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Transport of Samarium(III) and Uranium(VI) across a Silicone-Supported Liquid Membrane Using Di(2-ethylhexyl)phosphoric Acid and Tributyl Phosphate as Mobile Carriers

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ABSTRACT

Transport of actinides and lanthanides from dilute acidic solutions through silicone membranes prepared in this laboratory was studied using di(2-ethylhexyl)-phosphoric acid (D2EHPA) and tributyl phosphate (TBP) as mobile carriers. It was found that transport of uranyl and samarium ions increased with an increase in carrier concentration dissolved in kerosene in the membrane phase. However, the metal ion flux was optimum at 1 M D2EHPA and 30% (v/v) of TBP, after which it decreased. It was also observed that the higher nitrate ions concentration in the feed enhanced the transport of U(VI) species with TBP carrier. In general, the performance of our silicone membrane compares well with those of other extensively used supported membranes, such as polypropylene and PTFE.

Key Words. Silicone membrane; SLM; TBP; D2EHPA; Transport; Flux

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INTRODUCTION

The recovery of metals of value from dilute and impure solutions is a frequent requirement in the hydrometallurgical processing as well as for effluent treatment. Solvent extraction is one of the well-known processing schemes for achieving this goal, particularly for metals like lanthanides and actinides. In the area of solvent extraction technology, liquid membrane extraction (LME) has emerged as a novel technique and finds many interesting applications. One feasible type of LME is supported liquid membrane (SLM), which uses a porous polymer membrane to carry the extractant (carrier) in pores. The impregnated membrane acts as a common interface between the feed and the strip solution, and it aids in the selective transport of metal species of interest. The permeation of metal ion species through the SLM can therefore be described as a simultaneous extraction and stripping operation in a single stage under nonequilibrium conditions.

In comparison to the traditional solvent extraction technique, SLM offers many advantages such as 1) the possibility of using a high feed to strip volume to achieve a larger concentration of the transported species, 2) the economic use of expensive extractants due to its low inventory, 3) the elimination of the phase separation problem, 4) negligible organic phase entrainment, and 5) high selectivity. The success of SLM is, however, closely dependent on a number of desired properties for porous supports, namely (a) high porosity (>50%), (b) small pore diameters (<0.1 μm) and narrow size distribution, (c) low wall thickness (<100 μm), (d) a hydrophobic nature, (e) chemical resistance, (f) good wettability with the extractant, and (g) low cost. The choice of a suitable membrane is therefore an important aspect of the solution treatment scheme.

Studies of lanthanides and actinides are very important in nuclear energy programs. The process of solvent extraction has been used extensively for this purpose, and the technique of SLM has been extended to these studies. A large number of papers have been published dealing with SLM systems (1–7) as applied to the extraction of lanthanides and actinides, using extractants like bis(2-ethylhexyl)phosphoric acid (D2EHPA) (8, 9, 13) tributyl phosphate (TBP) (10, 11), LIX (12), etc. in porous membranes made of polypropylene, PTFE, polysulfone, and cellulose acetate.

In our laboratory we have synthesized and characterized silicone membranes (14). These membranes find applications in gaseous separation and pervaporation where they exhibit high permeability and selectivity (1, 15, 16). The present paper deals with the novel application of silicone membranes in the field of SLM. Studies were conducted on the transport

TABLE 1
Characteristic Properties of Silicone Membranes

Membrane batch no.	Water uptake (wt%)	Kerosene uptake (wt%)	Swelling (vol%)	N_2 gas permeability [cc(NTP)·cm/cm^2/s/atm × 10^6]	Tensile strength (kg/cm^2)
GR 220	0.27	156.5	120	3.05	3.0
GR 219	0.12	67.9	83	4.19	15.0
GR 218	0.25	49.1	64	4.66	22.0
GR 204	0.00	38.2	51	3.16	61.0
GR 208	0.24	27.0	36	4.57	58.3
GR 211	0.00	22.0	28	4.95	67.0

of uranyl and samarium ions with D2EHPA and of uranyl nitrate with TBP as carriers, loaded into the pores of silicone membranes.

EXPERIMENTAL

Materials

Among the various silicone membranes prepared earlier in this laboratory (14), those with the composition of batch GR 211 (Table 1) were chosen as it exhibited the least swelling characteristics and the best tensile strength. Because the membrane was too thin to handle with ease, it was coated/laminated on cellulose filter paper before use in such a way that the coated side became hydrophobic while other side remained hydrophilic. In addition to silicone, other membranes, like polypropylene (PP) and PTFE, were examined for comparison. Their characteristics along with those of silicone membrane GR 211, are given in Table 2.

TABLE 2
Physical Characteristics of Different Membranes Used for SLM Studies

Membrane type	Polymeric network	Thickness (μm)	Pore size (μm)	Porosity (v/v %)
GR 211	Silicone	60	—	34[a]
Celgard 2400	Polypropylene	25	0.02	38
SM 11807 Sartorious	PTFE	65	0.20	—

[a] Obtained from dodecane uptake.

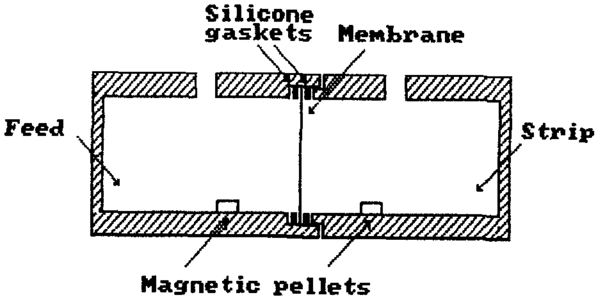

FIG. 1 Transport cell.

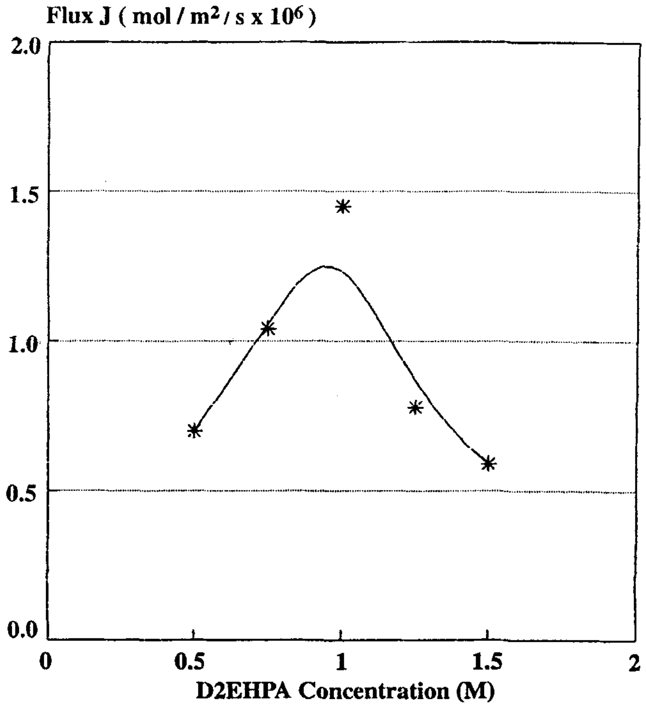

FIG. 2 Uranyl ion flux as a function of D2EHPA concentration.

Experimental Setup

The main experimental set up (i.e., the transport cell) used in this study was made from Perspex material as shown in Fig. 1. It consisted of two compartments, each with a capacity of 30 mL. Feed solution was introduced into one compartment, and the other compartment was used for the strip solution. A membrane loaded with the carrier was placed between the two compartments and sealed with a silicone rubber gasket. The feed and the strip solutions were stirred with magnetic stirrers.

Viscosity Measurements

An Ostwald viscometer with a 0.5-mm capillary was used to measure the viscosities of TBP/kerosene solutions at 25°C.

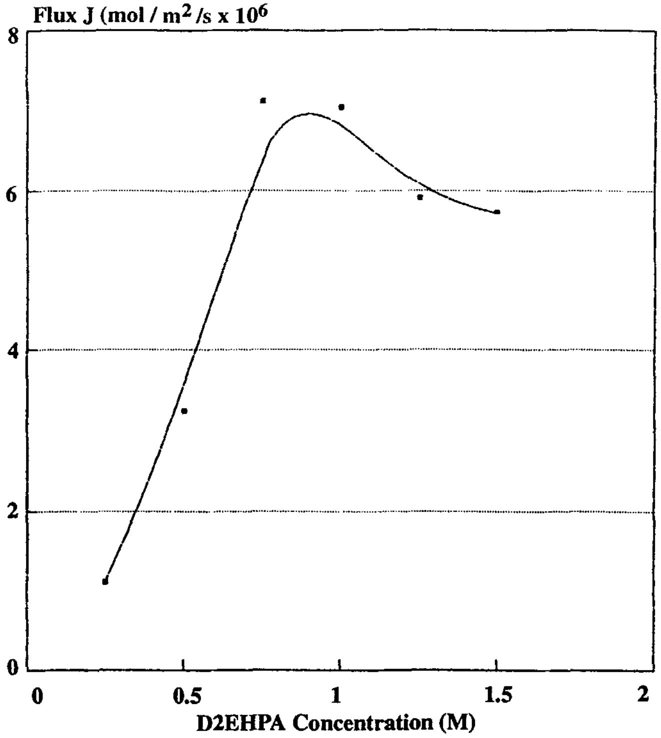

FIG. 3 Samarium ion flux as a function of D2EHPA concentration.

Procedure

In a typical experimental procedure, the membrane was first impregnated with the carrier solution in kerosene for 20 minutes and then placed between the two compartments of the transport cell.

For studies with the D2EHPA carrier, dilute solutions of UO_2^{2+} and of Sm^{3+} with concentrations of 2.76 and 4.70 mM, respectively, were used as feed solutions, while 0.5 M HCl was used as the strip solution. With TBP as the carrier, a feed solution of $UO_2(NO_3)_2$ (concentration 2.94 mM) and a strip solution of 0.5 M Na_2CO_3 were employed. The feed and the strip solutions were stirred with magnetic stirrers at a speed of ≥200 rpm. Samples from both strip and feed compartments were taken at regular intervals and analyzed by the spectrophotometric Arsenazo III method.

The rate of ion transfer through the membrane, J (mol/m^2·s), was evaluated from the initial slope of the metal ion concentration in the strip compartment vs time plot. The rate was calculated by using a linear regression technique.

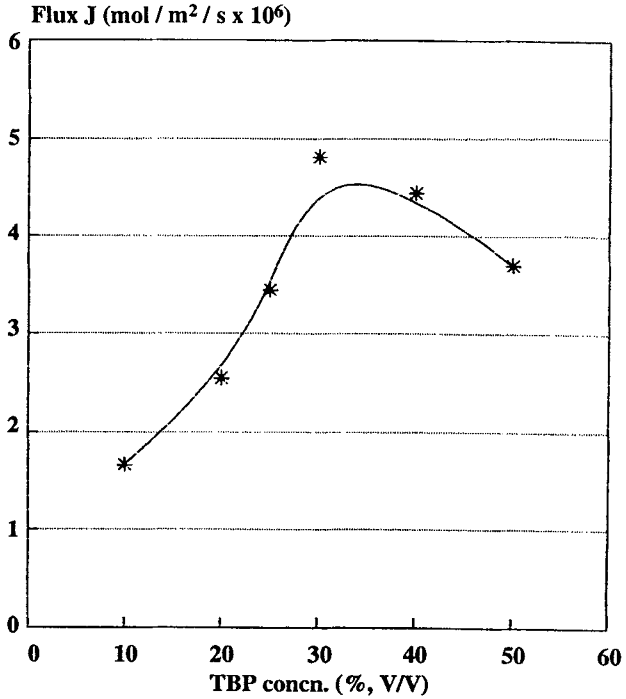

FIG. 4 Uranium flux as a function of TBP concentration.

In order to see the effect of carrier concentration in the membrane organic phase, experiments were done employing membranes loaded with different carrier concentrations in kerosene. The results are given in Figs. 2–4.

For the uranyl nitrate–TBP system, because the nitrate ion concentration in the feed affected the distribution coefficient K_d, different amounts of sodium nitrate were added to the feed of the uranyl nitrate solution, and its transport was studied on SLMs loaded with 30% TBP. The results are given in Fig. 5.

Finally, transport studies were carried out with commercial polypropylene and PTFE membranes. The performance of our silicone membrane is compared with them in Fig. 6.

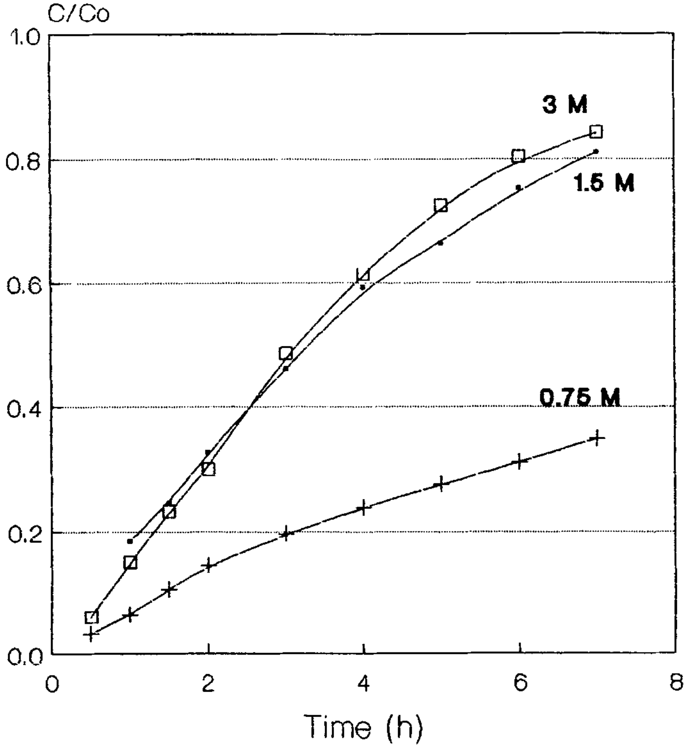

FIG. 5 Uranium transport with varying amounts of sodium nitrate in the feed. C_0 is the initial U(VI) feed concentration.

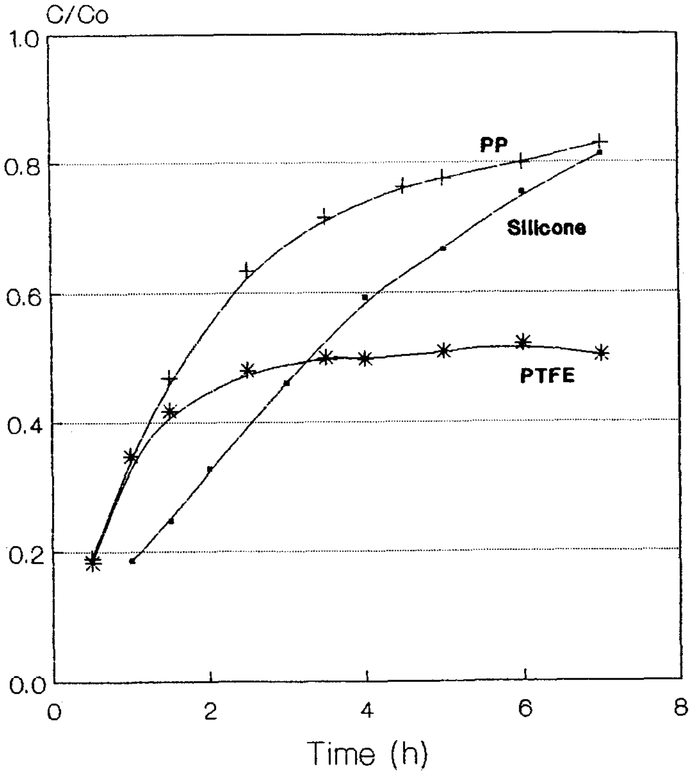

FIG. 6 Uranium transport using different SLMs. C_0 is the initial U(VI) feed concentration.

RESULTS AND DISCUSSION

D2EHPA extracts a trivalent lanthanide ion (Ln^{3+}) and a uranyl ion (UO_2^{2+}) through the cation-exchange reaction expressed by the following equations:

$$Ln^{3+}(aq) + 3(HX)_2(org) \rightleftharpoons LnX_3 \cdot 3HX(org) + 3H^+(aq) \qquad (1)$$

$$UO_2^{2+}(aq) + 2(HX)_2(org) \rightleftharpoons UO_2X_2 \cdot 2HX(org) + 2H^+(aq) \qquad (2)$$

where HX is D2EHPA and aq and org stand for aqueous and organic, respectively.

Extraction of uranyl nitrate by TBP is shown in the following equation:

$$UO_2^{2+}(aq) + 2NO_3^-(aq) + 2TBP(org) \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP(org) \qquad (3)$$

When D2EHPA is used as a carrier, the permeation of the metal ion species is by a countertransport process wherein equivalent H^+ ions move from the strip to the feed solution as metal ions move from the feed to the strip side. However, a carrier cotransport process is followed with TBP.

Figures 2 and 3 show that the transport rates (flux) of UO_2^{2+} and Sm^{3+} exhibit a maxima at around 1 M D2EHPA. The increase in transport rate with an increase in carrier concentration is natural, as the distribution coefficient (K_d) value increases simultaneously. However, the decrease in rate in the higher carrier concentration region is most probably caused by a decrease of K_d due to an increase in the viscosity of carrier solution (Table 3) as given by the Schulz equation (3):

$$J = \frac{k}{\eta}[(MX_n)_1 - (MX_n)_2] \tag{4}$$

where η is the viscosity of the carrier solution in the membrane, k is a constant, and the expression in brackets refers to metal–carrier complex concentration at the feed–membrane and the membrane–strip interfaces, respectively.

Similarly, in the transport flux for the $UO_2(NO_3)_2$–TBP system a maxima is observed at 30% TBP concentration (Fig. 4). From experiments using varying amounts of sodium nitrate in the feed solution containing 0.5 M HNO_3, it is observed (Fig. 5) that uranium transport is enhanced with the increase in the sodium nitrate concentration in the feed, as expected from the following equation:

$$K_d = K_{eq}[NO_3^-(aq)]^2[TBP(org)]^2 \tag{5}$$

where K_{eq} is the equilibrium constant as given by Eq. (3).

TABLE 3
Viscosity of TBP Extractant in Kerosene

Concentration of TBP solution in kerosene (wt%)	Viscosity (cPs)
0	1.26
10	1.32
20	1.35
25	1.41
30	1.46
40	1.57
50	1.68

TABLE 4

	Flux (mol/m^2·s)		
	D2EHPA		
Membrane	$UO_2^{2+} \times 10^6$	$Sm^{3+} \times 10^6$	TBP, $UO_2(NO_3)_2 \times 10^6$
Silicone	1.45	7.03	4.8
PP	—	—	9.0
PTFE	—	—	8.0

The transport flux of 1.45×10^{-6} mol/m^2/s with UO_2^{2+} ions was found to be lower than that obtained with Sm^{3+} (7.03×10^{-6} mol/m^2/s) using D2EHPA as the carrier (Table 4). However, the uranium flux using TBP as the carrier was found to be higher than that obtained with D2EHPA. The performance of our silicone membrane has been found to be comparable with those of PP and PTFE under similar experimental conditions, as shown in Fig. 6.

CONCLUSIONS

Based on the results of this study, the following conclusions were made.

1. The transport fluxes for UO_2^{2+} and Sm^{3+} have been obtained as 1.45×10^{-6} and 7.03×10^{-6} mol/m^2/s with a D2EHPA carrier. However, with TBP as the carrier, the value of uranium transport flux has been found to be 4.8×10^{-6} mol/m^2/s, which is higher than that obtained for the UO_2^{2+}–D2EHPA system.
2. The transport flux increases with an increase in the carrier concentration to a maximum and then falls due to the increased viscosity of the carrier.
3. In the uranium–TBP system, an increase in the nitrate ion concentration in the feed leads to enhancement of the uranium transport flux.
4. With D2EHPA as the carrier, the samarium transport flux was found to be larger than the uranyl flux.
5. The performance of a silicone membrane prepared in this laboratory compares well with such other commercial membranes as PP and PTFE. Our silicone membranes are also useful in gaseous separation and pervaporation.

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