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SELECTIVE AND UPHILL TRANSPORT OF URANYL ION IN THE PRESENCE OF SOME BASE METALS AND THORIUM ACROSS BULK LIQUID MEMBRANE BY DI (2-ETHYLHEXYL) PHOSPHORIC ACID

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SELECTIVE AND UPHILL TRANSPORT OF URANYL ION IN THE PRESENCE OF SOME BASE METALS AND THORIUM ACROSS BULK LIQUID MEMBRANE BY DI (2-ETHYLHEXYL) PHOSPHORIC ACID

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ABSTRACT

Di (2-ethylhexyl) phosphoric acid has been successfully used as a selective carrier for the transport of uranyl ion across a bulk liquid membrane of chloroform. More than 98% uranium is selectively transported from a binary or a multi component mixture of cations in less than 3 hr. The pH of the feed solution was kept between 4.0 and 5.0 while 0.1 *M* hydrochloric acid served as a stripping agent in the receiving compartment. The co-transport of Zn^{2+} and Fe^{3+} was significantly small ($<4\%$) but that of thorium was very high.

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However, the interference from Th(IV) and transition metal ions could be eliminated by the addition of EDTA (E. Merck (India) Ltd., Mumbai) to the feed solution. Different experimental parameters affecting the transport process were optimized and the membrane separation method was applied to the recovery and pre-concentration of uranium from synthetic seawater sample. It was concluded that approximately 98% of uranium could be recovered and a hundred fold pre-concentration of the metal could be accomplished in less than 3 hr.

Key Words: D2EHPA; Uranium; Thorium; Uphill; Bulk membrane; Selective

INTRODUCTION

Carrier facilitated transport of metal ions through a liquid membrane has attracted the attention of many separation scientists due to the application of the technique in various fields such as recovery of metal ions from waste, hydrometallurgy, and the biological model systems. It is some times possible to choose an organic ligand as carrier, which selectively forms complex with a metal ion and leads to its selective transport from a mixture. In some cases, the experimental conditions could be adjusted for a selective complexation and transport of the metal ion. Crown ethers, for example, have been successfully used as a carrier for the selective transport of alkali metal ions[1] where the selectivity is based on the cavity size of the macrocyclic ionophores. Selective permeation of uranyl ion through Nafion membrane[2] and the transport of the cation by crown ethers as its anionic thiocyanato complex have been reported.[3] In a recent communication we have also reported the selective transport of Th(IV) by di (2-ethylhexyl) phosphoric acid(D2EHPA).[4] In that study, we observed that the selective transport of Th(IV) was greatly affected by the presence of uranyl ion in the feed solution. Suitable masking agents could eliminate the interference from most of the transition metal ions but it was not possible to mask uranium by such agents. It was therefore, of interest to study the carrier activity of D2EHPA toward the selective transport of uranium in the presence of thorium and other interfering ions.

Selective extraction of uranium has received a lot of attention primarily due to its possible recovery from a poor source like seawater where the concentration of the element is remarkably low. The need for the development of such a recovery and pre-concentration process is primarily due to the application of the metal in nuclear industry. The solution to this difficult problem is associated with the unusual structure of the coordination complexes of UO_2^{2+} ion, which favors a pseudo planner penta, or hexa coordinated structure.

In general, the phosphorus containing ligands show good extracting ability for lanthanides and actinides. A few extracting agents such as carbamoyl methyl phosphonic oxide (CMPO) and its derivatives,[5] calixarenes, etc.,[6,7] have been tried with considerable success, but these extractants are difficult to synthesize and the production cost is very high. However, these reagents could possibly be used as carriers in membrane systems so that the recovery and pre-concentration of the metal ion could be accomplished at a much lower cost. In the present paper, the authors have chosen to conduct some initial studies using D2EHPA as a selective carrier for the transport of uranium from a synthetic mixture of transition metal ions and thorium followed by the application of the process to the recovery and pre-concentration of the metal from seawater.

EXPERIMENTAL

Reagents

1. Di-(2-ethylhexyl) phosphoric acid (G.R grade) obtained from E. Merck, Germany was used without further purification.
2. Chloroform was obtained from S.D. Fine chemicals, Mumbai, India. Stock solution (0.01 *M*) of D2EHPA in chloroform was prepared and diluted further when required for transport studies.
3. EDTA (BDH, A.R. grade) 0.01 *M* solution of the disodium salt of the reagent was prepared in deionised water and used in feed solution for masking Th^{4+} and transition metal ions.
4. Xylenol orange (S.D. Fine—Chem Ltd., India, A.R. grade). A 0.001 *M* solution of the reagent was prepared in deionised water and used as a complexing agent for spectrophotometric analysis[10] of all the metal ions except uranium.
5. A nitrogen laser based fluorimeter fabricated at the Center for Advanced Technology was used for fluorimetric determination of uranium.
6. Tetra-sodium diphosphate-10-hydrate, $Na_4P_2O_7 \cdot 10H_2O$ (B.D.H. U.K., A.R. grade) 5% solution prepared in deionised water and pH adjusted to 7.0–7.2 was used as a fluorescence enhancing agent in the determination of uranium.
7. Feed solution: Nitrate or chloride salts of the metal ions were used to prepare the feed solutions with pH adjustment between 5.0 and 5.5 with sodium acetate.
8. Receiving solution: Hydrochloric acid diluted with deionised water was used as a stripping agent in the receiving compartment of the permeation cell. All other reagents used were of analytical grade.

9. Permeation cell: The experimental setup including the cell used in the permeation studies has been described elsewhere.[3,4] All the transport experiments were carried out at ambient temperature. In a typical experiment, the volumes of the feed, the receiving, and the membrane solutions were maintained at 5, 10, and 25 mL, respectively. The pH of the feed solution was kept between 5.0 and 5.5 while that of the receiving solution was maintained at 1.0 with hydrochloric acid. All the three phases (two aqueous and one organic) were magnetically stirred with a Teflon coated magnetic bar placed in the organic phase. Uranium in the solution was determined fluorimetrically. The concentrations of thorium and transition metal ions were measured with a spectrophotometer (Perkin Elmer) using xylenol orange reagent. A pH meter with a combination electrode (Toshniwal Brothers, India) was used for pH measurements.

The permeation of uranium from a sodium chloride (2.5%) solution containing K^+, Mg^{2+}, and Ca^{2+} (0.1% each) were also studied. For this, 300 mL of feed solution containing approximately 2.8 ppb of uranium was used as feed solution and the pre-concentrated uranium was collected in 3.0 mL of 0.1 *M* HCl serving as receiving solution.

RESULTS AND DISCUSSION

Organic phosphoric acids have been widely studied as extracting agents for various metal ions[8,9] and as carriers for the transport of lanthanides across a liquid membrane.[10] There has also been considerable interest in the studies on the speciation of the permeating metal complexes of D2EHPA across the liquid membrane. In the course of these studies, it has been established that the reagent D2EHPA exists as dimer in the organic phase.[11] It is thus reasonable to assume that the complex formation reaction between UO_2^{2+} and D2EHPA can be represented as:

$$UO_2^{2+} + 2(HC)_2 = UO_2C_2(HC)_2 + 2H^+$$

During the de-complexation (stripping) of the metal ion at the receiving compartment, protons from the stripping agent would combine with the free reagent anion and diffuse back to the feed—membrane interface. It recombines with free UO_2^{2+} and results in the continuous and uphill transport of the metal ion. This is represented schematically in Fig. 1. Thus the ion exchange mechanism as suggested in the case of Th(IV) transport[4] also holds good in the present system. In the feed side, high pH was favorable for complexation and absorption of UO_2^{2+} in the membrane phase whereas a low pH was necessary for the stripping and

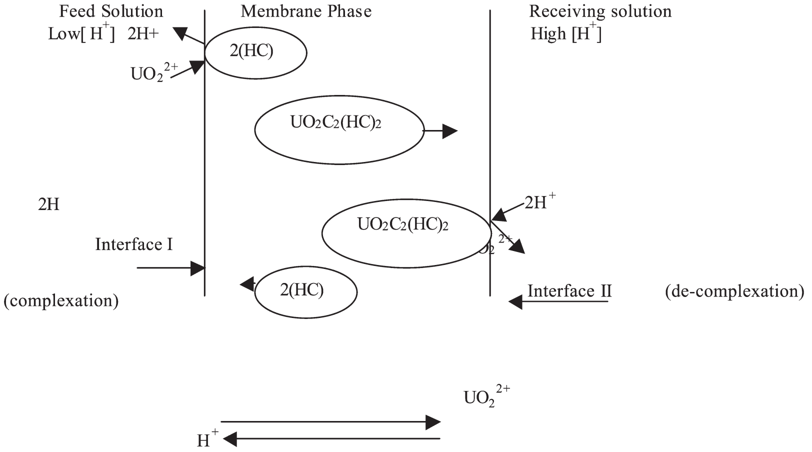

Figure 1. Schematic representation of the uphill transport of uranyl ion across bulk liquid membrane.

maintaining the continuous and uphill transport of the metal ion. The higher acidity of the receiving solution did not permit recombination of the metal ion with the carrier. The concentration polarization of the different species was minimized by continuous and uniform stirring of the membrane phase through out the experiment.

Table 1 shows the effect of pH variation of the feed solution on the transport of uranyl ion. The variation of pH of the feed solution was restricted to a narrow range in order to avoid probable hydrolysis and precipitation of uranyl ion in high pH region. The results of the pH variation studies on the receiving solution are shown in Table 2. It is seen that there is a reduction in the permeation

Table 1. Variation of pH in the Feed Solution

Feed pH	% Uranyl Ion in Receiving Phase	% Uranyl Ion in Feed Solution	% Uranyl Ion in Membrane Phase
1.00	44.9	48.2	6.9
1.52	79.0	20.3	0.7
2.15	98.8	0.4	0.8
2.60	98.9	0.3	0.8
3.92	≥ 99.0	Nil	≤ 1.0
5.05	>99.0	Nil	<1.0

Source phase, $1.0 \times 10^{-4} M$ UO_2^{2+}; carrier concentration, $5.0 \times 10^{-4} M$ D2EHPA; receiving solution, $1.0 \times 10^{-1} M$ HCl; duration, 2 hr.

Table 2. Variation in the Acidity of Receiving Solution

Strippant, HCl (*M*)	% Uranyl Ion in Receiving Phase	% Uranyl Ion in Feed Solution	% Uranyl Ion in Membrane Phase
5.0×10^{-3}	11.9	33.8	54.1
1.0×10^{-2}	28.6	31.4	40.0
5.0×10^{-2}	92.7	6.9	0.4
1.0×10^{-1}	98.8	0.4	0.8
5.0×10^{-1}	97.1	2.1	0.8

Source phase, $1.0 \times 10^{-4}\,M$ UO_2^{2+}; carrier concentration, $5.0 \times 10^{-4}\,M$ D2EHPA; duration, 2 hr; Feed pH, 2.15.

of uranium at lower acidity of the receiving phase. This may be attributed to the incomplete stripping of the metal ion from the membrane phase. At higher acidity ($>0.1\,N$) the variation of the transport with the increase in the acidity is insignificant presumably due to the near quantitative stripping of the metal ion. Thus the difference in the pH of the feed and the receiving solution resulted in the uphill transport of uranyl ion.

The variation in the concentration of the carrier in the membrane phase was also studied and the results are given in Table 3. In the absence of carrier in the membrane phase, no transport of uranium could be observed whereas a near quantitative permeation of the cation under optimum experimental conditions suggests definite carrier activity of D2EHPA.

It can be seen from the table that at higher concentration of the carrier, the extraction of UO_2^{2+} into the membrane phase was very high but the high carrier concentration does not favor the release of metal ion. It was only partially

Table 3. Variation of Carrier Concentration

Carrier Concentration D2EHPA (*M*)	% Uranyl Ion in Receiving Phase	% Uranyl Ion in Feed Solution	% Uranyl Ion in Membrane Phase
1.0×10^{-2}	9.0	0.12	90.9
5.0×10^{-3}	30.2	1.62	68.2
1.0×10^{-3}	96.8	0.9	2.26
5.0×10^{-4}	98.8	0.4	0.82
1.0×10^{-4}	20.7	75.8	3.43
5.0×10^{-5}	5.8	93.7	0.5

Source phase, $1.0 \times 10^{-4}\,M$ UO_2^{2+} (pH 2.1); receiving phase, $1.0 \times 10^{-1}\,M$ HCl; duration, 2 hr.

released into the receiving phase. This accounts for the low permeation of uranyl ion at high carrier concentration. At very 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 $5.0 \times 10^{-4}\,M$. Under these conditions, the transport of uranyl ion was nearly quantitative. Hence, in all further experiments, the carrier concentration and the pHs of the feed and the stripping solutions were maintained accordingly. The optimum conditions for maximum transport of UO_2^{2+} depends on the specific conditions used in the transport experiment. For example, the volume of the membrane phase and the type of membrane is expected to alter the transport time remarkably. The transport is expected to be quicker for a smaller volume of the BLM and similar result is expected for supported liquid membrane (SLM) and emulsion liquid membrane (ELM). The variation of the concentration of UO_2^{2+} in the feed (5.0 mL) and the receiving solution (10 mL) as function of time is shown in Fig. 2. It is seen from the figure that UO_2^{2+} is readily extracted into the organic membrane phase but the permeation sets in slowly. The metal ion is rapidly stripped out into the receiving phase after a time lag and the equilibrium reached in about 2 hr.

The selectivity of the permeation of uranyl ion was determined by carrying out the transport studies in the presence of other metal ions and EDTA as masking agent in the feed solution. The results are shown in Table 4. It is seen that D2EHPA behaves as a selective carrier for uranyl ion in the presence of thorium and transition metal ions like Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The

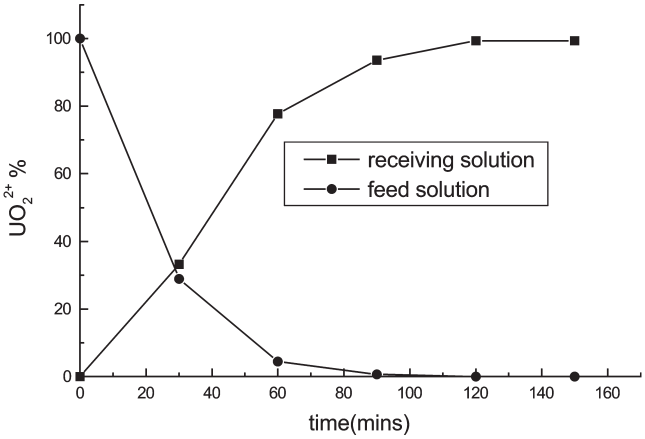

Figure 2. Variation of uranium concentration in feed and receiving phase as a function of time. Conditions: Source phase, $1.0 \times 10^{-4}\,M$ UO_2^{2+} (pH 5.0); receiving phase, 0.1 M hydrochloric acid; Membrane phase, $5.0 \times 10^{-4}\,M$ D2EHPA in chloroform.

Table 4. Studies on the Selectivity of Uranium Permeation

M^{n+} [EDTA] 1.0×10^{-3} [EDTA]* 6.0×10^{-3}	pH of Feed Solution Mixture	% Permeation of UO_2^{2+} in Receiving Phase
Th^{4+}	3.58	99.2, nil
Cu^{2+}	5.38	98.9, nil
Co^{2+}	5.12	99.1, nil
Mn^{2+}	5.40	99.2, nil
Ni^{2+}	5.46	99.0, nil
Zn^{2+}	5.47	99.1, <2.0
Fe^{3+}	5.25	99.0, <4.0
Mixture*, above ions	5.36	89.7

Source phase, mixture of $1.0 \times 10^{-4} M$ UO_2^{2+} and $1.0 \times 10^{-4} M$ (each) M^{n+}; concentration of D2EHPA, $5.0 \times 10^{-4} M$ D2EHPA; receiving solution, $1.0 \times 10^{-1} M$ HCl; duration, 2 hr.

concentrations of these metal ions in the binary mixtures were $1.0 \times 10^{-4} M$ and the initial concentration of UO_2^{2+} was $1.0 \times 10^{-4} M$. For the masking of thorium and transition metal ions mentioned above, $1.0 \times 10^{-3} M$ solution of di-sodium salt of EDTA was used in every binary mixture maintained at pH 5.0 (approx). Table 4 shows that a near quantitative and selective transport of UO_2^{2+} takes place from the binary mixture as well as mixture containing all the metal ions. The presence of Fe^{3+} and Zn^{2+} in the feed solution does not affect the selectivity and there was no significant change in the individual permeation of uranyl ion. As only $<4.0\%$ of Fe^{3+} permeated along with UO_2^{2+}, the interference of Fe^{3+} was ignored and no other masking agent except EDTA was used to eliminate the interference completely. The permeation of zinc along with uranyl ion was only $>2.0\%$. So its interference may also be neglected. In a separate experiment, thorium and all the six transition metal ions were taken together with uranyl ion in the feed solution. The concentration of the uranyl ion was $1.0 \times 10^{-4} M$ and those of thorium and transition metal ions were $1.0 \times 10^{-4} M$ each with pH maintained at 3.5–5.5. It is clear from Table 4 that thorium and transition metal ions do not interfere in the permeation of uranyl ion and selectivity of uranium transport is maintained even in the presence of a mixture of cations in the feed solution.

The selective permeation of UO_2^{2+} in the presence of other transition metal ions and EDTA is understandable from a consideration of the stability constants of their EDTA complexes. The $\log K$ for UO_2^{2+} is 7.4, whereas the corresponding values for Th^{4+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, and Fe^{2+} are 23.2, 18.8, 16.3, 14.0, 18.6, 16.5, and 14.3, respectively.[12,13] The concentration of free UO_2^{2+} will

Table 5. Recovery and Pre-concentration of Uranium from Synthetic Seawater

Experiment	Composition of Feed Solution	% Recovery of UO_2^{2+} in Receiving Solution
I	UO_2^{2+}—10^{-4} *M*	UO_2^{2+}—98.8%
	NaCl 2.5%	$Na^+ < 0.01\%$
	K^+, Mg^{2+}	$K^+ < 0.01\%$
	Ca^{2+} 0.1% each	Mg^{2+}, Ca^{2+}, <2%
II	UO_2^{2+}—2.38 ppb	UO_2^{2+}—97.9%
	Na^+, K^+, Mg^{2+}, and Ca^{2+} same as I	Na^+, K^+, Mg^{2+}, and Ca^{2+} same as I

Concentration of D2EHPA in membrane, 5.0×10^{-4} *M*; HCl concentration in receiving solution, 0.1 *M*; time of permeation, 3 hr.

be reasonably high due to the low *K* value while those of the other metal ions are expected to be too low to compete for the permeation. Moreover, the EDTA complexes of all the interfering ions are anionic and highly hydrophilic. This prevents the transport of these ions across the organic membrane as their EDTA complexes.

An attempt was made to apply the above transport studies to the recovery and pre-concentration of uranium from seawater. Uranium spiked with the synthetic seawater was subjected to the membrane separation process and the result obtained in two different experiments are given in Table 5. In the first experiment, the concentration of uranium was kept at 10^{-4} *M* in a sample matrix of Na^+, K^+, Ca^{2+}, and Mg^{2+}. The recovery was as high as 98.8%. Seawater normally contains 0.3–3.0 ppb of uranium.[14] Hence in the second experiment, a large volume (300 mL) of the synthetic seawater containing 2.38 ppb of uranium was used as feed solution and the transported metal ion was collected in 3.0 mL of 0.1 *M* HCl serving as receiving phase. The results indicate 97.9% recovery and a hundred-fold pre-concentration of uranium. This is highly satisfactory and it appears that the carrier-facilitated transport may be practically useful for the recovery of uranium from seawater.

CONCLUSION

It is clear from the above studies that di (2-ethyl hexyl)phosphoric acid can be successfully used as a carrier for selective and efficient transport of UO_2^{2+}. The pH of the feed and the receiving solutions should be carefully adjusted and the concentration of the carrier should be maintained nearly at 5.0×10^{-4} *M* for the best results. The EDTA is a suitable and effective masking agent for thorium and transition metal ions. Our work indicates that application of the membrane separation process to the recovery and pre-concentration of uranium from seawater appears to be promising.

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