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Studies on the Recovery of Uranium from Phosphoric Acid Medium by D2EHPA/ n-Dodecane Supported Liquid Membrane

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Abstract: Present studies deal with the application of supported liquid membrane (SLM) technique for the separation of uranium (VI) from phosphoric acid medium using Di-2 ethyl hexyl phosphoric acid (D2EHPA)/n-dodecane as a carrier and ammonium carbonate as a receiving phase. The studies involve the investigation of process controlling parameters like feed acidity of phosphoric acid, carrier concentration, stripping agents, and the effect of thickness and the pore size of the membrane. The transport of uranium decreases with increase in the concentration of phosphoric acid in feed solution whereas it increases with increase in carrier concentration in supported liquid membrane. More than 90% uranium (VI) is recovered in 360 minutes using 0.5 M D2EHPA/dodecane as carrier and 0.5 M ammonium carbonate as stripping phase from the 0.001 M H_3PO_4 feed. Lower concentration of phosphoric acid and higher carrier concentration is found to be the most suitable condition for maximum transport of uranium (VI) from its lean sources like commercial phosphoric acid and analytical wastes generated from the analysis of uranium by Volumetric (Davis-Gray) method.

Keywords: Di-2 ethyl hexyl phosphoric acid, flux, phosphoric acid, supported liquid membrane, uranium

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INTRODUCTION

In the context of the growing world population with increasing energy demands, nuclear power looks to be an attractive option particularly in the developing countries (1). At present the nuclear power production is broadly based on uranium fuel cycle. With limited resource position and the increased rate of its consumption uranium has become an important nuclear material. Efforts are being made to investigate newer resources of uranium. Emphasis is put on the secondary resources of uranium which can be proved to be a dependable source of uranium (2). Most natural phosphates contains several tens and hundreds parts per million of uranium. A high percentage of uranium in commercial phosphate rocks is present as an intrinsic component of the apatite mineral lattice (3,4). When the phosphate rocks are processed to produce phosphoric acid by a wet process method, most of the uranium is taken into the solution. Uranium present in phosphoric acid becomes a potential source of uranium. Since phosphoric acid is useful both for the fertilizer industries and for food applications, it is desired to remove uranium from wet process phosphoric acid as well as from commercial merchant grade phosphoric acid (5–7). It is also of greater interest to recover uranium from these secondary resources since it can serve as an additional source of uranium for nuclear applications. In the radiochemical laboratories, a significant quantity of analytical waste in phosphoric acid medium is generated while analyzing uranium (VI) by Devies-Gray method (8). It is desired to recover the uranium from this waste for its safe disposal. The separation of an element from a system containing the element of interest may be carried out using different separation techniques like solvent extraction, extraction chromatography, ion exchange, precipitation etc. (9,10). As all these processes have their own limitations and drawbacks such as solvent degradation, third phase formation, resin degradation, crud formation etc. and so they are not suitable for the separation and recovery of the desired metal ions from secondary resources like wet process phosphoric acid, merchant grade phosphoric acid where uranium concentration is low. To overcome these drawbacks, liquid membrane seems to be a good alternative. Supported liquid membrane (SLM) technique has potential application for industrial scale separation and enrichment of metal salt species (11–13). Its use in environmental applications, separation and recovery of important metals including nuclear material from its low level sources as well as from its nuclear wastes and in cleaning up of effluent streams has also received attention (14–18). Consequently substantial research is being carried out worldwide on optimizing the parameters for membrane processes for the removal of toxic or valuable metal ions from its lean sources (19,20).

A membrane is a semipermeable barrier separating two phases of different composition and is often used for separation and purification of aqueous waste streams with the objective to recover and concentrate valuable metals. Selective transport through a membrane is based on differences in permeability of the species to be separated. Permeability is determined by the driving forces for entering and leaving the membrane phase, the thickness of the membrane, the mobility of the species and the reaction or interaction with other species inside the membrane. The specific receptor molecules called carrier are generally used in liquid membrane which selectively forms complexes with particular metal ions and carry them through the membrane from one side to the other side where the metal ions are released. By complexation they increase the solubility of the specific metal ions in the membrane phase which in turn induces the selective transport of specific metal ions. The success of the process depends on the permeation rate of the metal ion and this is decided by the nature of extractant used in the membrane and by the kinetics and equilibrium constants of the exchange process (21). It is therefore necessary to understand the chemistry of the membrane process in order to use this technique effectively for the desired separation process. The advantages of SLMs based separation process are low energy requirements, low capital and operating cost, and the possibility of achieving a high separation factor. The simpler modular design with no moving parts make it simple to operate. High feed to strip volume ratios can be achieved, which leads to large concentration factors of the transported species. No phase separation problem is encountered because the organic and aqueous phases are never mixed. Negligible organic phase entrainment occurs in the feed and strip aqueous solutions. Guided by these factors, the efforts were made to optimize the various process parameters for the separation of uranium from phosphoric acid medium using D2EHPA as carrier by SLM.

EXPERIMENTAL

Reagents

The uranium standard was prepared by dissolving weighed amounts of $UO_2\ (NO_3)_2 \cdot 6H_2O$ (supplied by B.D.H. Mumbai) in phosphoric acid of the desired molarity. A suitable concentration of AR grade $(NH_4)_2CO_3$ (supplied by S.D. Fine Chemical Ltd, Mumbai) was used as stripping agent in the receiver compartment. Di-2-ethyl hexyl phosphoric acid (D2EHPA) and dodecane (supplied by Fluka AG. Buchs Ltd, Switzerland and Aldrich) were used as supported liquid membrane.

PTFE membranes used were procured from Millipore (India) Pvt. Ltd, Mumbai. All other reagents were used of AR grade. ^{233}U radio tracer was used as the spike throughout this study. ^{233}U was estimated at a different interval of time in both the feed and the receiver compartment using α Scintillation counter having ZnS, Silver activated detector.

Density and Viscosity Measurements

Densities and viscosities of the D2EHPA/solvents solutions were measured for comparison of uranium transport properties with the physical properties of the carrier-diluent organic phase. Viscosities were measured at 25°C using an Ubbelhode viscometer and densities were determined by weighing a known volume of solution using a pyknometer.

Membrane Cell

Details of glass SLM transport cells are described elsewhere (22). Single-stage SLM measurements were carried out with two compartment permeation cell in which a source aqueous solution (10 mL) was separated from the aqueous receiving solution (10 mL) by a supported liquid membrane with an effective membrane area of 5.15×10^{-4} m^2. The source and receiving solutions were mechanically stirred at room temperature using a magnetic stirrer to avoid concentration polarization conditions at the membrane interfaces and in the bulk solutions. Membrane permeabilities were determined by monitoring the uranium concentration radiometrically, primarily in the receiving phase, as a function of time.

Membrane Supports

During the entire course of this study, flat- sheet type PTFE (Poly-tetra-fluoro-ethylene) hydrophobic microporous polymeric membrane support was used. The porosity of the membrane was about 84%. The single membrane used had an average thickness of 160 µm and pore diameter of 0.22 µm and 0.45 µm. Filling the pores of these dry support polymers with the carrier solution was accomplished by immersing the membrane in the organic phase for at least 8–10 h before use. The pores were immediately and apparently quantitatively filled with the carrier solution by capillary action. This type of SLM with polymeric support eliminates the transport of water through the membrane and was free from osmotic effects. The Uranium (VI)-D2EHPA complex can diffuse across the membrane supported through the microporous structure. The concentration of uranium solution used in the present study was deliberately kept very dilute. The organic membrane phase was prepared by diluting a weighed amount of D2EHPA in dodecane to provide carrier solutions of varying concentrations which were subsequently equilibrated with acid solutions of the desired molarity before use. Various membrane experiments give the permeation results reproducible to approximately ±10%. All the batch experiments were carried out at room temperature i.e. $25 \pm 1°C$.

Flux and Permeability Coefficient

The flux is defined as the rate of mass transport of the solute through the SLM, and it is the criterion used to evaluate the performance of SLM. According to Fick's first law of diffusion, the rate of diffusion (dc/dt) of a solute across an area (A), known as flux (J) is calculated as (considering the initial concentration in receiving phase is zero)

$$J = (C_U, \text{receiving} \times V)/(A \times t) \tag{1}$$

where

C_U, receiving = U concentration in the receiving phase, moles/dm^3, V = volume of receiving phase, dm^3, A = effective area of the membrane, m^2, t = time elapsed, seconds.

Permeability coefficient is calculated using the equation

$$-\ln(C_t/C_0) = (A \times P/V) \times t \tag{2}$$

where

P = Permeability coefficient, m/s, C_0 = the concentration of uranium in feed phase at time zero, moles/L, C_t = the concentration of uranium in receiving phase at the time t, moles/L, A = effective area of the membrane, m^2 and V = volume of receiving phase, dm^3.

Liquid-Liquid Distribution Measurements

15 mL of U standard feed was prepared in 0.5 M phosphoric acid and 1 mL of ^{233}U radio tracer was spiked in it. 16 mL of 0.1 M D2EHPA/n-dodecane was added to the separating funnel containing feed solution and equilibrated for 30 minutes. After clear phase separation the organic and aqueous phases were collected in different beakers.

2 mL of the extracted organic phase was equilibrated with 2 mL of various stripping agents for 30 minutes and centrifuged for 5 minutes. Material balance of both the layers was checked by monitoring the alpha counts of ^{233}U by α-scintillation counter.

MECHANISM

D2EHPA is classified as an acidic metal extractant which normally exists as dimer and extraction of metal species from their aqueous solutions is effected by a cation exchange mechanism. The anion is extremely hydrophobic and can chelate a metal cation from the aqueous phase to form a soluble organic neutral metal complex.

$$M^{n+}_{(Aq)} + n(HR)_{2\,(Org)} \longleftrightarrow M(HR_2)_{n\,(Org)} + nH^{+}_{(Aq)} \tag{3}$$

The above reaction clearly indicates that the degree of extraction is strongly pH dependent. D2EHPA is considered to be a universal metal extractant because of its extractability of a majority of metal ions. At lower D2EHPA concentration, the influence of D2EHPA on solvent properties is less in view of its lower concentration and hence D2EHPA acts only as an extractant. At higher D2EHPA concentration, however, the effect on the extractant probably increases as indicated by enhanced acid and water extraction. This interferes with uranium extraction probably by a change in the nature of the extracted species and a competition for uranium between D2EHPA and water/acid. The membrane transport is closely related to the solvent extraction process for the recovery of the corresponding metal ion. The extractant D2EHPA employed in the present case is a liquid cation exchanger and extracts metal ions by a cation exchange mechanism. The extractant D2EHPA generally exists as a dimmer.

The formation of a chelate ring confers additional stabilization for the structure. In view of its hydrophobic nature, the reagent acts as a good extractant for metal ions. Moreover, uranium has a tendency to form strong complexes with phosphorous containing ligands. Hence D2EHPA was chosen as the supported reagent in the membrane. Therefore, on the basis of liquid-liquid extraction behavior of D2EHPA for uranium, the mechanism for the membrane transport is depicted in the Fig. 1.

In the feed Uranium-phosphate complex will dissociate as follows

$$UO_2(H_2PO_4)_2 \longleftrightarrow UO_2^{++} + 2H_2PO_4^{-} \tag{4}$$

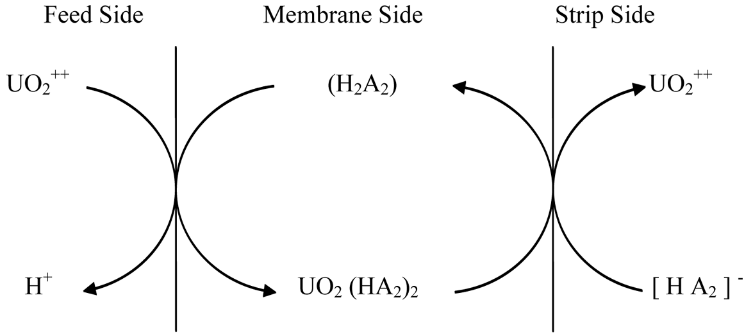

Figure 1. Scheme representing transport mechanism of metal ion from feed to receiver phase.

$$UO_2(HPO_4) \longleftrightarrow UO_2^{++} + HPO_4^{--} \tag{5}$$

And in the membrane phase H_2A_2 will dissociate as given below

$$H_2A_2 \longleftrightarrow [HA_2]^- + H^+ \tag{6}$$

At Feed-Membrane Interface the UO_2^{2+} will make complex with $(HA_2)^-$ and form $UO_2(HA_2)_2$ as per the equation given below

$$UO_2(H_2PO_4)_2 + 2H_2A_2 \rightleftarrows UO_2(HA_2)_2 + 2H_3PO_4 \tag{7}$$

$$UO_2(HPO_4) + 2H_2A_2 \rightleftarrows UO_2(HA_2)_2 + H_3PO_4 \tag{8}$$

In the membrane phase as the concentration of $UO_2(HA_2)_2$ goes on building at the membrane side of the feed membrane interface, it will diffuse towards the membrane-strip interface because of the concentration gradient.

At the membrane-strip interface, the complex $UO_2(HA_2)_2$ will come in contact with CO_3^{-2} ions present in strip solution and stripped as the uranyl carbonate at strip side and $[HA_2]^-$ will move back to the membrane side.

RESULTS AND DISCUSSION

Effect of Phosphoric Acid Concentration in Feed on Uranium Transport

Single ion transport of uranium (VI) across D2EHPA/n-dodecane SLM from an aqueous feed adjusted to 0.001–3.5M phosphoric acid is tested.

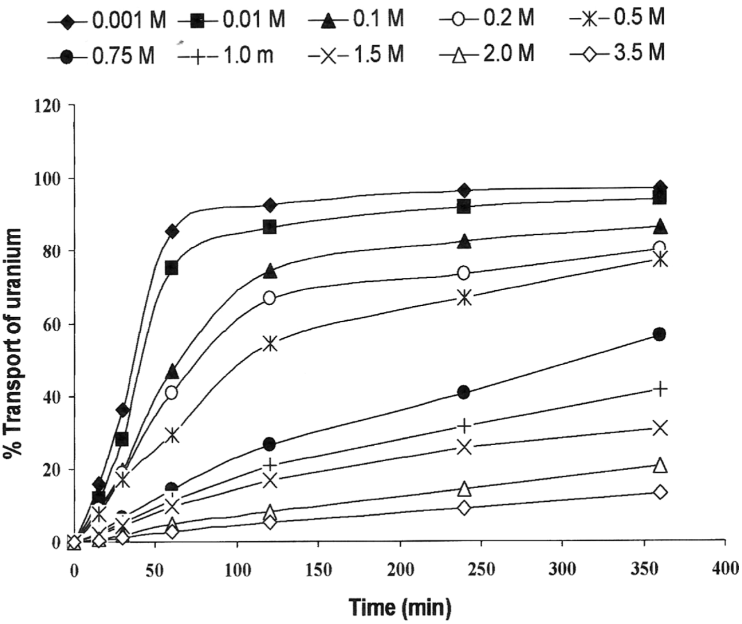

Figure 2. Percentage of transport of uranium as a function of feed acidity of H_3PO_4 [U]. In feed: 1.29×10^{-3} moles/L, Strippant: 0.5 M $(NH_4)_2CO_3$, [Carrier]: 0.1 M D2EHPA/dodecane.

In the present study the carrier concentration of D2EHPA/n-dodecane is kept 0.1 M in the membrane phase and the acid concentration of phosphoric acid in the feed is varied from 0.001–3.5M, keeping 0.5 M ammonium carbonate as a strippant. The uranium (VI) transport increases with the decrease in phosphoric acid concentration in the feed. The maximum extent of uranium transport of around 96% (Fig. 2) could be achieved by using 0.001 M phosphoric acid in feed after about 360 min across D2EHPA/n.dodecane supported liquid membrane. Only 13% of the uranium (VI) could be transported while keeping the acidity of the feed to 3.5 M of phosphoric acid. The permeability coefficients and average flux are found to be 5.63×10^{-5} m/s, 1.12×10^{-6} moles/m^{2}s and 0.14×10^{-5} m/s, 0.15×10^{-6} moles/m^{2}s for 0.001 M and 3.5 M phosphoric acid respectively as indicated in Table 1.

Figure 3 shows the trend of flux of uranyl ions at various concentrations of H_3PO_4 in the feed solution. Initially the flux increases and reaches maxima and then decreases. This is because the metal ion flux is associated with its concentration present in the feed phase. Initially the membrane phase starts saturating with the carrier-metal complex

Table 1. Permeation of uranium as a function of source phase phosphoric acid molarity

(H_3PO_4) (M)	[Uranium] in source phase (moles/L)	[Uranium] in receiving phase (moles/L)	Uranium permeation (%)	Flux (moles/m^2s)	Permeability coefficient (m/s)
0.001	1.29×10^{-3}	1.25×10^{-3}	96.37	1.12×10^{-6}	5.63×10^{-5}
0.01	1.29×10^{-3}	1.21×10^{-3}	93.33	1.09×10^{-6}	4.32×10^{-5}
0.1	1.29×10^{-3}	1.11×10^{-3}	85.55	0.99×10^{-6}	2.94×10^{-5}
0.2	1.29×10^{-3}	1.05×10^{-3}	81.57	0.95×10^{-6}	1.73×10^{-5}
0.5	1.29×10^{-3}	9.94×10^{-4}	76.82	0.89×10^{-6}	1.73×10^{5}
0.75	1.29×10^{-3}	7.24×10^{-4}	55.92	0.66×10^{-6}	0.70×10^{-5}
1.0	1.29×10^{-3}	5.33×10^{-4}	41.13	0.48×10^{-6}	0.54×10^{-5}
1.5	1.29×10^{-3}	3.97×10^{-4}	30.68	0.36×10^{-6}	0.43×10^{-5}
2.0	1.29×10^{-3}	2.64×10^{-4}	20.38	0.24×10^{-6}	0.19×10^{-5}
3.5	1.29×10^{-3}	1.69×10^{-4}	13.08	0.15×10^{-6}	0.14×10^{-5}

Initial feed concentration: 1.29×10^{-3} moles/L uranium in varied amount of phosphoric acid.

Carrier concentration: 0.1 M D2EHPA/dodecane.

Strippant: 0.5 M Ammonium carbonate.

Time: 360 minutes.

and a very small amount of the metal ion transport to the receiving side hence we get low values of flux. Once the membrane phase is saturated, because of the concentration gradient the maximum metal ion transported to the receiving phase therefore the flux reaches maxima. Then the flux decreases as the concentration of metal ion decreases at the feed side or the concentration gradient decreases.

This is partly in agreement with the expected trend since the flux of a cation varies with $H_2PO_4^-$ ion concentration according to the relationship given below (23)

$$J_M = AT/\eta[H_2PO_4^-]^n_{aq}\ [\mathrm{Carrier}]^n_{org} C_{M,feed} \tag{9}$$

Where A, is the area of membrane (m^2), T is absolute temperature (K), η is viscosity (cp), and CM is the concentration of metal in feed (mol/L).

There should be an increase in flux with increase in phosphoric acid concentration. But the reverse trend has been observed. It is because at the high concentration of phosphoric acid, the dissociation of phosphoric acid decreases.

$$H_3PO_4 \longleftrightarrow H_2PO_4^- + H^+ \tag{10}$$

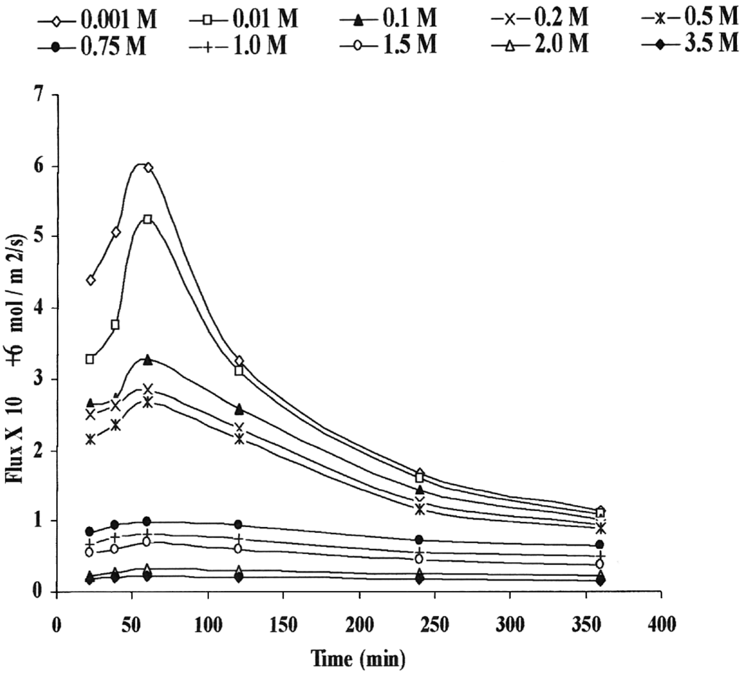

Figure 3. Flux vs time for varying concentration of H_3PO_4 in feed side. [U] In feed: 1.29×10^{-3} moles/L, [Carrier]: 0.1 M D2EHPA/n-Dodecane, Strippant: 0.5 M $(NH_4)_2CO_3$.

$$H_2PO_4^- \longleftrightarrow HPO_4^- + H^+ \tag{11}$$

Hence, the undissociated phosphoric acid is present more and the availability of $H_2PO_4^-$ ions in feed will be less which is mainly responsible for the flux as per eq. (9). Figure 4 shows the trend of average flux of uranyl ions at various concentration of H_3PO_4 in the feed solution.

Effect of Carrier Concentration on Permeation

To model the organic membrane phase at the feed interface, various concentrations of D2EHPA/dodecane solutions, already equilibrated with the feed solution, were studied. From the results, it is quite clear that there is a significant increase in viscosity with increase in carrier concentration, especially when the same is complexed with uranium. As per Table 2, it is evident that as the D2EHPA concentration is increased from

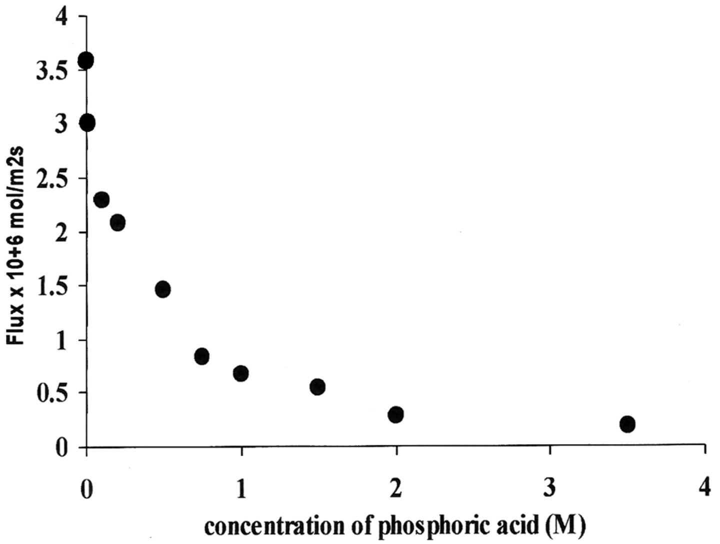

Figure 4. Average Flux vs. acidity of varying concentration of phosphoric acid after 360 minutes. [U] In feed: 1.29×10^{-3} moles/L, [Strippant]: 0.5 M $(NH_4)_2CO_3$, [Carrier]: 0.1 M D2EHPA/n-dodecane.

0.01 M to1.0M the viscosity increased from 1.497 to 3.174 cp which is nearly more than twice the initial viscosity whereas the change in density is nominal from 0.75 to 0.81 × gm/ml.

Table 2. Variation in viscosity and density of D2EHPA with change in concentration of D2EHPA in n-Dodecane at 25°C

Conentration of D2EHPA in n-Dodecane [M]	Viscosity Centipoises (cp)	Density Gm/mL
0.01	1.497	0.749
0.02	1.508	0.75
0.03	1.50	0.749
0.05	1.527	0.751
0.10	1.578	0.754
0.20	1.681	0.761
0.30	1.802	0.767
0.50	2.104	0.781
0.75	2.562	0.797
1.0	3.174	0.812

The liquid membrane pertraction of metal cations involves a heterogeneous chemical reaction between an organic carrier and the aqueous metal ion and so the metal flux (J_M) will be governed by the diffusion rates of the reactants in the presence of fast kinetics of interfacial reaction. The diffusion coefficient of a solute D, across the membrane is defined by the following Stokes-Einstein equation (22).

$$D = kT/6\pi\eta r \tag{12}$$

Where k is the Boltzmann constant, T is the absolute temperature (K), r the molecular radius (Angstrom) of the uranium complex, and η(cp) is the viscosity of the organic phase equilibrated with the aqueous phase. Since the flux is inversely proportional to the viscosity, an increase in the viscosity should reduce the uranium flux, as is the case in the present study. Evidently, the organic phase viscosity proves to be a controlling parameter in the optimum carrier concentration for a liquid membrane system.

Table 3 summarizes data on the effect of D2EHPA concentration on flux, percentage permeation and permeability coefficient. Generally an increase in carrier concentration will produce an increase in cation flux; however, the concurrent increase in viscosity results in a steady decrease in the diffusivity of the carrier as well as of the metal-carrier complex. Figure 5 represents the trend of flux at varying concentration of the carrier. It is also obvious that the transport of uranium should be

Table 3. Permeation of uranium as a function of carrier concentration (D2EHPA)

(H_3PO_4) (M)	[Uranium] in source phase (moles/L)	[Uranium] in receiving phase (moles/L)	Uranium permeation (%)	Flux (moles/m^{2}s)	Permeability coefficient (m/s)
0.01	1.29×10^{-3}	2.57×10^{-4}	19.56	0.23×10^{-6}	2.16×10^{-6}
0.02	1.29×10^{-3}	3.65×10^{-4}	28.26	0.33×10^{-6}	3.24×10^{-6}
0.05	1.29×10^{-3}	8.82×10^{-4}	68.18	0.79×10^{-6}	9.44×10^{-6}
0.1	1.29×10^{-3}	9.93×10^{-4}	76.82	0.89×10^{-6}	1.75×10^{-5}
0.2	1.29×10^{-3}	1.08×10^{-3}	83.54	$0.97 \times 10^{-}$	2.18×10^{-5}
0.3	1.29×10^{-3}	1.16×10^{-3}	89.75	1.04×10^{-6}	2.64×10^{-5}
0.5	1.29×10^{-3}	1.23×10^{-3}	95.17	1.11×10^{-6}	3.72×10^{-5}
0.75	1.29×10^{-3}	1.18×10^{-3}	91.43	1.06×10^{-6}	3.24×10^{-5}
1.0	1.29×10^{-3}	1.03×10^{-3}	79.83	0.93×10^{-6}	2.40×10^{-5}

Feed acidity: 0.5M of H_3PO_4.
Strippant: 0.5M Ammonium carbonate.
Time: 360 minutes.

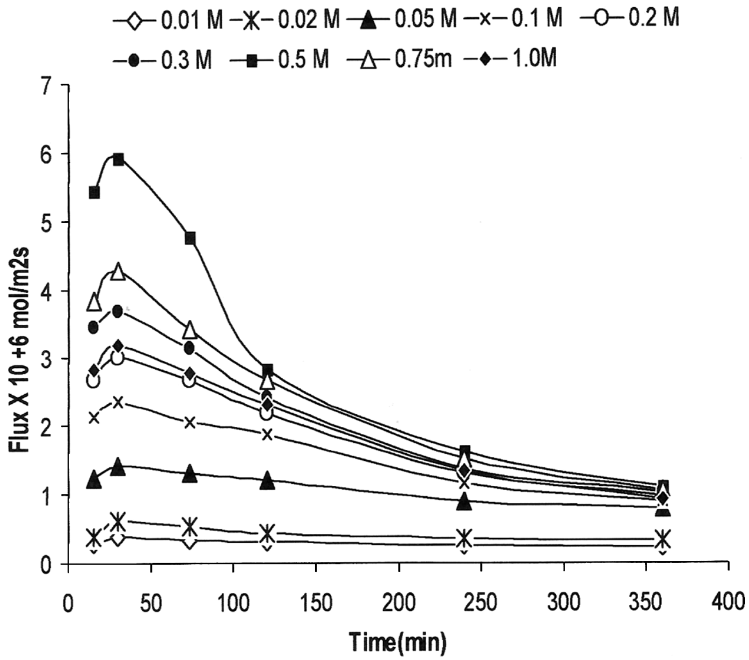

Figure 5. Flux vs time for varying carrier concentration of D2EHPA in n-dodecane. Feed acidity: 0.5 M H_3PO_4, [U] In feed: 1.29×10^{-3} moles/L, Strippant: 0.5 M $(NH_4)_2CO_3$.

a function of both the distribution coefficient and diffusion coefficient because the transfer of uranyl ions through the membrane may be considered diffusive in nature. However, in carrier-mediated transport of uranium with D2EHPA, a more complex behavior is seen. From the results, it is evident that the transport of uranium increases upto 0.5 M of carrier concentration and then decreases. Babcock et al (24) have assigned the dominant effects that cause this "maximal phenomenon" to be due to:

(i) the concentration gradient of the carrier-complex species,
(ii) the viscosity of the membrane phase, and
(iii) hindered diffusion of metal complex caused by aggregation of the complex.

Here, the amount of uranium that could be extracted into the membrane and the viscosity of the organic solution have increased. Since an increase in viscosity of D2EHPA solutions may lead to decrease of the diffusion coefficient and hence permeability of the diffusing species, these opposing effects resulted in a maximum permeation at about 0.5.M D2EHPA. Above this concentration, the permeation decreased with increasing carrier concentration. The permeation coefficients and average flux are found to be 3.72×10^{-5} m/s, and 1.11×10^{-6} moles/m^{2}s for 0.5 M D2EHPA in dodecane. The difference in permeability between experiments with varying feed acidity, carrier concentration, and uranium molarity can be understood by considering the probable expression for the rate of formation of the diffusing species at the feed interface:

$$D[UO_2(H_2PO_4)_2 \cdot 2D2EHPA]/dt = k^*[D2EHPA]^2[H_2PO_4^-]^2[UO_2^{2+}] \tag{13}$$

Where k* is rate constant for the formation of the UO_2^{2+}-D2EHPA complex. This equation is based on the stoichiometry of uranium (VI) extraction established earlier (25). The rate of diffusion of metal species will thus depend upon any changes in $H_2PO_4^-$, D2EHPA and UO_2^{2+} concentration in the feed side.

Effect of Strippant on the Permeation of Uranium

Detailed experiments were carried out to demonstrate that the transport of uranyl ions across D2EHPA/dodecane membranes is strongly dependent upon the nature and concentration of a strippant present on the receiver side of the membrane. It is apparent that out of several aqueous strippants such HCL, H_2SO_4, HNO_3, $(NH_4)_2CO_3$, citric acid, urea, sodium salt of E.D.T.A, and H_2O were tested. $(NH_4)_2CO_3$ proved to be the most efficient for stripping uranium from the loaded organic phase. Figure 6 shows that near quantitative recovery of uranium was possible with ammonium carbonate and around 80% uranium was back stripped by using sulphuric acid. All other strippants were able to transport only less than 42% of uranium from the SLM.

Effect of Pore Size of Membrane Support on Uranium Permeation

Figure 7 presents the trend of uranium transport with varying pore size of membranes. The percentage permeation of uranium was found to 75% and 60% in the case of 0.45 μm and 0.22 μm pore size respectively. The membrane porosity better known as the void volume of the membrane is a vital parameter responsible to guide the permeation and flux. In general the membrane porosity lies between 30 to 85%. The capillary force is

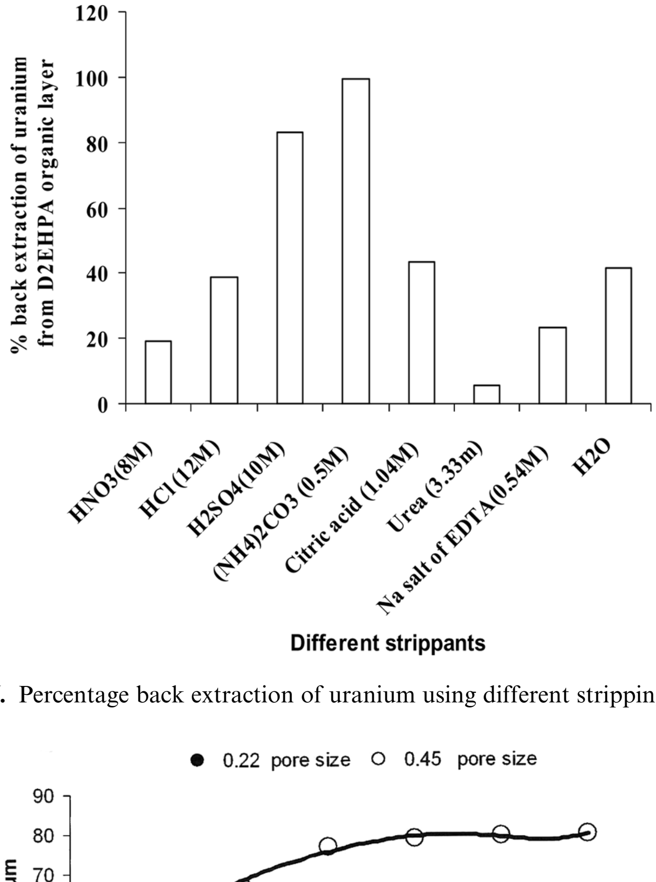

Figure 6. Percentage back extraction of uranium using different stripping agents.

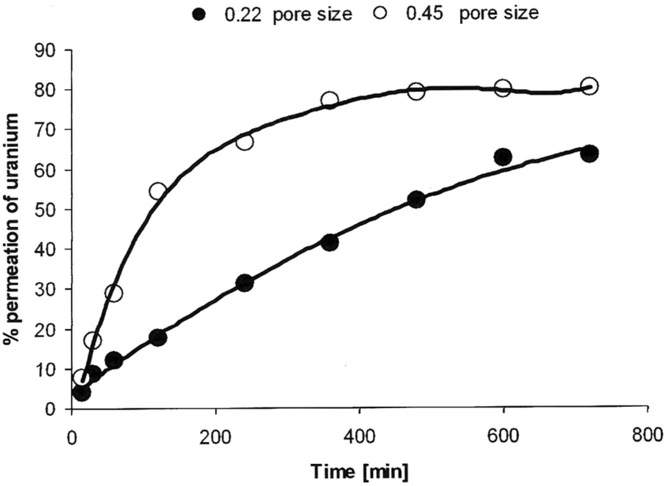

Figure 7. Percentage permeation of uranium vs Time using two different pore size membrane. Pore Size: 0.22 μm and 0.45 μm, [U] In feed: 1.29×10^{-3} moles/L, Feed acidity: 0.5 M of H_3PO_4, [Strippant]: 0.5 M $(NH_4)_2CO_3$, [Carrier]: 0.5 M D2EHPA/n-dodecane.

Table 4. Permeation of uranium as a function of thickness of PTFE membrane at particular source phase acidity

	160 μm thick membrane		320 μm thick membrane		480 μm thick membrane	
Time (min)	Uranium permeation (%)	Flux (moles/m^{2}s)	Uranium permeation (%)	Flux (moles/m^{2}s)	Uranium permeation (%)	Flux (moles/m^{2}s)
15	6.79	1.91×10^{-6}	5.96	1.67×10^{-6}	5.04	1.41×10^{-6}
30	14.23	2.00×10^{-6}	12.32	1.73×10^{-6}	11.73	1.65×10^{-6}
60	27.12	1.90×10^{-6}	22.67	1.59×10^{-6}	20.56	1.44×10^{-6}
120	49.86	1.75×10^{-6}	41.45	1.45×10^{-6}	36.62	1.28×10^{-6}
240	66.17	1.16×10^{-6}	59.56	1.04×10^{-6}	47.53	0.83×10^{-6}
360	76.94	0.90×10^{-6}	64.5	0.75×10^{-6}	55.72	0.65×10^{-6}

Initial feed concentration: 1.29×10^{-3} moles/L uranium in Varied amount of phosphoric acid.

Carrier concentration: 0.1M D2EHPA/dodecane.

Feed acidity: 0.5M of H_3PO_4.

Strippant: 0.5M Ammonium carbonate.

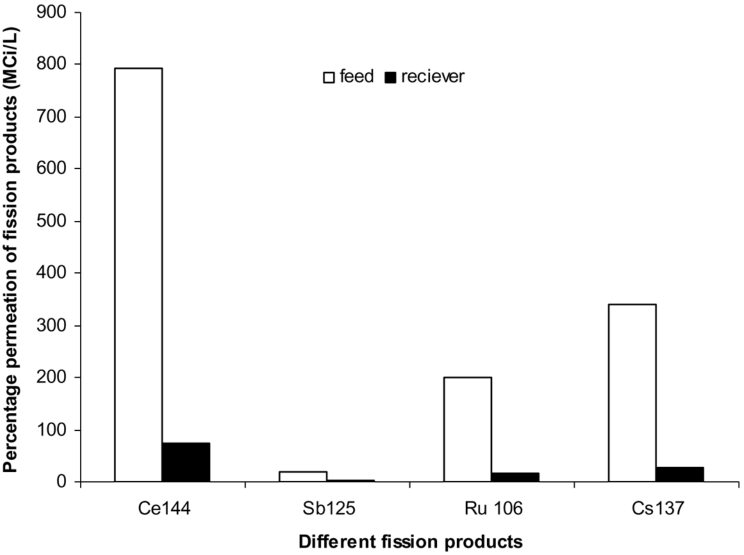

Figure 8. Fission products permeation from the analytical waste generated by Davis-Gray analysis through D2EHPA/Dodecane liquid immobilized Membrane in 360 minutes. Feed Acidity: 2.5–2.6M ($H_3PO_4 + H_2SO_4$), [Feed] in receiver: [$U^{(VI)}$] 187 ppm, [Fe^{++}] 373 ppm [$Mo^{(VI)}$] 22 ppm, [K^+] 119 ppm [$Cr^{(III)}$] 159 ppm, [Na^+] 2 ppm, [Carrier]: 0.5 M D2EHPA/n-dodecane, [Strippant]: 0.5 M $(NH_4)_2CO_3$.

the pressure by which the membrane phase is expelled from the support and it depends on the pore size and its distribution. It is known that the higher the membrane porosity it results in higher permeation and flux. The diffusion limited flux through a supported liquid membrane is influenced by the support porosity (θ) and tortuosity factor (β). The tortuosity factor can be reduced substantially with larger-pore size of membrane, leading to higher diffusion constants attainable in porous media. The tortuosity β is related to (τ) (average pore length/membrane thickness) by a correction for difference in pore diameter (α) according to $\tau = \alpha\beta^2$. The increase in transmembrane flux with increasing membrane pore size may be related to the enhanced mass transport process. It is observed that the percentage permeation increases as the pore size of the supports increases.

Effect of Thickness of Support on Uranium Permeation

Membrane thickness plays a significant role in dictating the resistance to mass transfer. An increase in membrane thickness linearly increases the

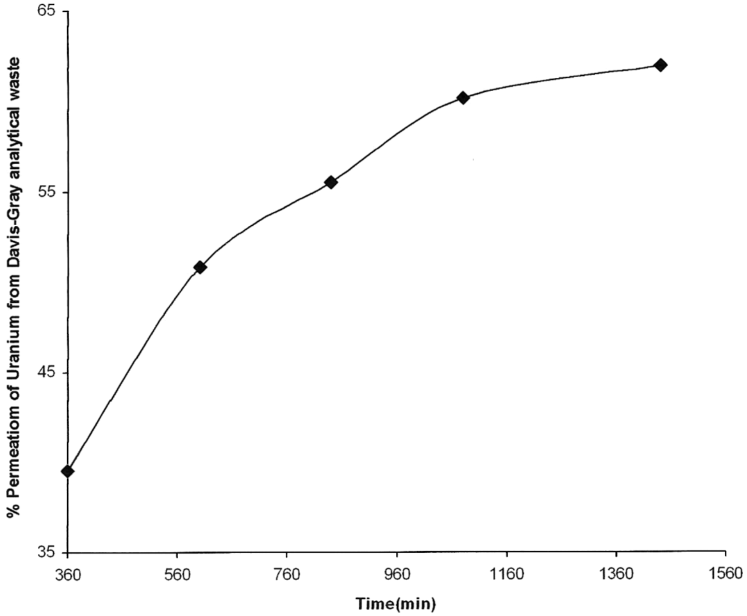

Figure 9. Uranium permeation from the analytical waste generated by Davis Gray analysis through D2EHPA/Dodecane liquid immobilized Membrane. Feed Acidity: 4.32 M of H_3PO_4 & H_2SO_4. [Feed] in receiver: [$U^{(VI)}$] 187 ppm, [Fe^{++}] 373 ppm [$Mo^{(VI)}$] 22 ppm, [K^+] 119 ppm [$Cr^{(III)}$] 159 ppm, [Na^+] 2 ppm, [Carrier] : 0.5 M D2EHPA/n-dodecane, [Strippant]: 0.5 M $(NH_4)_2CO_3$.

diffusional resistance (d_m/D_m) of the membrane (21). The permeate flux is inversely proportional to the membrane thickness. Thus as the thickness of the membrane increases, the flux decreases. It is evident from the results that the % transport also decreases with increase in membrane thickness. The % transport of Uranium (VI) was decreased from 77% to 56% while increasing the thickness of the membrane from 160 μm to 480 μm. To obtain a high permeability flux the membrane should be as thin as possible. However, this effect may be small in the case where the reaction kinetics is slow. The overall effect can be seen by measuring the flux as a function of membrane thickness. It is observed that as the thickness of the membrane increases the average flux decreases. The observed average flux are 1.60×10^{-6} moles/m^2s, 1.37×10^{-6} moles/m^2s and 1.21×10^{-6} moles/m^2s for 160 μm, 320 μm and 480 μm thickness of the membrane respectively (Table 4).

APPLICATIONS

Transport of uranium and fission products (produced during irradiation of natural uranium metallic fuel in nuclear research reactors) was investigated using 0.5 M D2EHPA/n-Dodecane supported liquid

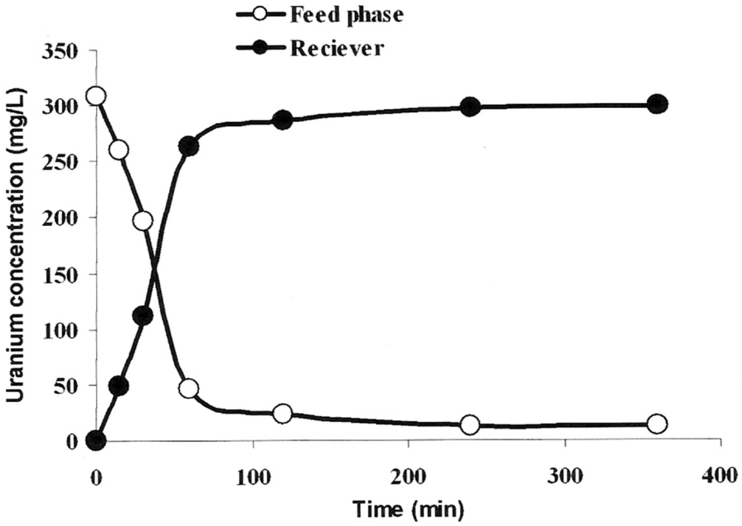

Figure 10. Concentration of uranium in feed and receiver side at condition given below. [Feed Acidity]: 0.001 M of H_3PO_4, [Carrier]: 0.1 M D2EHPA/ n-Dodecane, [Strippant] : 0.5 M $(NH_4)_2CO_3$.

membrane. The feed solution contains the actual radio analytical waste generated after volumetric analysis of uranium by DAVIS-GRAY method. It is evident from Fig. 8 that around 10% or less of major fission products were transported in 360 minutes. Figure 9 shows that around 60% of uranium was permeated through 0.5 M D2EHPA/dodecane supported liquid membrane in 1440 minutes. This may be attributed to the presence of other anions and cations in the analytical waste which reduces the permeation rate of uranium. However, it is significant to note that the concentration of uranium can be reduced substantially in feed by increasing the contact time. Figure 10 shows the concentration profile of feed and receiving phase with time under optimum conditions.

CONCLUSION

The transport of uranium (VI) by D2EHPA/dodecane supported liquid membrane (SLM) is studied and found that uranium (VI) can be effectively separated from the phosphoric acid medium. It is established that maximum uranium permeation is attained with feed acidity of 0.001 M phosphoric acid and 0.5 M D2EHPA/n-dodecane as carrier in the supported liquid membrane using support of PTFE (Poly-tetra-fluoro-ethylene) of 0.45 μm pore size and of 160 μm thickness. The 0.5 M ammonium carbonate has been found to be the best strippants for uranium (VI) for the receiving phase and it was observed that the same was efficient for quantitative recovery of uranium in 360 minutes. In the case of actual Davis-Gray analytical waste it was observed that around 10% or less of major fission products and 60% of uranium were transported. The driving force for the separation is not only the carrier concentration but also the degree of dissociation of H_3PO_4 for the transport of uranyl ions.

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