



## Effects of alkyl substituents of organophosphorous extractants on uranium permeation for recovery from uranyl nitrate raffinate

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Received 17 February 2011; Accepted 17 July 2011

### ABSTRACT

Carrier mediated transport of uranium from nitric acid medium has been investigated using supported liquid membrane (SLM). Microporous polytetrafluoroethylene (PTFE) membrane (pore size : 0.45  $\mu\text{m}$ , diameter : 47 mm, unless stated otherwise) was used as a solid support and various neutral donor organophosphorous extractants like tributyl phosphate (TBP), tris (2-butoxyethyl) phosphate (TBEP), and tris(2-ethylhexyl) phosphate (TEHP) dissolved in *n*-paraffin (a mixture of  $\text{C}_{12}$ - $\text{C}_{14}$ ) were used as carriers. Effects of various parameters like feed acidity, carrier concentration, uranium concentration, pore size, and membrane thickness on transport of uranium were investigated. Uranium transport with different carrier solutions followed the order: TEHP  $\geq$  TBP > TBEP. Transport of uranium increased with feed acidity and reached a maximum at 3.3 M  $\text{HNO}_3$  and decreased thereafter with increased nitric acid concentration. The permeation of uranium across SLM increased with increased membrane pore size and decreased with increased membrane thickness. These extractants were also evaluated for uranium recovery from uranyl nitrate raffinate (UNR) waste. TEHP appeared promising for efficient and selective extraction of uranium from such waste solutions.

*Keywords:* Supported liquid membrane; Organophosphorous extractant; Uranium; Transport

### 1. Introduction

The membrane based separation processes have gained considerable attention in the past few decades for the treatment of industrial effluents, water purification and gas separation etc. [1–3]. Carrier mediated transport of metal ions across liquid membranes is one of the promising options for the recovery of valuable metals from various waste streams [4–7]. This is of particular relevance in the nuclear industry in view of the

stringent nuclear waste management regulations. Liquid membranes are considered to be an improved version of solvent extraction which is widely used in hydrometallurgical separations, because of its high efficiency, selectivity, less power consumption, as well as use of lower organic solutions. The transport of metal ions across a supported liquid membrane (SLM) is generally considered as a combination of extraction and stripping process simultaneously. The transport mechanism is basically same as in liquid-liquid extraction, but the transport process is governed by various diffusion parameters across the membrane interface. Several studies

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on the recovery of actinides like uranium, plutonium, americium etc. from solutions of different nature/origin using various extractants by SLMs have been described earlier [8–14]. Separation of uranium from fission products using tributyl phosphate (TBP) as carrier in SLM has been reported earlier [7,8,12,13]. Alamine-336 (trioctyl/decyl amine), LIX-63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime) and crown ethers were also employed as carriers in SLM by researchers to separate actinides from acidic solutions [4,6,14].

The raffinate generated during the purification of uranium yellow cake (diuranate) by TBP route generally contains significant amounts of uranium (0.4–1 g/l) (Table 1). It is treated with MgO or calcium hydroxide to precipitate uranium as magnesium or calcium diuranate and disposed as a solid waste [15]. It is desirable to develop a process flow sheet to recover uranium from uranyl nitrate raffinate (UNR). In this context, solvent extraction and membrane separation studies on the recovery of uranium(VI) from nitric acid medium have been reported using PC88A as extractant either alone or in combination with neutral extractants such as TBP, trioctyl phosphine oxide (TOPO), and dioctyl sulphoxide (DOSO) [16,17].

TBP has been the work horse as an extractant for the nuclear industry in the back-end of nuclear fuel cycle for the reprocessing of spent fuels. TBP solution in aliphatic hydrocarbon has been employed for the last four to five decades as a versatile solvent for the recovery and purification of uranium and plutonium from spent nuclear fuels in the PUREX process [18]. However, the experiences gained over several years of reprocessing by the PUREX process, have revealed that the use of TBP as an extractant is associated with certain drawbacks such as relatively high aqueous solubility, poor decontamination of U, Pu with respect to fission products due to the formation of acidic degradation products (mono-, dibutyl phosphoric acids), and third-phase formation due to limited solubility of tetravalent metal ions. Therefore, there is a need to look for alternative extractants of TBP. Siddall postulated that other trialkyl phosphates and possibly dialkyl alkylphosphonates might be even more advantageous in processing irradiated uranium [19]. Simi-

Table 1

Major components of a typical raffinate solution (of uranium purification cycle)

Component	Concentration
U	0.4–1.4 g/l
Free acidity	1.1–2.0 M
Soluble Solid <sup>#</sup>	6.4% (w/v)
Suspended Solids <sup>##</sup>	0.2% (w/v)

<sup>#</sup>Determined by gravimetry.

<sup>##</sup>Suspended Solids were removed by filtration prior to membrane transport studies.

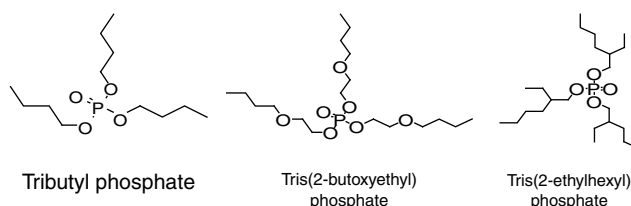


Fig. 1. Structural formulae of different trialkyl phosphates used in the present study.

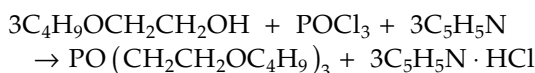
larly, Suresh et al. demonstrated that though tri-*n*-amyl phosphate (TAP) was analogous to TBP, however, it exhibited higher distribution ratios for uranium, plutonium, and thorium from nitric acid solutions [20]. Pathak et al. compared the distribution behavior of uranium and thorium from aqueous phases at different nitric acid concentrations using tris(2-ethylhexyl) phosphate (TEHP) and TBP solutions in *n*-dodecane as solvents. These results indicated that TEHP was a better choice than TBP for the separation of U from Th matrix [21]. Biswas et al. investigated the extraction behavior of U(VI) and Th(IV) from nitric acid medium tris(2-butoxyethyl) phosphate (TBEP) in *n*-paraffin as solvent. The effects of diluents, nitric acid concentration as well as extractant concentration on the extraction of U(VI) and Th(IV) were evaluated [22]. The extraction mechanism was typical of neutral organophosphorous extractants. It was observed that TBEP could be a potential extractant for separation of uranium from a mixture of U(VI) and Th(IV) in nitric acid medium.

In view of these findings, an attempt has been made in the present paper to compare the uranium transport behavior across SLM using trialkyl phosphates having different alkyl substituents viz. TBP, TBEP, and TEHP as the carriers. The effects of various experimental parameters such as feed acidity, carrier, and receiver phase composition on uranium transport have been investigated. The study has been extended for uranium recovery from UNR waste generated during uranium purification from yellow cake. Fig. 1 represents the structure of various organophosphorous extractants used in the present study.

## 2. Experimental

### 2.1. Synthesis and characterization of TBEP

TBEP was synthesized in our laboratory using the following reaction [23]:



Desired quantities of dry 2-butoxy ethyl alcohol and pyridine were refluxed in a round-bottom flask. The solution was stirred and allowed to cool up to ~5°C using an ice-salt mixture. Phosphorus oxychloride

(b.p.:106–107°C) was added drop wise with efficient stirring such that the temperature did not exceed 10°C. After complete addition, the reaction mixture was stirred for two hours and thereafter was cooled to room temperature. Water wash was given to reaction mixture to remove pyridine. Benzene and other low-boiling materials were removed by distillation at 40–50 mm of Hg until the temperature of the distilling vapor reached 90°C. Water was removed by anhydrous sodium sulfate. The tris(2-butoxyethyl) phosphate fraction was collected at 160–162°/15 mm of Hg and the yield of the product was ~70%. The elemental analysis was performed on a Thermo Finnigan Flash EA TM 1112 analyzer. The results are as follows: C = 54.2% (Calculated C = 54.3%), H = 9.78% (Calculated H = 9.79%), O = 28.2% (Calculated O = 28.1%), P = 7.77% (Calculated = 7.78%). The purity of TBEP was found to be ~99% [22].

## 2.2. Materials and techniques

TBP (BDH, purity: >95%), TEHP (E-Merck, purity: >97%) were used as received. Nuclear grade natural uranium oxide and UNR waste solutions were received from Uranium Extraction Division, BARC, Mumbai. All other reagents used in these studies were of AR grade. Uranium oxide was dissolved and diluted in nitric acid as per requirements. The acidity of the feed and strip solutions was determined by using standard method described elsewhere [24]. 1.1 M carrier solutions of TBP, TBEP and TEHP were prepared by weighing the required amounts and making up the volume with *n*-paraffin (a mixture of C<sub>12</sub>–C<sub>14</sub>). Tables 1 and 2 show the compositions (minor/major components) of a typical UNR solution used in this study. The uranium concentrations in strip as well as in feed solutions were determined by 2-(5-bromo-2-pyridylazo-5-diethylaminophenol) (Br-PADAP) method with the relative standard deviation

Table 2  
ICP-AES analysis of minor components in a typical UNR waste solution (obtained after uranium purification cycle)

Element	Concentration, µg/ml	Element	Concentration, µg/ml
Al	257	Fe	238
B	0.4	Mg	37.5
Cd	0.5	Mn	3.8
Ce	0.7	Ni	6.8
Co	0.4	Sm	<0.1
Cr	9.3	Y	0.3
Dy	<0.1	Yb	<0.1
Eu	<0.1		

Detection limit (3σ) of non-transition elements: <0.2 ppb, transition elements: <1 ppb and rear earths elements: <3 ppb. Standard deviations of the measurements are with in 2–5%.

of ±2% [25]. The trace impurities in UNR as well as in feed and strip solutions were determined by Inductively Coupled Emission Spectroscopy (ICP-AES) with the relative standard deviation of 2–5%. The detection limit (3σ) of the instrument for non-transition elements: <0.2 ppb, transition elements: <1 ppb and rear earths elements: <3 ppb. It should be noted that suspended solids were removed by filtration prior to membrane transport studies to avoid membrane fouling.

Commercially available polytetrafluoroethylene (PTFE) membranes (pore size: 0.45 µm; diameter: 47 mm) procured from Sartorius, Germany, were used (unless stated otherwise) as a solid support. Porosity of the membrane was determined as 72% by measuring the volume of dodecane that membrane could hold in the pores and by scanning electron microscopy (SEM) technique [26]. The SLMs were prepared by soaking PTFE membranes in the desired carrier solutions overnight. The excess organic phase was removed by using a jet of distilled water.

## 2.3. Membrane transport experiments

The transport studies were performed using a Pyrex glass cell consisting of two equal compartments each having 25 ml capacity. The measured effective geometric membrane area was 4.94 cm<sup>2</sup>. Distilled water was used as receiver phase in these studies. The feed and strip solutions were stirred using Teflon coated magnetic spin bar at constant speed of 200 rpm and at room temperature. The SLM was positioned in between the two compartments of the glass cell, joined by glass flanges. The concentration of uranium in feed as well as in strip solution was monitor by taking 0.1 ml samples.

## 2.4. Transport equation

The transport process of metal ions in supported liquid membranes can be divided in to three basic steps, viz. extraction at the feed-membrane interface, diffusion inside the membrane, and stripping at the membrane-receiver interface. The driving force behind the transport of metal ion across SLM is the concentration gradient of metal ion at the aqueous feed-membrane interface and at membrane-aqueous strip interface. Under experimental conditions of the present work, the transport processes of metal ions are generally diffusion controlled, and the distribution ratio of metal ion ( $D_M$ ) is much greater at the aqueous feed-membrane interface as compared to the membrane-aqueous strip interface, the flux ( $J$ ) of the system is given as [26–29]:

$$J = PC_f \quad (1)$$

where  $P$  is the permeability coefficient (cm/s) at the feed-membrane interface and  $C_f$  is the concentration of

the metal ion at the feed side. Similarly, the flux ( $J$ ) can also be calculated by the following equation:

$$J = -(1/Q) dV_f C_f / dt \quad (2)$$

where  $V_f$  is the feed volume (ml) and  $Q$  is the effective surface area ( $\text{cm}^2$ ) of the membrane used in the experiment. If volume of the feed does not change significantly during the experiment ( $V_f = V$ ), then combination of Eqs. (1 and 2) followed by integration gives:

$$\ln(C_{f,t}/C_{f,0}) = -QP_f t/V \quad (3)$$

where  $C_{f,0}$  and  $C_{f,t}$  represent the concentration of feed at time 0 and after time  $t$ , respectively.  $V$  is the time average aqueous feed volume (in ml).  $Q$  represents the product of geometrical surface area ( $A$ ) and the porosity of the membrane ( $\epsilon$ ). The permeability coefficient ( $P$ ) values were calculated by the Eq. (3). The percentage transport of U(VI) (%  $T$ ) across SLM is calculated as:

$$\%T = (C_{r,t}/C_{f,0})100 \quad (4)$$

where  $C_{f,0}$  and  $C_{r,t}$  are the concentrations of U(VI) in feed and in receiver compartments at time 0 and  $t$ , respectively.

### 3. Results and discussion

#### 3.1. Effect of alkyl substituents on U(VI) transport

To understand the effect of alkyl substituents of neutral oxodonor, U(VI) transport studies were carried out employing 1.1 M solutions of TBEP, TBP and TEHP in *n*-paraffin as carriers.  $2 \times 10^{-3}$  M U(VI) at 1.12 M  $\text{HNO}_3$  and distilled water were used as feed and receiver solutions, respectively. There was a distinct effect of alkyl substituents on U(VI) transport and it followed the order: TEHP  $\geq$  TBP  $>$  TBEP (Fig. 2). The lower transport of U(VI) in case of TBEP was attributed to the presence of extra oxygen atom in the alkyl substituents, which decreased the basicity/donor capacity of the P=O group. On the other hand, marginal difference in the uranium transport was observed in the case of TBP and TEHP. Burger reported the correlation between P=O bond stretching frequency (reflecting the basicity of the ligand) and the distribution data of various organophosphorous extractants [30]. More shift of IR stretching frequency of P=O bond in lower side indicated higher basicity of the ligand and better extraction of metal ions. The phosphoryl IR absorption bands shifted towards lower wave numbers in the order:  $(\text{RO})_3\text{PO} > (\text{RO})_2\text{RPO} > (\text{RO})\text{R}_2\text{PO} > \text{R}_3\text{PO}$ . The absorption bands at  $1273 \text{ cm}^{-1}$  for TBP and  $1275\text{--}1270 \text{ cm}^{-1}$  for

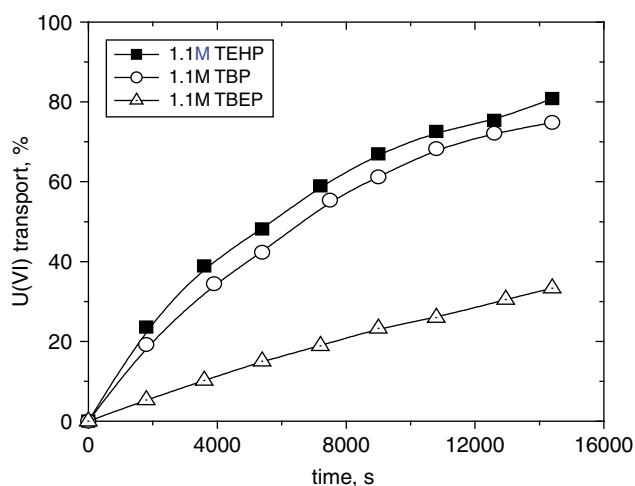


Fig. 2. Uranium transport across supported liquid membrane impregnated with various organophosphorous extractants; Carrier: 1.1 M TBP/TBEP/TEHP in *n*-paraffin;  $[\text{U(VI)}]_{\text{feed}}: 2 \times 10^{-3}$  M at 1.12 M  $\text{HNO}_3$ ; Receiver phase: Distilled Water.

TEHP suggested that the basicities of the two ligands are almost similar. The U(VI) transport from  $\text{HNO}_3$  medium through SLM using TBP as a carrier has been investigated by many authors [8,14]. However, our literature search suggested that U(VI) transport from  $\text{HNO}_3$  medium across SLM using TEHP as a carrier, has not been studied as yet and compared with that of TBP. TEHP was, therefore, chosen for further experiments because of its high selectivity towards U(VI) over other metal ions [21]. Experiments were also carried out to compare the performance of TEHP vis a vis TBP and TBEP, with respect to uranium transport.

#### 3.2. Effect of feed acidity

The transport of U(VI) was investigated from feed solutions at various nitric acid concentrations ( $\sim 2 \times 10^{-3}$  M U(VI) at 1.1–3.3 M  $\text{HNO}_3$ ) employing 1.1 M TBP/TBEP/TEHP solutions in *n*-paraffin as carriers. Fig. 3(a) shows an increase in uranium transport with increased feed acidity. Both TBP and TEHP display similar transport behavior of uranium at all acidities. Typically,  $\sim 90\%$  uranium transport was observed in 4 h for TBP and TEHP at 3.3 M  $\text{HNO}_3$  as feed acidity. By contrast, only  $\sim 80\%$  uranium transport was observed in the case of 1.1 M TBEP under identical experimental conditions. The increased transport of U(VI) from 2.1 M  $\text{HNO}_3$  to 3.3 M  $\text{HNO}_3$  as feed acidity was attributed to salting out effect by nitrate ions. Therefore, it was of interest to study U(VI) transport at higher acidities (up to 6 M  $\text{HNO}_3$ ) using 1.1 M TBEP/*n*-paraffin as the carrier. However, further increase in the feed acidity suppressed

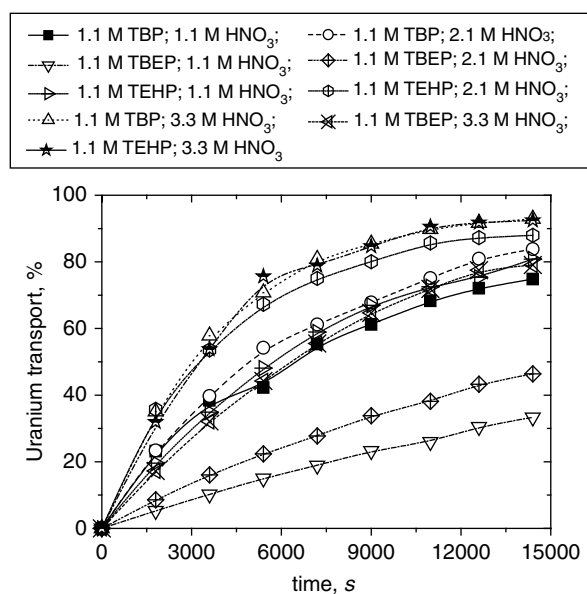


Fig. 3(a) Comparison of uranium transport across supported liquid membrane impregnated with different carriers and with different feed solutions; Carrier(s): 1.1 M TBP/TBEP/TEHP in *n*-paraffin; Feed solution(s):  $2 \times 10^{-3}$  M U(VI) at 1.1–3.3 M  $\text{HNO}_3$ ; Receiver phase: Distilled Water.

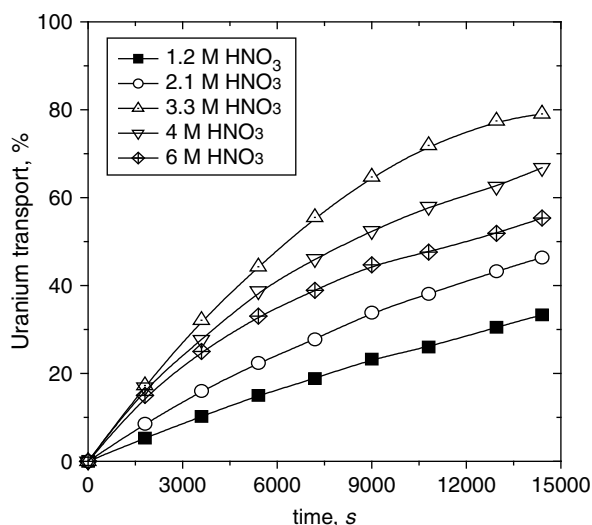


Fig. 3(b) Effect of acidity on uranium transport using 1.1 M TBEP in *n*-paraffin as a carrier;  $[\text{U(VI)}]_{\text{feed}}: 2 \times 10^{-3}$  M; Receiver phase: Distilled Water.

U(VI) transport (Fig. 3(b)), which was due to increased strip phase acidity leading to poor stripping from the membrane phase. Typically, the acid transport from 1.1–6 M  $\text{HNO}_3$  feed solutions were found to be as high as 15% in 4 h. The transport of U(VI) by neutral organophosphorous extractant occurs via cotransport mechanism where  $\text{NO}_3^-$  ion is anion Fig. 4 [18,21,22].

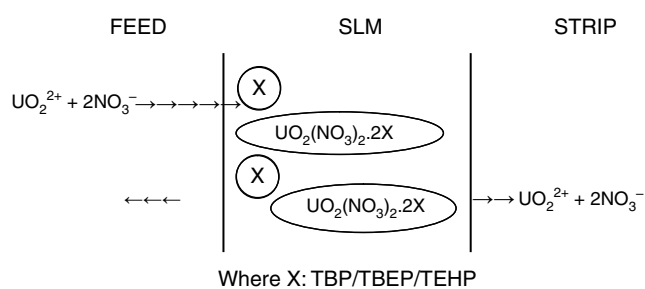
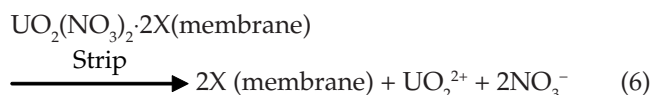
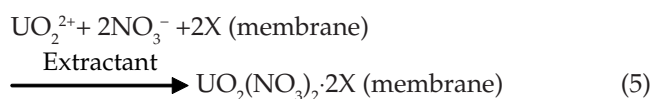


Fig. 4. Schematic for uranium transport across Supported Liquid Membrane.

The chemical reaction for this coupled transport is given as follows:



where  $\text{X} = \text{TBEP, TBP or TEHP}$ .

From Eq. (5) it is observed that the transport of U(VI) through membrane will increase with increase in nitrate ion concentration in feed and hence with nitric acid concentration. The decrease in transport of U(VI) after 3.3 M  $\text{HNO}_3$  is due to the formation of ' $\text{HNO}_3 \cdot \text{X}$ ' complexes which lower both the concentration of  $\text{NO}_3^-$  ions in feed as well as extractant ' $\text{X}$ ' in the membrane phase.

### 3.3. Effect of extractant concentration

Uranium transport was studied as a function of TEHP concentration employing  $2 \times 10^{-3}$  M U(VI) solution at 4 M  $\text{HNO}_3$  as feed and distilled water as receiver phase. Table 3 shows the variation of permeation

Table 3

Effect of carrier concentration on U(VI) transport from  $\text{HNO}_3$  medium using TEHP/*n*-paraffin, U(VI):  $2 \times 10^{-3}$  M, PTFE membrane pore size: 0.45  $\mu$ ; Porosity: 72%, Volume of feed and strip solutions: 25 ml; Feed acidity: 4 M  $\text{HNO}_3$ ; Stripant: Distilled water; Stirring speed: 200 rpm

Carrier concentration	$\text{P} \times 10^4, \text{cm/s}$	%T
0.1 M TEHP	4.0	70
0.2 M TEHP	7.9	88
0.3 M TEHP	9.6	93
0.5 M TEHP	11.1	96
1.1 M TEHP	11.4	97

coefficient ( $P$ ) of U(VI) with varying concentrations of TEHP/*n*-paraffin. Uranium transport increases initially with increased carrier concentration in the membrane phase up to 0.5 M beyond which no appreciable increase was observed. It appears that the increased viscosity of the carrier was responsible for slow increase in uranium permeation across the membrane [17,29].

### 3.4. Effect of uranium concentration

Fig. 5 shows the variation of flux with uranium concentration ( $4.2 \times 10^{-4}$  to  $3.4 \times 10^{-3}$  M) at 2 M  $\text{HNO}_3$  as feed acidity, distilled water as receiver phase using 1.1 M TEHP/*n*-paraffin as carrier. As expected, there was a linear increase in the flux (though small) with increased metal ion concentration in the feed solution, which was attributed to the presence of limited ligand in the membrane phase. However, transport of U(VI) initially increased with metal ion concentration and became maximum at  $0.8 \times 10^{-3}$  M U(VI) (Fig. 6), any further increase in metal ion concentration caused a decrease in transport of the metal ion. Initially, U(VI) ions at lower concentrations can not saturate the carrier present. However, the carrier gets saturated by metal ions beyond  $0.8 \times 10^{-3}$  M U(VI) in the feed solution.

### 3.5. Effect of pore size

The transport rate depends on the amount of carrier held in the membrane pores, pore structure/size, the membrane thickness, porosity and tortuosity (defined as effective diffusion path length) etc. [31]. Membrane pore size plays an important role in the permeation rate of metal cations across supported liquid membranes. With increasing membrane pore size, porosity of the membrane increases where as tortuosity of the membrane decreases.

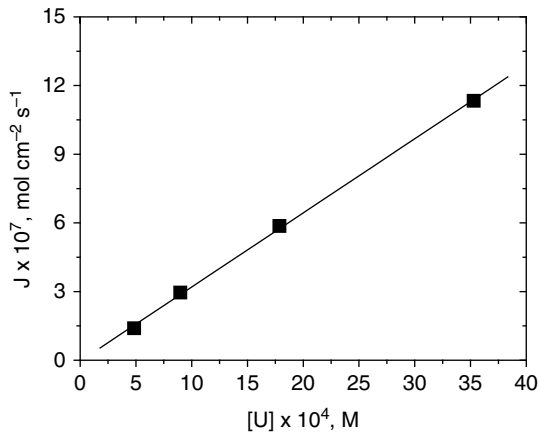


Fig. 5. Variation of flux ( $J$ ) with U(VI) concentration in the feed solution; Carrier: 1.1 M TEHP/*n*-paraffin; Feed acidity: 2 M; Receiver phase: Distilled Water.

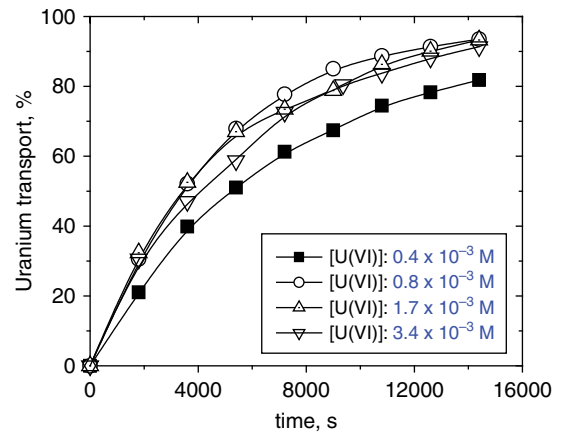


Fig. 6. Effect of U(VI) concentration in the feed solution on its permeation; Feed acidity: 2 M  $\text{HNO}_3$ ; Carrier: 1.1 M TEHP in *n*-paraffin; Receiver phase: Distilled Water.

In order to understand the effect of membrane pore size on U(VI) transport, two membranes with different pore sizes and porosities ( $0.20 \mu\text{m}$ , 55% and  $0.45 \mu\text{m}$ , 70%) impregnated with 1.1 M TEHP/*n*-paraffin were used for permeation studies. Fig. 7 shows that uranium transport increased with membrane pore size suggesting that larger pore size provides relatively easy passage for the metal cations. However, it has to be noted that too large a pore size ( $\geq 5 \mu\text{m}$ ) would lead to poorer holding of the carrier molecules in the pores of the membrane and therefore may leach out of the membrane. The diffusion coefficient of the metal-carrier complex  $D$ , across the membrane is inversely related to the radius of the diffusing complex defined by the following Stokes–Einstein Eq. (7):

$$D = \frac{kT}{6\pi\eta r} \quad (7)$$

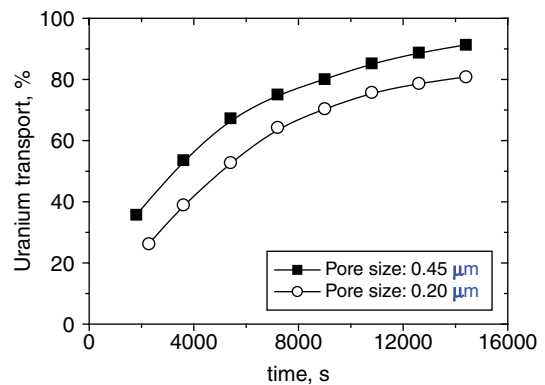


Fig. 7. Effect of membrane pore size on U(VI) transport across SLM employing 1.1 M TEHP/*n*-paraffin; Feed:  $2 \times 10^{-3}$  M U(VI) at 2 M  $\text{HNO}_3$ ; Receiver phase: Distilled Water.

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature (K),  $r$  is the ionic radius (Å) of solute and  $\eta$  is the viscosity of the organic phase equilibrated with the aqueous phase. The effect of porosity and tortuosity can be expressed by the following Eq. (8).

$$D_m = D \left( \frac{\theta}{\tau} \right) \quad (8)$$

where  $D_m$  is the diffusion coefficient of the complex,  $\theta$  and  $\tau$  are the porosity and tortuosity of the membrane, respectively. Therefore, with increasing membrane pore size, porosity of the membrane increases whereas tortuosity of the membrane decreases [31]. So both these effects result in an enhancement in the transport rate of metal with increasing membrane pore size. Therefore, higher the pore size, lower is the resistance experienced by the complex species which results in higher transport rate for higher pore size membranes. Similar observations were made during the transport of Am(III), and U(VI) using dimethyldibutyltetradecyl-1,3-malonamide (DMDBTDMA), a tertiary amine and TEHDGA, as carriers [4,26,31]. The hindered diffusion of the metal-carrier complex across the membrane pores indicates predominant contribution from tortuosity.

### 3.6. Effect of membrane thickness

In diffusion controlled transport process, permeability ( $P$ ) of the metal ion is dependent on the effective diffusion path length in the membrane phase. The permeability coefficient ( $P$ ) depends on the distribution coefficient ( $D_U$ ) by the following equation [32,33]:

$$P = D_U / \{D_U(d_a/D_a) + (d_m\tau/D_m)\} \quad (9)$$

where  $d_a, d_m$  are the thickness of diffusion layer of aqueous phase and membrane;  $\tau$  is the tortuosity of the membrane; and  $D_a, D_m$  are the diffusion coefficient of the metal ion and the complex (metal ion & carrier) in aqueous phase and in membrane phase, respectively. Uranium transport experiments were carried out by compressing a number of membranes (pore size: 0.45  $\mu\text{m}$ , and effective thickness: 60  $\mu\text{m}$ ) using 1.1 M TEHP/*n*-paraffin,  $2 \times 10^{-3}$  M U(VI) at 2 M  $\text{HNO}_3$  and distilled water as carrier, feed, and the receiver phase, respectively. The membranes were immersed separately in to the carrier solution of desired concentration and were stacked together to increase the thickness. In diffusion controlled transport process, permeability ( $P$ ) of the metal ion is dependent on the effective diffusion path length in the membrane phase. With increase in membrane thickness, there was a gradual decrease in permeability of uranium across SLM (Fig. 8) which is a characteristic property of diffusion controlled process.

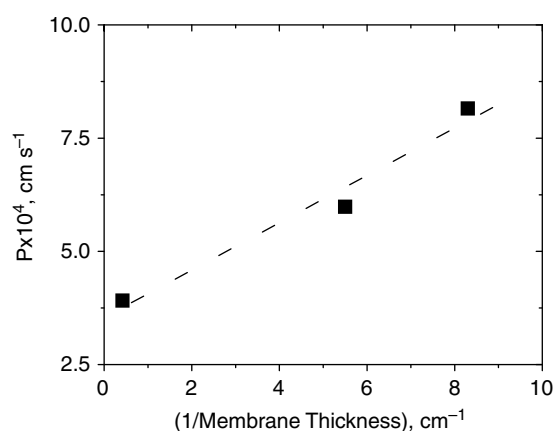


Fig. 8. Effect of membrane thickness on U(VI) transport across SLM employing 1.1M TEHP/*n*-paraffin; Feed:  $2 \times 10^{-3}$  M U(VI) at 2 M  $\text{HNO}_3$ ; Receiver phase: Distilled Water.

### 3.7. Separation of uranium from raffinate waste solution

The UNR waste generated during a typical purification cycle by TBP route contained  $\sim 0.5$  g/l U(VI) at 1.1 M  $\text{HNO}_3$  and a large number of other metal ions as impurities (Table 2). An attempt was made to compare the uranium transport from UNR waste (after removal of suspended particles) using 1.1 M solutions of TBP, TBEP and TEHP in *n*-paraffin as carrier solutions and distilled water as the receiver phase. It is evident that change in alkyl substituents has no significant influence on the selectivity of extractants towards impurities (Table 4). However, the presence of butoxyethyl group significantly suppresses uranium transport which can be attributed to reduced basicity of the TBEP as compared to those of TBP

Table 4

Transport (%) of various elements from UNR waste solution across SLM impregnated with different carriers; Carrier solution: 1.1 M TBP/TBEP/TEHP solutions in *n*-paraffin; Volume of feed and strip solution: 25 ml; Feed acidity: 1.1 M  $\text{HNO}_3$ ; Strippant: Distilled water; Stirring speed: 200 rpm

Elements	%Transport, 4 h		
	TBEP	TBP	TEHP
U	39	81	84
Al	<1	<1	<1
Co	<1	<1	<1
Cr	1	1	<1
Fe	2	2	<1
Mg	2	3	<1
Mn	1	1	<1
Ni	1	3	2
Y	1	2	<1

and TEHP. Contaminants transport appeared to be negligible under the experimental conditions of present study.

#### 4. Conclusions

Uranium transport from nitric acid medium was studied using various neutral donors such as TBEP, TBP, and TEHP across SLM. Transport of uranium increased with feed acidity and reached a maximum at 3.3 M HNO<sub>3</sub> and decreased thereafter with increased nitric acid concentration. At a fixed feed acidity, uranium transport with different carrier solutions followed the order: TEHP ≥ TBP > TBEP. The permeation of uranium across SLM increased with increased membrane pore size and decreased with increased membrane thickness. TEHP appeared suitable for uranium recovery from UNR waste solutions. Contaminants transport was negligible under the conditions of these studies.

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