bombay, February 4–7, 1991.

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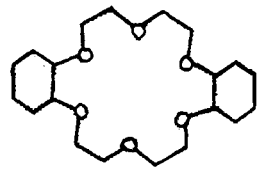
INTRODUCTION

Liquid membrane separation, combining the processes of extraction, diffusion, and stripping in a single step, has aroused much interest in recent years since these constitute one of the cheapest separation techniques because of their relatively smaller inventory and low running costs. Energy consumption is quite low and organic losses are often negligible under proper conditions. For this purpose, macrocyclic crown compounds have proven to be an excellent choice due to their profound selectivity with particular cations (*1*). The obvious mode of exploiting the selectivity of macrocycles for cation separations would be to use them as ionopores in liquid membranes. Cation transport across various liquid membrane configurations, viz., bulk liquid, emulsion liquid, and supported liquid membranes, exhibit great potential, particularly in processing dilute metal solutions for the recovery and separation of metals (*2*, *3*). Numerous practical applications of such membranes have also been envisaged for the recovery of metals from hydrometallurgic leach solutions; removal of uranium, plutonium, and americium removal from nitric acid waste streams generated by plutonium recovery operations in the Purex Process (*4–8*).

Considering the strategic importance as well as biotoxicity of plutonium, it becomes almost imperative to recover it from low as well as high level active nitrate wastes. Supported liquid membranes (SLM) have proved to be the best alternative in transferring and concentrating plutonium from nitrate solutions (*9*).

With this in view, a comprehensive work program has been initiated by us to explore the applications of liquid membranes, especially for treating dilute plutonium solutions employing a neutral macrocyclic carrier, 2,3,11,12-dicyclohexano-1,4,7,10,13,16-hexaoxacyclo-octadecane (dicyclohexano-18-crown-6; DC18C6), which has been found to be highly selective and effective for plutonium in a toluene medium (*10*). DC18C6 dissolved in toluene was selected as the mobile carrier in the facilitated transport of Pu(IV) across an organic bulk liquid membrane (BLM) as well as SLM. The effect of important parameters that affect cation flux in liquid membranes, such as feed acidity, carrier (DC18C6) concentration in the organic



Dicyclohexano-18-Crown-6.
(DC18C8)

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membrane phase, nature and type of strippant in the receiving phase, and chemical stability of the polypropylene membrane against the solvents toluene and nitric acid, were evaluated. Enka Accurel polypropylene (PP) films were tested as the flat solid supports for SLM.

EXPERIMENTAL

All the chemicals were of AR or GR grade unless specified otherwise. DC18C6, obtained from Aldrich Chemicals, USA, was used as supplied.

Plutonium-239 tracer (1 mg/dm^3), purified by the usual ion-exchange method (*11*), was used throughout this study. Tetravalency of plutonium in the feed was adjusted with sodium nitrite (ca. 0.05 mol/dm^3). Permeation of the fission products was checked with an unpurified plutonium nitrate solution of the following composition received from reprocessing operations: Pu, 50 mg/dm^3; Cs-137, 2.63 μCi/dm^3; Ru-106, 4.28 μCi/dm^3; Sb-125, 0.69 μCi/dm^3.

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Liquid Membrane Cells

Details of the glass BLM and SLM transport cells used are described elsewhere (*9*). The BLM cells (Shulman bridge type) consisted of a bulk DC18C6/toluene phase separating the aqueous source phase (10 cm^3) and receiving phase (capacity 2.4 cm^3). Single-stage SLM measurements were carried out with simple two compartments permeation cell which consisted of a feed solution (generally 2.4 cm^3) separated from a product solution chamber (2.4 cm^3) by a liquid membrane having an effective membrane area of 1.13 cm^2. The feed and product samples were mechanically stirred at about 120 rpm at room temperature (24 ± 1°C) to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. Membrane permeabilities were determined by monitoring the plutonium concentration radiometrically in the receiving phase as a function of time. Plutonium concentration in the various phases was found to be reproducible within ±10% of the stated values. The plutonium flux, J_M, was computed by the following equation:

$$J_M = C_{Pu,\text{receiving}} \times V/(A \times t)$$

where $C_{Pu,\text{receiving}}$ = initial Pu concentration in the receiving phase, mol/dm^3

V = volume of receiving phase, dm^3

A = effective area of the membrane, m^2

t = time elapsed.

The organic membrane phase was prepared by dissolving a weighed quantities of DC18C6 in toluene to obtain carrier solutions of varying

concentrations. It was subsequently equilibrated with solutions of the desired molarity of nitric acid before use.

Membrane Support

Throughout this study, Enka Accurel PP thin, flat-sheet type hydrophobic microporous polymeric membranes, coded as 2E HF-PP, were used. These membranes were about 130–180 μm thick and had a nominal porosity of about 70%, with an average pore diameter of the order of 0.2 μm. Filling the pores of these dry supports with the carrier was accomplished by immersing the membrane in the organic phase for at least 6–7 h before use.

Density and Viscosity Measurements

The densities and viscosities of the DC18C6/toluene solutions were measured in order to relate the plutonium transport properties with the physical properties of the carrier/diluent organic phase. Viscosities were measured at 25 ± 1°C by using an Ubbelhode viscometer, and densities were determined by weighing a known volume of solution using a pycnometer.

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Liquid–Liquid Distribution Measurements

Equal volumes (1 mL) of Pu-239 tracer in nitric acid of the desired molarity and DC18C6 dissolved in toluene were pipetted into a 15-mL glass-stoppered tube and mechanically stirred for nearly half an hour at room temperature (23–25°C). After settling for about 30 min, aliquots from both phases were withdrawn for radioassay. The distribution ratio (D_M) of plutonium, defined as the ratio of its concentration in the organic phase to that in the aqueous phase, was calculated. From knowledge of D_M, of the volume of the aqueous phase (V_w), and of the volume of the organic phase (V_o), the percentage of extraction ($\%E$) was obtained:

$$\%E = 100D_M/D_M + (V_w/V_o)$$

For the back-extraction studies, aliquots from the loaded organic phase were withdrawn and subsequently back-extracted for about 10 min with the same volume of the strippant.

RESULTS AND DISCUSSION

Liquid–Liquid Extraction

The liquid–liquid extraction of plutonium(IV) into toluene by DC18C6 from HNO_3 solutions is fairly selective and effective, primarily because of

the optimum fit of the Pu^{4+} cation (radius = 0.96 Å) into the crown cavity of DC18C6 (radius = 1.34–1.43 Å). Distribution ratios are quite high, and quantitative extraction is possible for plutonium(IV) under optimum conditions. With increasing acidity, the extraction of Pu(IV) first increased, passed through a maximum between 4 to 5 mol/dm^3, and then decreased. With an enhanced macrocycle concentration up to 0.2 mol/dm^3, the extraction was maximum at 3–4 mol/dm^3 acidity. No detectable extraction of commonly associated long-lived fission product contaminants, such as Cs-137, Ru-106, and Sb-125, took place at any acidity.

To examine the nature of the plutonium(IV) species extracted, the dependence of D_{Pu} on the macrocycle concentration was studied, keeping $[HNO_3]$ constant at 3 *M*. The extraction of Pu^{4+} by a crown ether (CE) can be represented by

$$Pu_a^{4+} + 4NO_{3a}^- + xCE_o \leftrightarrow Pu(CE)_x(NO_3)_{4o}$$

where the subscripts *a* and *o* denote the aqueous and organic phases, respectively.

The equilibrium constant, K_{Pu}, is given by

$$K_{Pu} = D_{Pu}/[NO_3^-]_a^4[CE]_o^x \quad (1)$$

with

$$D_{Pu} = [Pu(CE)_x(NO_3)_4]_o/[Pu^{4+}]_a$$

and it follows that

$$\log D_{Pu} = \log K_{Pu} + 4 \log [NO_3^-]_a + x \log [CE]_o \quad (2)$$

As seen from Eq. (2), a plot at constant $[HNO_3]$ of log D_{Pu} vs log $[CE]_o$ should be a straight line with a slope equal to the number x of extractant molecules attached to the Pu^{4+} cation in the organic phase. For Pu(IV), the slope is nearly +2, i.e., the complex is 1:2 (Fig. 1). The plutonium is extracted as a cationic sandwich associated with nitrate ions, presumably of the type $Pu(CE)_2^{4+} \cdot 4NO_3^-$, in accord with an earlier study (*10*).

A log K_{Pu} value of 4.44 for the Pu(IV) complex with DC18C6/toluene reflects the relatively high extractability of Pu(IV) and justifies the idea of selecting this crown ether as a carrier for liquid membrane systems.

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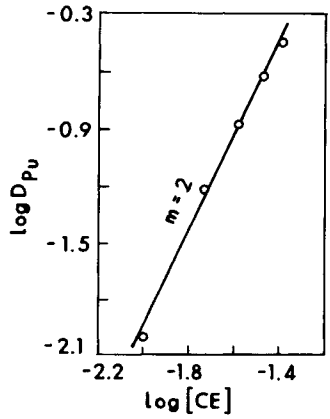

FIG. 1. Plot of extraction of Pu(IV) into toluene by DC18C6 from 3 mol/dm^3 HNO_3 aqueous medium as a function of the initial concentration of the macrocycle.

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Carrier Mediated Transport

DC18C6 dissolved in toluene served as the organic membrane in both BLM and SLM permeability measurements. Plutonium(IV) is highly extractable by DC18C6/toluene from nitric acid media and therefore it permeates easily across these liquid membranes. Carrying out control experiments with no DC18C6 in the membrane solvent proved that there was no permeation of plutonium(IV) across the membrane by the membrane solvent itself.

The receiving phase strippants hydroxylamine hydrochloride, oxalic acid, sodium carbonate, sulfuric acid, and dilute nitric acid were tested. More than 90% of the plutonium was recovered with 0.5 *M* sodium carbonate. With the rest of the strippants, except for hydroxylamine hydrochloride, the maximum recovery never exceeded 60%.

Permeation through BLM

The driving force for plutonium transport is provided by the concentration gradient of the nitrate ion between the source and receiving phases. For cation transport from higher to lower acidity, it is important to study the effect of nitric acid concentration. Results for the single-ion transport of nearly 1.0 mg Pu/dm^3 from an aqueous feed adjusted to different nitric acid molarities through a DC18C6/toluene BLM membrane using sodium carbonate as strippant are summarized in Table 1. A maximum plutonium recovery of over 90% and a maximum flux of 1.6×10^{-8} mol/m^2/s were reached after about 1 h of the transport process from a relatively low feed acidity up to 3 *M* HNO_3 while enhanced acidity, to about 5 *M*, adversely

TABLE 1
Flux and Permeation of Plutonium as a Function of Source Phase Nitric Acid Molarity[a]

Source phase acidity, HNO_3 (mol/dm^3)	Time elapsed (h)	Plutonium flux, J_M ($\times 10^{-8}$ $mol/m^2/s$)	Plutonium permeation (%)
1	1	—	—
	2	0.2	9.8
	3	0.2	11.7
	4	0.2	15.3
	5	0.2	18.6
	6	0.2	20.8
2	1	0.8	10.8
	2	0.7	20.2
	3	0.5	24.6
	4	0.4	25.1
	5	0.3	27.4
	6	0.3	31.6
3	1	1.6	28.6
	2	1.5	53.5
	3	1.5	74.9
	4	1.4	97.0
	5	0.9	97.5
	6	0.7	98.0
4	1	0.6	9.2
	2	0.6	18.5
	3	0.9	33.2
	4	0.6	39.5
	5	0.5	45.3
	6	0.5	52.2
5	1	0.1	4.3
	2	0.3	18.8
	3	0.6	27.2
	4	0.8	40.4
	5	0.7	43.3
	6	0.6	45.3
6	1	0.3	5.3
	2	0.2	7.4
	3	0.3	14.2
	4	0.4	23.5
	5	0.3	27.2
	6	0.3	30.1

[a]Initial feed concentration: 1.0 mg/dm^3 plutonium in HNO_3
Carrier concentration: 0.2 mol/dm^3 DC18C6/toluene
Strippant: 0.5 mol/dm^3 sodium carbonate
Volume ratio of feed to strippant: 4:1

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affected the plutonium transport and plummeted to 45% and lower. This is partly in accord with the expected trend since the flux of a cation varies with the NO_3^- ion concentration according to the relationship:

$$J_M = A(T/\eta)[NO_3^-]_a^n[DC18C6]_o^n C_{Pu},\text{feed}$$

and, hence, there should be an increase in permeability with an increase in proton or nitric acid concentration. Evidently this is true up to 3 mol/dm^3 nitric acid concentration (Fig. 2), and thereafter the Pu^{4+} ions form acido complexes with nitric acid of the $HPu(NO_3)_5$ and $H_2Pu(NO_3)_6$ types (*12*). Uptake of nitric acid by DC18C6 is also an important factor in reducing the cation flux because of its complexation with DC18C6 to form complexes of the DC18C6·nHNO$_3$ type.

Studying the effect of the initial concentration of plutonium (1–81 mg/dm^3) in the feed solution, when the product side contained a negligible concentration of plutonium, revealed that the cation flux initially increased sharply and then decreased with increasing plutonium molarity. Results of plutonium permeation through the membrane as a function of elapsed time (and thus of the extraction of Pu(IV) into the organic phase at various initial plutonium concentrations in the feed) are shown in Fig. 3. Most interestingly, a further increase in the feed plutonium concentration to 81 mg/dm^3 resulted in a significant decrease in the percent transport of plutonium to as low as 33%, probably due to membrane saturation and a lower effective membrane area in the BLM.

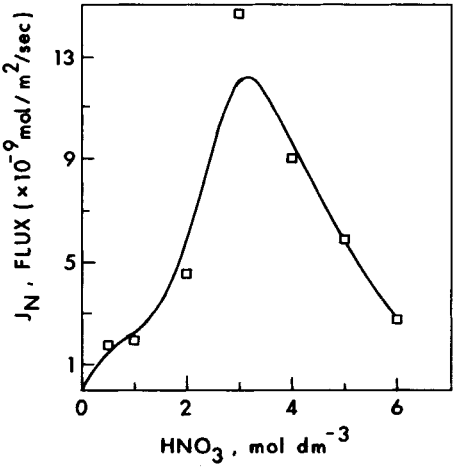

FIG. 2. Flux of plutonium as a function of HNO_3 concentration in the source phase (feed). (Mean value of the flux measured after 5 h of transport process.)

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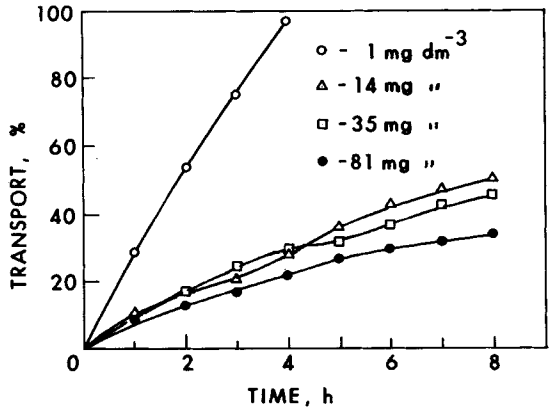

FIG. 3. Effect of initial plutonium concentration in the feed solution on its transport. Membrane: 0.2 mol/dm³ DC18C6/toluene. Source phase acidity: 3 mol/dm³ HNO_3. Strippant: 0.5 mol/dm³ sodium carbonate.

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As seen from Eq. (2), the value of D_{Pu} should increase with the aqueous nitrate concentration. Therefore, the "pumping" effect in a BLM study can be enhanced by increasing the ratio of the nitrate concentration in the source phase to the nitrate concentration in the receiving phase. Thus, in order to distinguish the driving force for cation transport across the crown ether/toluene membrane, experiments were performed with decreasing amounts of nitric acid mixed with ammonium nitrate while maintaining the total [NO_3^-] concentration at 3 *M* to simulate partial neutralization of the acid waste. From the results given in Table 2, it is clear that no significant change in plutonium transport took place when the source phase

TABLE 2
Flux and Permeation of Plutonium at a Fixed [NO_3^-] Concentration in the Source Phase[a]

[HNO_3] (mol/dm³)	[NH_4NO_3] (mol/dm³)	Plutonium flux,[b] ($\times 10^{-8}$ mol/m²/s)	Plutonium (%)
3.0	0.0	1.3	97.0
1.5	1.5	1.3	92.8
0.5	2.5	1.3	95.4

[a]Aqueous feed composition: 3 mol/dm³ NO_3^- (HNO_3 + NH_4NO_3)
Initial plutonium concentration: 1 mg/dm³ plutonium in HNO_3
Carrier (DC18C6) concentration: 0.2 mol/dm³ DC18C6/toluene
Strippant: 0.5 mol/dm³ sodium carbonate
[b]Mean value of the flux measured after 5 h of operation.

acidity was decreased while the nitrate molarity was kept constant, i.e., 3 *M*. Hence, the NO_3^- ion—not the H^+ ion—seems to be the driving force for plutonium(IV) transport under the present conditions. Thus, the best condition for transfer among those tested is 0.5 *M* HNO_3 + 2.5 *M* NH_4NO_3 which requires relatively smaller amounts of nitric acid to adjust the nitrate concentration.

The difference in permeability among experiments with varying feed acidities, carrier concentrations, and plutonium concentrations can be understood by considering the probable expression for the rate of formation of the diffusing species at the feed interface:

$$d[Pu(CE)_2(NO_3)_4]/dt = k^*[CE]^2[NO_3^-]^4[Pu^{4+}]$$

where k^* is the rate constant for the formation of the plutonium(IV)–crown ether complex. This equation is based on the stoichiometry of plutonium extraction as detailed elsewhere (*10*). The rate of diffusion of metal species will thus depend upon any changes in CE, NO_3^-, and Pu^{4+} concentrations in the feed side.

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Effect of Carrier Concentration on Plutonium Transport

The composition of the organic solution has a marked effect on cation flux. When transport across a membrane occurs via a carrier, as in facilitated transport, the flux is generally expected to increase with increasing carrier concentration. However, in carrier-mediated transport of plutonium with DC18C6, a more complex behavior is seen. Table 3 summarizes data on plutonium flux vs DC18C6 concentration in the membrane. Figure 4 shows that with increasing carrier concentration in an inert diluent like toluene, plutonium transport gradually increases, reaching a maximum (>95%) at about 0.3 mol/dm^3 DC18C6 within 4–5 h, and thereafter there is a significant decrease at 0.4 to 0.5 mol/dm^3 DC18C6. This seems to be due to insufficient stripping from the BLM containing the high concentration of DC18C6. The optimum carrier concentration is thus around 0.3 *M*, taking into account complete stripping from BLM.

This behavior probably also occurs because the viscosity of 0.5 *M* DC18C6/toluene is greater than that of a lower concentration of DC18C6 (Table 3), and therefore the diffusion coefficient in the membrane decreases with an increase of the viscosity of the diluent, which probably may be explained by the Stokes–Einstein equation:

$$D = kT/6\pi r\eta$$

where k, T, r, and η denote the Boltzman constant, the absolute temperature, the molecular radius of the plutonium complex, and the viscosity of

TABLE 3
Flux and Permeation of Plutonium as a Function of Carrier (DC18C6) Concentration in the Organic Membrane[a]

DC18C6 concentration in toluene (mol/dm³)	Viscosity (cP)	Time elapsed (h)	Plutonium flux, J_M ($\times 10^{-8}$ mol/m²/s)	Plutonium permeation (%)
0.05	0.559	1	0.4	6.1
		2	0.5	13.7
		3	0.6	22.8
		4	0.5	28.0
		5	0.3	30.7
		6	0.2	32.5
0.1	0.563	1	1.4	9.5
		2	1.9	49.7
		3	1.6	64.5
		4	1.4	73.0
		5	1.1	76.7
		6	0.9	77.8
0.20	0.569	1	1.6	28.6
		2	1.5	53.5
		3	1.5	74.9
		4	1.4	97.0
		5	0.9	97.5
		6	0.7	98.0
0.30	0.572	1	3.5	61.6
		2	2.7	79.3
		3	1.8	88.5
		4	1.7	95.0
		5	1.1	95.8
		6	0.8	96.0
0.40	0.579	1	1.2	16.1
		2	1.7	43.0
		3	1.6	62.8
		4	1.3	66.2
		5	0.9	69.7
		6	0.7	70.8
0.50	0.586	1	0.6	18.7
		2	0.4	20.2
		3	0.4	26.2
		4	0.4	34.2
		5	0.3	36.8
		6	0.3	39.6

[a]Initial source phase acidity: 3 mol/dm³ HNO_3
Initial plutonium concentration: 1 mg/dm³
Strippant: 0.5 mol/dm³ sodium carbonate

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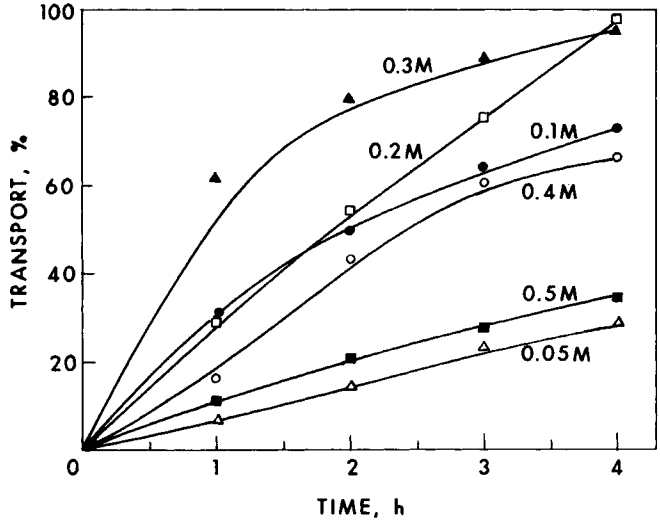

FIG. 4. Effect of carrier (DC18C6) concentration on the Pu(IV) transport across BLM as a function of permeation time. Source phase acidity: 3 mol/dm^3 HNO_3. Strippant: 0.5 mol/dm^3 sodium carbonate.

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the organic phase, respectively. The trend is shown to be true in Fig. 5 since the flux increases up to 0.3 mol/dm^3 DC18C6 and then decreases from 0.4 to 0.5 mol/dm^3 DC18C6/toluene. Babcock et al. (*13*) attributed the main cause of this behavior to the concentration gradient of the metal

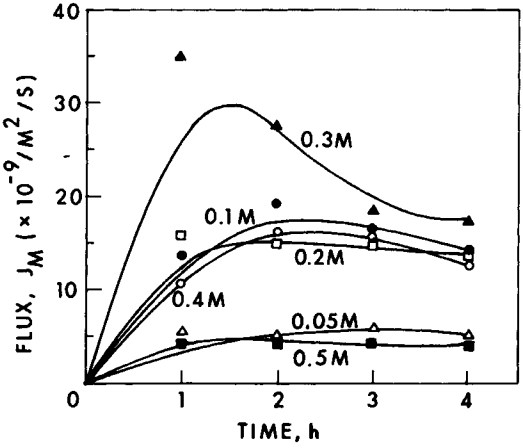

FIG. 5. Plots of plutonium flux against transport time for BLM using different concentrations of DC18C6 as the carrier (see details in Fig. 4).

complex, the viscosity of the organic phase and hindered diffusion of the metal complex caused by aggregation of the complex, and the tortuosity of the pores of the membrane.

Effect of Strippant on Plutonium Permeation

Detailed experiments were carried out to demonstrate that the transport of plutonium ions across the DC18C6/toluene membrane is strongly dependent upon the nature and concentration of the strippant present on the product side of the membrane. From Table 4, it is apparent that out of several aqueous strippants that were tested (oxalic acid, sulfuric acid, hydroxylamine hydrochloride, sodium carbonate), 0.5 *M* sodium carbonate proved to be the most efficient for stripping purposes. For example, $[Pu]_{p,5h}/[Pu]_{f,5h}$ is around 29, which happens to be the maximum under the present conditions. The effect of sodium carbonate concentration on the flux was also studied and was found to remain practically unchanged at nearly 1.5×10^{-8} mol/m^2/s (mean value of the flux measured after 5 h of transport process) while keeping the feed acidity at nearly 3M HNO_3 and the initial plutonium(IV) concentration around 1 mg/dm^3. The concentration range studied (0.5–2 mol/dm^3) indicated, in general, that there was no appreciable change in flux with increasing strippant concentration.

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TABLE 4
Effect of Aqueous Strippants on Plutonium Transport (5 h permeation time)[a]

Aqueous strippant	Concentration (mol/dm^3)	Flux ($\times 10^{-8}$ mol/m^2/s)	$[Pu]_{f,5h}$[b] ($\times 10^{-7}$ mol/dm^3)	$[Pu]_{p,5h}$[c] (mol/dm^3)	$[Pu]_{p,5h}/[Pu]_{f,5h}$
Na_2CO_3	0.1	0.2	8.2	1.5×10^{-6}	1.8
	0.5	1.5	4.1	1.2×10^{-5}	29.3
	1.0	1.1	5.6	7.7×10^{-5}	13.7
	2.0	1.2	5.0	6.7×10^{-5}	13.4
Oxalic acid[d]	1.0	0.6	2.6	1.2×10^{-6}	4.6
	2.0	0.7	2.3	1.3×10^{-6}	5.7
H_2SO_4	1.0	0.7	6.1	9.5×10^{-6}	15.6
	2.0	0.8	5.7	8.3×10^{-6}	14.6
$NH_2OH \cdot HCl$	0.05	0.7	5.2	1.2×10^{-5}	23.1
	0.10	1.0	4.2	1.1×10^{-5}	26.2

[a] $V_f = 10$ cm^3; $V_p = 2.4$ cm^3; $[Pu]_{f,0} = 4.2 \times 10^{-6}$ mol/dm^3. Feed acidity = 3 mol/dm^3 HNO_3.
[b] Concentration of Pu in the feed after 5 h of permeation.
[c] Concentration of Pu in the product side after 5 h of permeation.
[d] Dissolved in 0.05 mol/dm^3 HNO_3.

Effect of the Feed Volume

To concentrate plutonium from very dilute solutions, a high volume ratio, V_f/V_p, of feed to product solution is desirable because it yields the limiting concentration factor $[Pu]_{p,t}/[Pu]_{f,0}$. The J_M values were found to be inversely proportional to the feed volume. Thus, we should adjust the volume of the product solution to be as small as possible in order to obtain a high concentration factor, and to use a large membrane area to enhance the transport rate. Evidently, this can be achieved by means of a tubular or hollow fiber type of support for the carrier liquid.

Permeation through SLM

Based on the above findings with BLM on plutonium transport, the SLM measurements were operated only at the optimum concentration of feed acidity (3 mol/dm^3 HNO_3), carrier concentration (0.2 mol/dm^3 DC18C6), and strippant (0.5 *M* sodium carbonate). Under these conditions, more than 90% of plutonium(IV) (1 mg/dm^3) could be easily recovered within 7–8 h by employing an Accurel 2E-HF-PP membrane support. Nitric acid was observed to be cotransported through the supported liquid membrane:

$$DC18C6 + nHNO_3 \rightarrow DC18C6 \cdot nHNO_3$$

Experiments were also performed in which the feed and product solutions initially contained an equal plutonium concentration (0.79 mg/dm^3). Figure 6 shows the plutonium concentration in the acid feed and in the alkaline strip phases as a function of time. Efficient transport of plutonium still took place through this membrane against a concentration gradient.

To test the feasibility of the permeation of different oxidation states of plutonium, experiments were also conducted with SLM to observe the effect of different oxidation states like Pu(III) and Pu(VI). Negligible amounts of these were transported even after 8 h of operation because Pu(III) and Pu(VI) have very low distribution ratios in the DC18C6/toluene organic phase.

Permeation of Fission Product through BLM and SLM

Permeation of some long-lived fission products, such as Cs-137, Ru-106, and Sb-125 which often accompany plutonium, was also tested. It can be seen from Table 5 that no detectable amounts of these fission products permeated to the product side even after 12 h of operation. This was expected because these fission products are almost unextractable by DC18C6/toluene under similar conditions (*10*). The feasibility of a moderately clear-cut separation of plutonium from some of the fission product contaminants is thus clearly established by this study.

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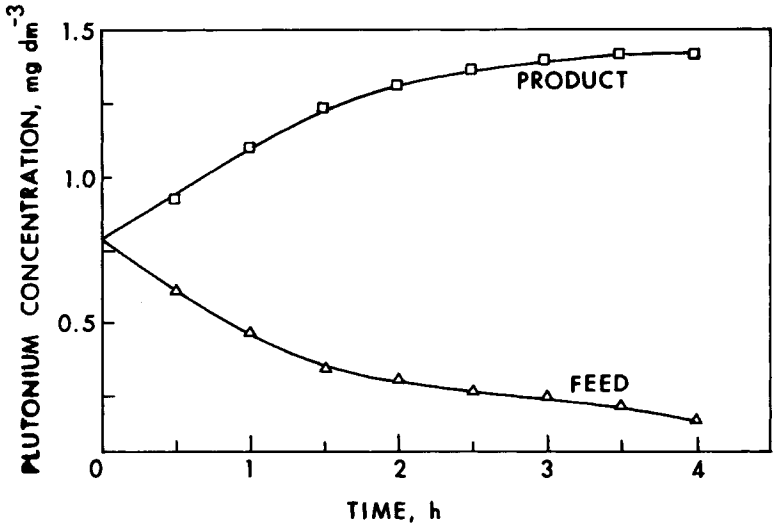

FIG. 6. Plot of plutonium concentration in the feed and product solution vs time. Membrane: 0.2 mol/dm^3 DC18C6/toluene. Source phase acidity: 3 mol/dm^3 HNO_3. Strippant: 0.5 mol/dm^3 sodium carbonate. Concentration of initial feed and product solutions: 0.79 mg/dm^3 Pu.

Chemical Stability, Regeneration, and Life Time of the Polymeric Support

Stability of the polymeric solid thin-film supports was tested by measuring the plutonium flux under optimum conditions. Before performing each new flux measurement, the feed and strip solutions were replaced

TABLE 5
Permeation of Various Fission Products (FP) through a Supported Liquid Membrane[a]

Fission product	Half life (years)	FP activity[b] in source phase (μCi/dm^3)	FP activity in the receiving phase (μCi/dm^3)	Permeation of fission products (%)
RU^{106}	1	4.28	0.72	16.8
Cs^{137}	28	2.63	0.44	16.5
Sb^{125}	2	0.69	0.08	11.6

[a]Initial feed concentration: 50.0 mg/dm^3 plutonium in HNO_3
Carrier concentration: 0.2 mol/dm^3 DC18C6/toluene
Strippant: 0.5 mol/dm^3 sodium carbonate
Volume ratio of feed to strippant: 6:1
[b]Activity of fission products was estimated by using a multichannel analyzer with a high purity germanium detector (HPGe).

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with fresh ones. At the end of the permeation experiment, the SLM was left in contact with the depleted feed and the plutonium-loaded strip solution. Loss of carrier was observed after about 12 h of continuous use. The stability probably depends on the capillary forces that hold the organic membrane solvent within the pores, as implied by the Young–Dupre equation (*14*):

$$P_c = (2\gamma/a) \cos \theta$$

where P_c, γ, a, and θ denote the capillary pressure, solvent–water interfacial tension, membrane pore size, and the contact angle, respectively. Danesi and Rickert (*15*) have concluded that the probable causes of SLM instability are loss of the carrier extractant by its solubility and progressive wettability of the support pores induced by a lowering of the interfacial tension.

Aromatic solvents possess relatively lower interfacial tension than do aliphatic ones (*16*), and this may account for the fast degradation of the SLM support in the toluene medium. To check the chemical resistance of the polypropylene membranes to toluene, they were periodically test-soaked in DC18C6/toluene over a period more than a month. At the end of each run, the SLM support was washed with toluene and stored in toluene. From data summarized in Table 6, it is evident that the flux was practically unaffected, thus showing that the integrity of the support was not seriously disturbed by the solvent and hence can be regenerated for reuse.

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Mechanism of Pu(IV) Transport

A possible scheme for the transport of Pu^{4+} ions from dilute HNO_3 across BLM as well as SLM systems containing DC18C6/toluene into Na_2CO_3 is presented in Fig. 7.

When the Pu^{4+} ions in the feed solution come in contact with DC18C6 (CE) in the liquid membrane in the presence of H^+ and NO_3^- ions (in the source phase), the following reaction takes place:

$$Pu^{4+} + 4NO_3^- + 2CE \rightarrow Pu^{4+}(CE)_2 \cdot 4NO_3^-$$

Because the $Pu^{4+}(CE)_2 \cdot 4NO_3^-$ complex forms on the membrane interface on the feed side, its concentration within the membrane is enhanced on that side. This complex then moves toward the stripping solution within the membrane as a consequence of concentration gradient. When the complex reaches the product side of the membrane, the following reaction takes place:

$$Pu^{4+}(CE)_2 \cdot 4NO_3^- + Na_2CO_3 \rightarrow Pu(CO_3)_2 + 2CE$$

TABLE 6
Stability and Lifetime of a Flat-Sheet Polypropylene Membrane Support[a]

Number of days[b]	Plutonium flux ($\times 10^{-9}$ mol/m^2/s)		Plutonium permeation (%)	
	1 h	4 h	1 h	4 h
1	15.7	13.7	28.6	97.2
7	15.2	13.5	27.9	96.5
13	14.9	13.3	27.5	96.0
19	15.1	13.6	28.0	97.0
25	15.4	13.2	27.8	96.5
31	15.6	13.4	28.0	96.9

[a]Initial source phase acidity: 3 mol/dm^3 HNO_3
Initial plutonium(IV) concentration: 1 mg/dm^3
Strippant: 0.5 mol/dm^3 sodium carbonate
Carrier concentration: 0.2 mol/dm^3 DC18C6/toluene
[b]Membrane was soaked in 0.2 mol/dm^3 DC18C6/toluene before the start of each run.

The CE molecules are left free in the organic membrane phase, and the $Pu(CO_3)_2$ species enters the stripping solution. The concentration of the $Pu(CE)_2^{4+}\cdot 4NO_3^-$ ion-pair complex in the liquid membrane remains high on the source phase side because the complex is continuously being formed

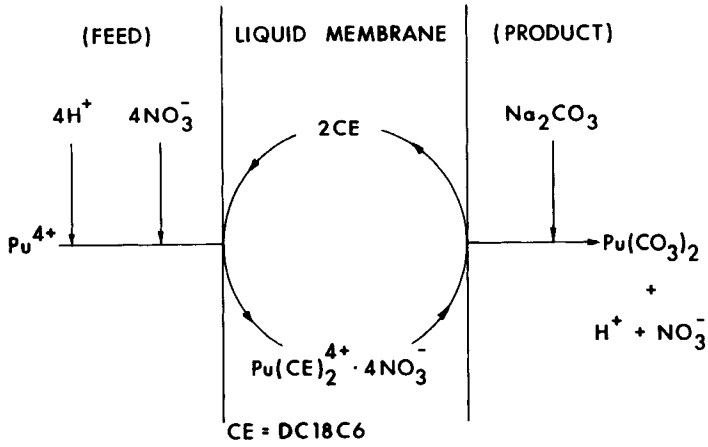

FIG. 7. Possible scheme for Pu(IV) transport from HNO_3 solution to dilute Na_2CO_3 through DC18C6/toluene-based bulk liquid/supported liquid membrane.

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on that side while its concentration remains very low on the product side. Consequently, the complex permeates continuously from the feed to the product side across the liquid membrane under its concentration gradient. The CE molecules become free on the receiving phase side of the membrane, resulting in a CE concentration gradient in a direction opposite to that of the Pu^{4+} ions, thus returning the CE molecules from the stripping to the feed solution side within the membrane. As the NO_3^- ions move in the direction of the Pu^{4+} ions, there is a coupled cotransport process. At high HNO_3 concentrations, a $CE \cdot nHNO_3^-$-type complex may also be formed, thus hindering acid transport because of the nitric acid concentrations.

CONCLUSIONS

It is concluded that maximum plutonium permeation through macrocyclic-based liquid membranes is attained with a feed activity of around 3 mol/dm^3 HNO_3 and 0.2 mol/dm^3 DC18C6 in toluene as the carrier. Dilute sodium carbonate was found to be the best strippant. Enrichment factors of the order of 6 or more are not difficult to achieve by properly manipulating the feed : strip volume ratios. Under these optimum conditions, both BLM and SLM are quite effective and selective for the removal of trace as well as milligram amounts of plutonium from acidic nitrate solutions. There is a need to expose this technique to large surface area membranes with high boiling point membrane solvents which minimize the loss of carrier from the membrane support. An 18-membered macrocyclic compound was shown to be the best candidate for liquid membranes owing to its high selectivity for plutonium(IV) even in the presence of some long-lived fission product contaminants, thus leading to novel applications of membrane technology in the nuclear industry.

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REFERENCES

1. R. M. Izatt, J. S. Bradshaw, S. A. Nielson, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev., 85,* 271 (1985).
2. H. K. Lonsdale, *J. Membr. Sci., 10,* 81 (1982).

3. J. D. Way, R. D. Noble, T. M. Flynn, and E. D. Sloan, *Ibid., 12,* 239 (1982).
4. P. R. Danesi, *Sep. Sci. Technol., 19,* 857 (1984–85).
5. P. R. Danesi, R. Chiarizia, P. Rickert, and E. P. Horwitz, *Solv. Extr. Ion Exch., 3,* 111 (1985).
6. A. C. Muscatello, J. D. Navratil and M. Y. Price, in *Liquid Membranes: Theory and Applications* (R. D. Noble and J. D. Way, eds.), (ACS Symp. Ser. 347), Washington, D.C., 1987.
7. R. D. Noble, C. A. Koval, and J. J. Pellegrino, *Chem. Eng. Prog.*, p. 58 (1989).
8. A. C. Muscatello and J. D. Navratil, "Americium Removal from Nitric Acid Waste Streams, in *Chemical Separations, Litarvan,* Vol. II, Denver, 1986, p. 439.
9. J. P. Shukla and S. K. Misra, *J. Membr. Sci.,* In Press.
10. J. P. Shukla, R. K. Singh, and A. Kumar, *Radiochim. Acta,* In Press.
11. D. E. Ryan and A. W. Wheelwright, *USAEC Report HW-55983* (1959).
12. F. Baroncelli, G. Scibona, and M. Ziffereo, *J. Inorg. Nucl. Chem., 24,* 541 (1962).
13. W. C. Babcock, R. W. Baker, E. D. La Chapelle, and K. L. Smith, *J. Membr. Sci., 7,* 89 (1980).
14. A. W. Adamson, *Physical Chemistry of Surfaces,* 2nd ed., Wiley, New York, 1967.
15. P. R. Danesi and R. G. Rickert, *Solv. Extr. Ion Exch., 4,* 149 (1986).
16. H. Takeuchi, K. Takahashi, and W. Goto, *J. Membr. Sci., 34,* 19 (1987).

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