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FACILITATED TRANSPORT OF Th(IV) ACROSS BULK LIQUID MEMBRANE BY DI(2-ETHYLHEXYL)PHOSPHORIC ACID

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ABSTRACT

Di(2-ethylhexyl) phosphoric acid (DEHPA) has been successfully used as a carrier for the selective and efficient transport of Th(IV) across a bulk liquid membrane (BLM) of chloroform. The feed comprised of a solution of pure Th(IV) or a binary mixture of Th(IV) and a cation, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Pb^{2+}, La^{3+}, Fe^{3+}, or UO_2^{2+}, in water maintained at pH 2, while 0.1 mol/L hydrochloric acid served as a stripping agent in the receiving compartment of the permeation cell. Greater than 99% of Th^{4+} selectively permeated across the membrane in less than 3 h, while the transport of other cations present along with thorium was less than 3% during the same time.

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Selectivity of the transport of thorium was greatly affected by the presence of Fe^{3+} and UO_2^{2+} in the feed solution. Fe^{3+} could be effectively masked by the addition of SCN^- or citric acid to the feed solution but the cotransport of UO_2^{2+} could only be partially reduced by the addition of carbonate or thiocyanate to the feed solution.

INTRODUCTION

In recent years, liquid membranes have widely been used in the studies of ion transport against a concentration gradient. Transport of metal ions across a membrane plays an important role in stimulating biological membrane functions (1,2) and separation technologies (3). Of the different types of membranes, bulk liquid membranes (BLMs) are considered to be the most suitable ones for industrial applications due to their simplicity, low operational cost, and high mechanical stability.

The carrier-facilitated transport generally results in uphill transport and higher selectivity. Many such transport studies on metal ions across the liquid membrane have been well documented (4–7). During the carrier facilitated transport of metal ions, the transportable ions get absorbed into the organic membrane phase due to the complexation of the latter with the carrier molecules at the interface between the feed solution and the membrane. At the interface between the membrane and the receiving solution, the metal ions are released into the receiving solution due to their decomplexation by a suitable stripping agent. The carrier activity and transport continues until the concentration of the transporting ions becomes so low that ions do not form complexes with the carrier molecules. The stripping agent added to the receiving solution not only releases the metal ions from the carrier complex but also prevents its back transport into the feed solution. The net result is the uphill transport of the metal ion from the feed side to the receiving side of the membrane.

Di(2-ethylhexyl) phosphoric acid (DEHPA) is a good extracting agent and an effective carrier for many metal ions (8,9). The aim of this work was to adopt the extraction of Th(IV) by DEHPA into organic solvent to a membrane process.

Recently the separation and purification of thorium has become very important due to its application in nuclear industries. Therefore, the studies on the selective and uphill transport of Th(IV) would be useful for the separation and preconcentration of the metal ion. In this paper, we outline the optimum conditions for effective transport of Th(IV) from a mixture containing various cations.

EXPERIMENTAL

Reagents

Reagents used in the study were obtained and used as follows:

1. DEHPA (G.R grade) was obtained from Merck-Schuchardt (Germany) and was used without further purification.
2. Chloroform was supplied by S.D. Fine Chemicals (Mumbai, India). A 0.01 mol/L stock solution of DEHPA in chloroform was diluted further when required for transport studies.
3. A 0.01 mol/L solution of EDTA (British Drug House) disodium salt was prepared in deionized water and standardized by titration against a standard calcium salt solution using Eriochrome Black T as indicator.

All other reagents were of analytical grade.

Feed Solution

Nitrate or chloride salts of the metal ions were used to prepare the feed solutions. In some cases metal oxides were dissolved in dilute nitric acid and pH was adjusted to 2.

Receiving Solution

Hydrochloric acid diluted with deionized water was used as a stripping agent in the receiving compartment of the permeation cell.

Permeation Cell

The experimental setup used in the permeation studies has been described elsewhere (6), and the permeation cell is shown in Fig. 1. All the transport experiments were carried out at ambient temperature. In a typical experiment, the volumes of the feed and the receiving solution were maintained at 5 mL and 10 mL, respectively. The volume of the membrane phase was 25 mL. The pH of the feed solution was adjusted to 2 while that of the receiving solution was maintained at 1 with hydrochloric acid. All 3 (2 aqueous and 1 organic) were magnetically stirred with a Teflon-coated magnetic bar placed in the organic phase as shown in the figure. Thorium concentration in the aqueous phase was determined by complexo-

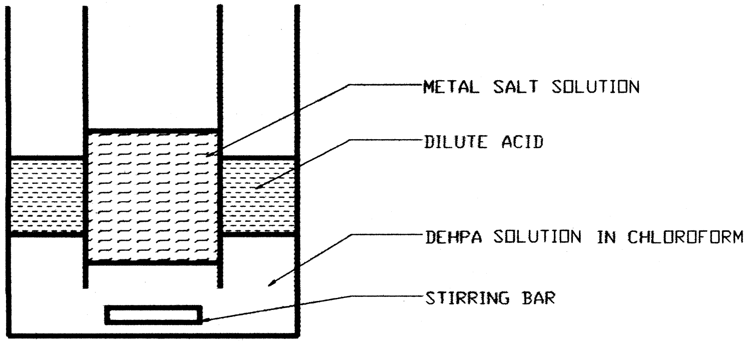

Figure 1. Permeation cell.

metric titration with EDTA (10). The concentration of alkali and alkaline earth metal ions were measured with a flame photometer (Elico India Pvt. Ltd). A nitrogen based laser fluorimeter, manufactured by the Centre for Advanced Technology, was used for the determination of the UO_2^{2+} concentration in the solution. A pH meter with a combination electrode (Toshniwal Brothers, India) was used for pH measurements.

RESULTS AND DISCUSSION

The mechanism of the transport of Th(IV) across the BLM has been schematically represented in Fig.2. The carrier DEHPA is a mono basic acid and is represented as HC in the figure. The metal ions are absorbed into the membrane

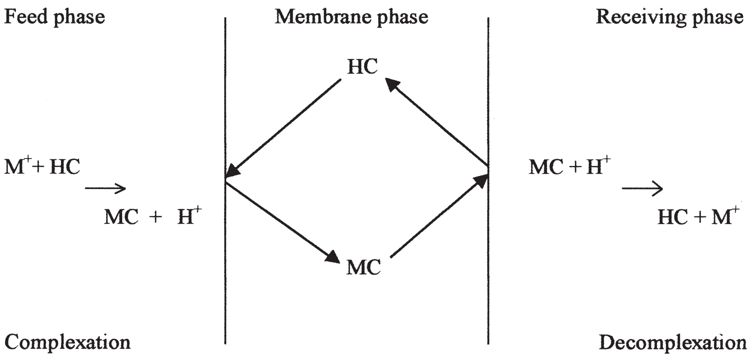

Figure 2. Complexation and decomplexation reactions at the membrane interfaces.

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due to the complex formation with DEHPA at the interface between feed and the membrane. The carrier complex diffuses to the other interface between the membrane and the receiving solution where Th^{4+} is released into the aqueous phase due to the stripping action of the H^+ ion .The free carrier diffuses back to the interface at the feed side to form another complex with available fresh Th^{4+} ions. The concentration polarization of the different species is avoided and their uniform concentration is maintained throughout by continuous and uniform stirring. The higher acidity of the receiving solution does not permit the recombination of the metal ions with the carrier and prevents the backward transport of thorium from the receiving to the feed solution. Thus the difference in the pH of the feed and the receiving solution resulted in the uphill transport of the metal ion.

Table 1 shows the effect of pH variation of the feed solution on the permeation of thorium. The variation experiments were restricted to a narrow pH range between 1 and 3.5. At very low pH (high acidity) the complexation of Th^{4+} does not take place and at higher pH (>3) thorium is precipitated as hydroxide. This explains the low permeation of thorium at pH above 3.5.

The effect of the variation in the acidity of the receiving solution on the permeation of Th^{4+} was also studied (Table 2). A reduction in the permeation at low acidity of the receiving phase was observed. This may be attributed to the partial stripping of the metal ion from the membrane. As thorium strips out quantitatively at higher acidity, its variation in the stripping solution above 0.1 N obviously does not show any significant increase in the permeation.

The concentration of DEHPA in the membrane phase also controls the permeation of thorium (Table 3). In the absence of the carrier in the membrane phase, no permeation of Th^{4+} could be observed in 5 h, whereas a near quantitative transport of the metal ions was observed under optimum experimental conditions. This suggests that the DEHPA has definite carrier activity toward the transport of Th^{4+}. It can be seen from Table 3 data that at higher concentrations of the carrier,

Table 1. Effect of Feed pH on Thorium Permeation

Feed pH	% Thorium Permeation	% Thorium in Feed	% Thorium in Membrane Phase
1.02	0.0	92.4	7.6
1.51	80.8	9.1	10.1
2.14	99.3	0.0	0.6
2.50	96.9	0.0	3.1
3.40	89.9	0.0	10.1

Permeation condition: source phase 1.0×10^{-3} mol/L $Th(NO_3)_4 \cdot 5H_2O$ (pH 2.14); carrier concentration 1.0×10^{-3} mol/L; stripping phase, 1.0×10^{-1} mol/L HCl; stirring duration 3 h.

Table 2. Effect of Strip Solution Acidity on Thorium Permeation

Strip Solution, mol/L HCl	% Thorium Permeation	% Thorium in Feed	% Thorium in Membrane Phase
1.0×10^{-3}	0.0	5.05	94.95
1.0×10^{-2}	5.05	5.05	89.9
5.0×10^{-2}	67.6	0.00	27.35
1.0×10^{-1}	99.4	0.00	0.6
5.0×10^{-1}	99.2	0.00	0.8

Permeation condition: source phase, 1.0×10^{-3} mol/L $Th(NO_3)_4 \cdot 5H_2O$ (pH 2.14); carrier concentration 1.0×10^{-3} mol/L; stirring duration 3 h.

the extraction of Th^{4+} into the membrane phase was very high but the high carrier concentration does not favor the release of metal ion. It was only partially released into the receiving phase. This accounts for the low permeation of thorium at high carrier concentration. At low carrier concentration, the permeation is again low due to the low absorption of the metal ion in the organic phase. The optimum carrier concentration was found to be 1.0×10^{-3} mol/L. Under these conditions, the transport of thorium was nearly quantitative. In all subsequent experiments, the carrier concentration and the pH of the feed and the stripping solutions were maintained at optimum levels.

The optimum conditions for maximum transport of Th^{4+} depends on the specific conditions used in the transport experiment. For example, the volume of the membrane phase and the type of membrane was expected to alter the transport time remarkably. The transport was expected to be quicker for a smaller volume of the BLM and similar results were expected for a supported liquid membrane and an emulsion liquid membrane.

Table 3. Effect of DEHPA Concentration on Thorium Permeation

Carrier Concentration, mol/L DHEPA	% Thorium Permeation	% Thorium in Feed	% Thorium in Membrane Phase
1.0×10^{-2}	3.0	0.0	97.0
5.0×10^{-3}	20.2	0.0	79.8
1.0×10^{-3}	>99.0	0.0	0.6
5.0×10^{-4}	98.9	0.0	1.1
1.0×10^{-4}	42.4	48.9	8.7
5.0×10^{-5}	22.2	73.2	4.6

Permeation condition: source phase, 1.0×10^{-3} mol/L $Th(NO_3)_4 \cdot 5H_2O$ (pH 2.14); stripping phase, 1.0×10^{-1} mol/L HCl (pH 1.48); stirring duration 3 h.

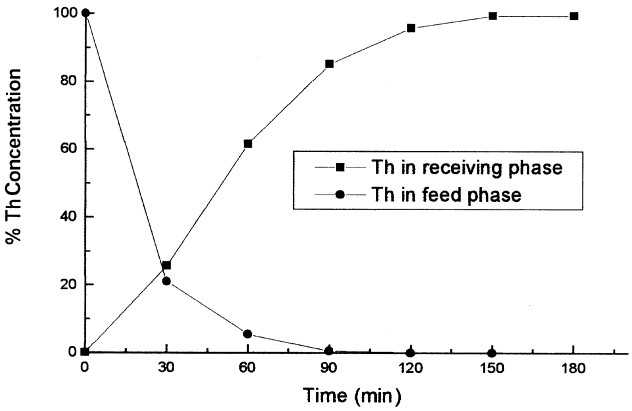

Figure 3. Time variation versus permeation of Th^{4+}. Permeation conditions: source phase, 1.0×10^{-3} mol/L $Th(NO_3)_4 \cdot 5H_2O$ (pH 2.14); receiving phase, 0.1 mol/L HCl (pH 1.48); membrane phase, 1.0×10^{-3} mol/L DEHPA in chloroform.

The variation of Th(IV) concentrations in the feed and the receiving solutions as a function of time is shown in Fig. 3. Th^{4+} was readily extracted into the organic membrane phase but the permeation was relatively slow. The metal ion rapidly was stripped into the receiving phase after a time lag and equilibrium was reached in approximately 2 h.

The selectivity of the permeation of thorium was determined through transport studies conducted with other metal ions in the feed solution. The results are shown in Table 4. DEHPA behaved as a selective carrier for thorium in the presence of many common ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Pb^{2+}, etc. The concentrations of these metal ions in the binary mixtures were 1×10^{-3} mol/L and the initial concentration of Th^{4+} was also 1×10^{-3} mol/L. Table 4 shows that a near quantitative and selective transport of Th^{4+} takes place from the binary mixture. The presence of Fe^{3+} and UO_2^{2+} in the feed solution seriously affected selectivity, but the permeation of thorium was not significantly changed. About 30% of Fe^{3+} permeated along with Th^{4+}, but the interference of Fe^{3+} could be eliminated by addition of SCN^- or citrate to the feed solution. The data for the transport of the Th^{4+} shown in Table 4 was obtained in the presence of excess of SCN^- in the feed solution. DEHPA is also a good carrier for UO_2^{2+}. So the interference of UO_2^{2+} could not be completely eliminated, but it could be considerably reduced by the addition of carbonate or SCN^- to the feed solution. Carbonate forms a strong complex with UO_2^{2+}. However, the complex is weak at pH 2, so the interference of UO_2^{2+} could not be eliminated completely. As the permeation of Th^{4+} was low at higher pH, the basicity of the feed solution could not be further increased. SCN^- is known to form a strong anionic complex $[UO_2(SCN)_4]^{2-}$ with

Table 4. Selectivity of Carrier for Cations in Binary Mixture

Mixture	% Permeated into Stripping Phase	% Left in Feed	% Remaining in Membrane
Th^{4+},	98.4	0.0	1.6
Na^{+}	2.3	74.7	23.0
pH 2.16			
Th^{4+},	97.5	0.0	2.5
K^{+}	2.4	81.1	16.5
pH 2.02			
Th^{4+},	98.5	0.0	1.5
Ca^{2+}	2.04	87.0	10.96
pH 2.17			
Th^{4+},	98.4	1.4	0.2
Mg^{2+}	<0.1	98.0	<2.0
pH 2.12			
Th^{4+},	98.9	0.0	1.1
Cu^{2+}	0.7	99.1	0.2
pH 2.07			
Th^{4+},	98.1	0.0	1.9
Pb^{2+}	2.3	75.4	22.3
pH 2.05			
Th^{4+},	98.2	0.0	1.8
La^{3+}	2.5	69.2	28.3
pH 2.00			
Th^{4+},	98.3	0.0	1.7
Fe^{3+}	<1.0	98.0	<2.0
pH 2.00			
Th^{4+},	98.5[a], 98.4[b]	0.0[a], 0.0[b]	1.5[a], 1.6[b]
UO_2^{2+}	28.0[a] , 9.7[b]	57.1[a], 85.5[b]	20.7[a], 4.8[b]
pH 2.12[a] , 2.05[b]			

Source phase: 1.0×10^{-3} mol/L of each cation in the binary mixture; receiving phase 1.0×10^{-1} mol/L HCl; membrane phase: 1.0×10^{-3} mol/L DEHPA in $CHCl_3$; stirring duration 3 h; a: in presence of carbonate; b: in presence of thiocyanate.

UO_2^{2+} at low pH (11). Hence the addition of KSCN to the feed solution effectively masked the UO_2^{2+} and lowered its permeation below 10% (Table 4).

CONCLUSION

DEHPA can be successfully used as a carrier for selective and efficient transport of Th^{4+}. The pH values of the feed and receiving solutions should be carefully adjusted, and the concentration of the carrier should be maintained at 1.0×10^{-3} mol/L for the best results. Most of the common cations do not affect the selectivity of thorium permeation. The interference from Fe^{3+} could be effectively eliminated by the addition of SCN^- to the feed solution, and UO_2^{2+} could be partially masked with thiocyanate and carbonate.

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