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Thorium Ions Transport across Tri-*n*-butyl Phosphate–Benzene Based Supported Liquid Membranes

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ABSTRACT

Transport of Th(IV) ions across tri-*n*-butyl phosphate (TBP) benzene based liquid membranes supported in microporous hydrophobic polypropylene film (MHPF) has been studied. Various parameters such as variation of nitric acid concentration in the feed, TBP concentration in the membrane, and temperature on the given metal ions transport have been investigated. The effects of nitric acid and TBP concentrations on the distribution coefficient were also studied, and the data obtained were used to determine the Th ions–TBP complex diffusion coefficient in the membrane. Permeability coefficients of Th(IV) ions were also determined as a function of the TBP and nitric acid concentrations. The optimal conditions for the transport of Th(IV) ions across the membrane are 6 $mol \cdot dm^{-3}$ HNO_3 concentration, 2.188 $mol \cdot dm^{-3}$ TBP concentration, and 25°C. The stoichiometry of the chemical species involved in chemical reaction during the transport of Th(IV) ions has also been studied.

INTRODUCTION

Supported liquid membranes (SLM) (1) are constituted of some liquid absorbed inside a microporous solid support by capillary action in its

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pores. The support may be some polymeric microporous hydrophobic film or tube. The organic liquid is held there because it is immiscible in the surrounding aqueous phases. Separations have been performed by using this technique by various workers (2–5) on different metal ions: Tc(VII), U(VI), Be(II), Mo(VI), Sr(II), Ti(IV), V(VI), and W(VII). Classical solvent extraction is normally a selective method for the separation of metal ions in which large amounts of carrier liquids are used with separate extraction and stripping stages. Normally Th(IV) and U(VI) ions have been extracted from other metal ions by using tri-*n*-butyl phosphate (TBP) as carrier, but no literature is available for Th(IV) ions extraction using a TBP-benzene based SLM. In the present investigation these membranes have been studied for the transport of Th(IV) ions. A stoichiometric study of the chemical reaction involved has also been performed by using the flux and viscosity data.

EXPERIMENTAL

Reagents

The organic phase was prepared by dissolving tri-*n*-butyl phosphate (GR grade, E. Merck) in benzene (GR grade, E. Merck) to obtain solutions of various compositions. It was equilibriated with an HNO_3 (Analar grade, B.D.H.) solution of the required concentration before use. Thorium nitrate hexahydrate (Analar grade, B.D.H.) was used for all solutions. Ultrapure water, purified by Milli-Q RO-cum-ion exchange units, was used in all solutions. All other chemicals were of analytical grade or equivalent and were used without further purification.

Apparatus

Membranes

Celgard 2400, a microporous polypropylene film from Celenese Corporation USA, was used throughout this study. Dry films were immersed in the organic phase for more than 24 hours before use and had an effective area of 23.8 cm^2, a thickness of 25 μm, a porosity of 38%, and a pore diameter of 0.02 μm.

Liquid Membrane Cell

The cell, shown in Fig. 1, was fabricated from Teflon with two compartments (half cells), each with a capacity of 145 cm^3, for holding the feed and strip solutions. The half cells had electric stirrers to agitate the cell liquids at a rate of more than 1000 rpm.

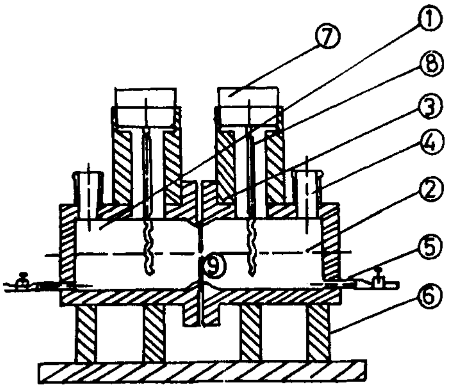

FIG. 1 Liquid membrane cell. (1) Feed solution compartment. (2) Product solution compartment. (3) "O" ring, 5 mm. (4) Feed and product solution inlets. (5) Outlets for drain. (6) Stand for cell. (7) Electric stirring motor. (8) Perspex stirrer. (9) Membrane.

Flux Measurement

The membrane was fixed between the two half cells. One half cell was filled with thorium solution (the feed solution). The other side of the membrane was filled with 0.943 mol·dm^{-3} Na_2CO_3 solution (the strip solution). After regular time intervals, 1 cm^3 was drawn from each side and analyzed using a spectrophotometric method (6). The Th(IV) ions flux was determined from the amount of Th(IV) ions transferred to the strip solution. The whole cell was immersed in a water bath of the required temperature.

Analytical Method

Thorium solution samples were analyzed spectrometrically (6) by using Arsenazo III as the complexing agent. Absorbance was measured at 660 nm.

Distribution Coefficient Measurement

Equal volumes (25 cm^3) of the feed and TBP solutions were agitated together for 30 minutes. The aqueous phase was analyzed for Th(IV) ions before and after stirring to determine the concentration in the organic aqueous phases. The ratio of concentrations in the organic and aqueous phases furnished the distribution coefficient. The initial aqueous phase contained a Th(IV) ions concentration of 0.431×10^{-3} mol·dm^{-3}.

Viscosity Measurement

Viscosity was measured by an Ubbelohde viscometer. The solution containing the viscometer was immersed in a 25°C water bath for sufficient time to attain this temperature.

RESULTS AND DISCUSSION

$Th(NO_3)_4 \cdot 6H_2O$ was used during this study. Earlier workers (7) indicated that at $pH < 3$, $Th(NO_3)_4$ is not hydrolyzed. Therefore, Th(IV) ions are extracted into the organic phase through the following reaction in a liquid–liquid extraction system:

$$Th^{4+} + 4NO_3^- + n\mathrm{TBP}_{org} \rightleftharpoons Th(NO_3)_4 \cdot n\mathrm{TBP}_{org} \tag{1}$$

The extraction coefficient K_e is given as

$$K_e = \frac{G[Th(NO_3)_4 \cdot n\mathrm{TBP}]_{org}}{[Th^{4+}]_{aq}[NO_3^-]_{aq}[\mathrm{TBP}]_{org}} = \frac{D}{[NO_3^-]^4[\mathrm{TBP}]_{org}} \tag{2}$$

where G is a factor based on the activity coefficients of the species involved in Reaction (1) and

$$D = \frac{[Th(NO_3)_4 \cdot n\mathrm{TBP}]_{org}}{[Th^{4+}]_{aq}} \tag{3}$$

D is the distribution coefficient of the Th(IV) ions.

The flux (J) of metal ions across the liquid membrane may be given by Fick's law of diffusion:

$$J = \frac{\overline{D}\epsilon}{l}(D_f C_f - D_s C_s) \tag{4}$$

where D is the diffusion coefficient of the species being transferred, ϵ is the membrane porosity, C_f and C_s are the concentrations of Th(IV) ions in the bulk feed and strip solutions respectively, D_f and D_s are the distribution coefficients of Th(IV) ions in the membrane from the feed and strip solutions respectively, and l represents the membrane thickness.

The complex formed at the membrane face on the feed side is extracted into the membrane, while at the strip side of the membrane there may be no or a negligible amount of such a complex. The concentration gradient thus developed forces the complex to travel through the membrane to its strip side. Due to the very low distribution coefficient of Th(IV) ions into the membrane on this side, D_s approaches zero and thus $D_s C_s \rightarrow 0$, and hence Eq. (4) is reduced to

$$J = \frac{D}{l} D_f C_f \tag{5}$$

From Eq. (2):

$$D = K_e[NO_3^-]^4[TBP]^n_{org} \tag{6}$$

By using Eqs. (5) and (6):

$$J = \frac{D\epsilon}{l} K_e[TBP]^n_{org}[NO_3^-]^4_{aq} \tag{7}$$

According to the Wilke–Change (8) equation, the diffusion coefficient is related to viscosity η and temperature T:

$$D = K' \frac{T}{\eta} \tag{8}$$

where K' is a constant. So

$$J = K' \frac{T\epsilon}{l\eta} K_e[TBP]^n_{org}[NO_3^-]^4_{aq} C_f \tag{9}$$

and thus at constant temperature, thickness of the membrane, and porosity:

$$J = \frac{A}{\eta} [TBP]^n_{org}[NO_3^-]^4_{aq} C_f \tag{10}$$

where $A = K'T/l$ and A is a new constant.

In the logarithmic form Eq. (10) becomes

$$\log \eta J = \text{constant} + n \log[TBP]_{org} + 4 \log[NO_3^-]_{aq} + \log C_{ft} \tag{11}$$

If the feed solution concentration at time t is C_{ft} and the nitrate ions concentration in the feed is kept constant, then from Eq. (11) the moles of TBP involved in the chemical reaction for the Th–TBP complex may be determined from a plot of log $J\eta$ versus log[TBP]. Although the concentration in the feed solution varies continuously, it may remain constant for a short time.

THORIUM IONS TRANSPORT AGAINST CONCENTRATION GRADIENT

Figure 2 provides Th(IV) ions concentrations in the feed and product solutions as a function of time. Beyond 80 minutes the concentration of

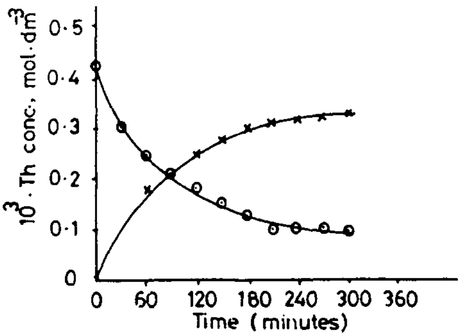

FIG. 2 Th concentration in the feed and stripping solution as a function of time.

Th(IV) ions in the feed solution is lower than that in the stripping solution and the Th(IV) ions still continue to transport from feed to strip solution, which quite clearly indicates (Fig. 2) the transport of Th(IV) ions against their concentration gradient.

Initially the feed concentration was 0.431 × 10^{-3} mol·dm^{-3} and there were no Th(IV) ions in the product solution. Thorium complex formation with TBP at the membrane is faster in the beginning because the higher concentration of Th(IV) ions makes the kinetics faster, but as transport of the ions proceeds, the concentration of Th(IV) ions at the feed side becomes lower and hence the flux is reduced as shown in Fig. 3. The complex diffuses toward the strip side through the membrane liquid, and

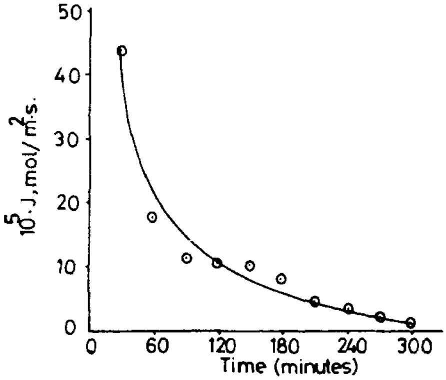

FIG. 3 Th(IV) ions flux, J, as a function of time.

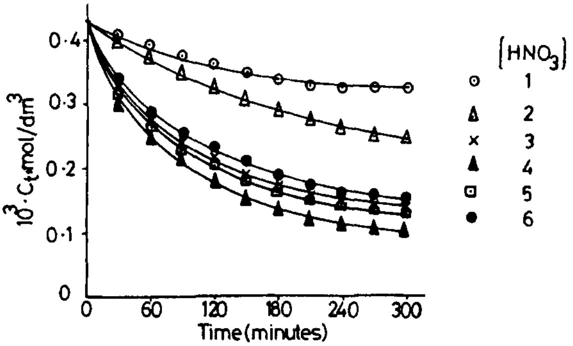

FIG. 4 Variation in Th concentration with time at different HNO_3 molarities.

due to the very low distribution coefficient (D.C.) of Th(IV) ions in basic aqueous solution, dissociates to release the Th(IV) ions into the strip solution. TBP molecules in the membrane diffuse back to the feed side of the membrane as a result of the concentration gradient developed for TBP. The reduced transport of Th(IV) ions with the passage of time is also attributable to the depletion of membrane solution with respect to TBP molecules which may enter the feed and strip solutions as a result of stirring both solutions.

The slope of the curve at different time intervals was evaluated from Fig. 4 as

$$\text{Slope} = \frac{dC_x}{dt} = \frac{C_{t1} - C_{t2}}{\Delta t} \tag{12}$$

C_{t1} and C_{t2} are the concentrations of Th(IV) ions in the bulk feed solution at times t_1 and t_2 respectively. The slope for time interval Δt was evaluated, and then the flux for each duration was evaluated by using Eq. (13):

$$\text{Flux } (J) = \frac{V(C_{t1} - C_{t2})}{a\Delta t} \quad (\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}) \tag{13}$$

V and a' refer to the half cell liquid volume and effective membrane area, respectively. Figure 3 indicates the flux of Th ions against time at [TBP] = 2.189 mol·dm^{-3} and [HNO_3] = 6 mol·dm^{-3}.

EFFECT OF NITRIC ACID CONCENTRATION ON FLUX

Figure 4 indicates the effect of nitric acid concentration on the transport of Th(IV) ions. By keeping the TBP concentration constant at 1.823

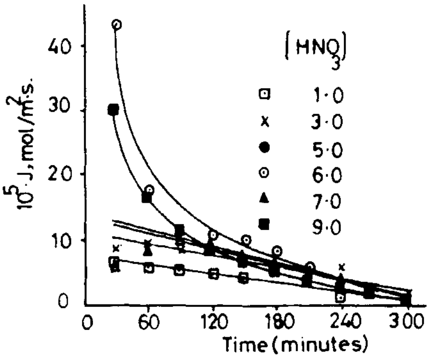

FIG. 5 Plot of flux, *J*, versus time at various nitric acid molarities.

mol·dm^{-3} and using Eq. (13) and plots of Fig. 4, Th(IV) ions flux for different time intervals has been evaluated and is shown in Fig. 5.

The flux of Th as a function of nitric acid concentration is given in Fig. 6. It is obvious that the flux increases with a rise in nitric acid concentration and reaches its maximum value at 6 mol·dm^{-3} concentration; with a further rise in acid concentration, the flux decreases. Figure 7 indicates that D.C. for Th(IV) ions increases with increasing acid concentration. Figure 8 shows that the viscosity of the membrane liquid containing a carrier decreases as the nitric acid concentration increases. According to D.C. data, the flux should increase with an increase in nitric acid concentration. Also, low viscosity for a high acid concentration should result in

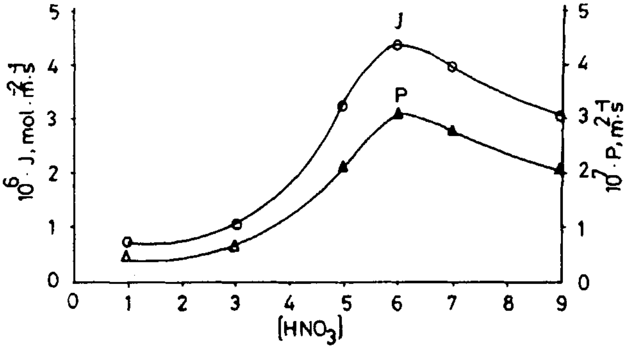

FIG. 6 Flux, *J*, and permeability, *P*, as a function of nitric acid molarities.

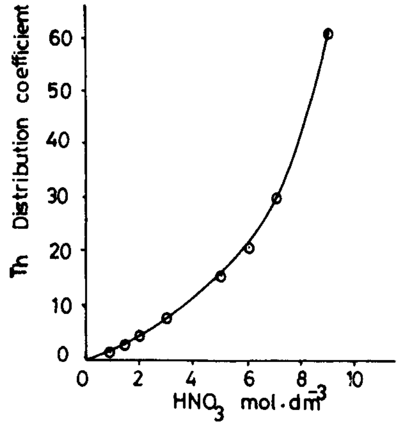

FIG. 7 Distribution coefficient of Th as a function of HNO_3 concentration in feed side aqueous solution. TBP = 1.823 mol·dm^{-3}. Th concentration = 0.431 × 10^{-3} mol·dm^{-3}.

a high diffusion coefficient, and thus the flux should be higher for higher acid concentrations up to 6 mol·dm^{-3}. The flux obtained may be predicted by D.C. and viscosity data, but at high acid concentrations the flux decreases. This is due to HNO_3 extraction and competition between the complexes $Th(NO_3)_4 \cdot n$TBP and TBP·HNO_3 (9) which results in reduced thorium flux at higher nitric acid concentrations. At lower acid/nitrate

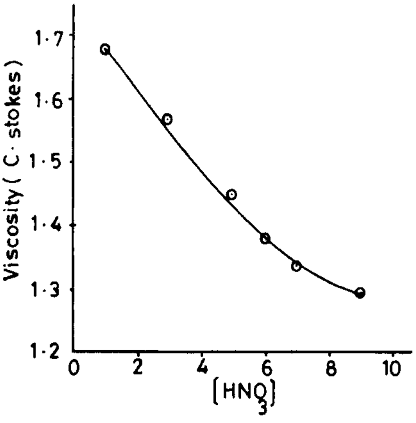

FIG. 8 Effect of nitric acid concentration on viscosity of TBP organic solution. [TBP] = 1.823. 25°C.

ions concentrations there is a co-ion effect which pushes the reaction forward. This behavior has also been observed for other metal ions by Korkisch (10) and Chaudry (5).

Figure 9 indicates diffusion coefficient variation with a change in nitric acid concentration. Starting from 1 to 3 mol·dm^{-3} acid concentration, the diffusion coefficient falls, increases up to 6 mol·dm^{-3}, and finally drops as the acid concentration increases further. The important point is that like other actinides, stoichiometric requirements of thorium extraction appear to be less straightforward where it has been demonstrated that two molecules of extractant are required for each actinide atom. This is according to Siddall (11), but Katzin (12) and Siddall (13) favored a thorium complex with 3 extractant molecules. So a thorium complex may be formed with 2 or 3 extractant molecules. It may be possible that at 3 mol·dm^{-3} acid concentration, $Th(NO_3)_4 \cdot 3TBP$ is a more favorable species than $Th(NO_3)_4 \cdot 2TBP$, and due to large size of the Th species, its diffusion coefficient decreases. At higher nitric acid concentrations (>6 mol·dm^{-3}), a $HTh(NO_3)_5$ type species develop. However, these species can also form a complex with TBP as $HTh(NO_3)_5 \cdot n\mathrm{TBP}$. Figure 6 indicates the variation in the permeability coefficient with an increase in acid concentration. This has been determined from a plot of $-\ln C_t/C_0$ versus time. The permeability coefficient of Th(IV) ions transported through the membrane is given by

$$\frac{pAt}{lV} = -\ln\frac{C_t}{C_0} \tag{14}$$

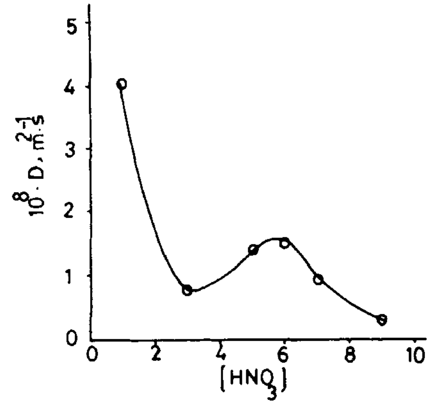

FIG. 9 Diffusion coefficient of Th in the membrane as a function of HNO_3 concentration in the feed. [TBP] = 1.823. 25°C.

The value of p from the slope of the line of a $-\ln C_t/C_0$ versus t plot can be obtained from Eq. (14).

The Th ions permeability variation with change in acid concentration follows the same trend as that of the flux variation. Thus up to 6 mol·dm^{-3} acid concentration species like $Th(NO_3)_4 \cdot nTBP$ permeable to basic Na_2CO_3 strip solution are there. As a result of further acid concentration rise, $TBP \cdot HNO_3$ may begin to form and compete with Th complex to reduce Th(IV) ions flux.

EFFECT OF TBP CONCENTRATION

The effect of TBP concentration on the transport of Th(IV) ions through a membrane is shown in Fig. 10. Flux (J) versus time plots of Th ions at different time intervals and TBP concentrations in the membrane plotted against time are shown in Fig. 11. In all these plots the flux is shown initially to be high and decreases with time. In the beginning, higher Th(IV) ions concentration makes the flux faster, which decreases with a decrease in Th(IV) ions concentration. This behavior may also be attributed to the deterioration of the membrane with respect to TBP molecules which may diffuse into aqueous solutions. The initial Th ions flux against TBP concentration plot is given in Fig. 12. TBP concentration variation also has an effect on the D.C. of Th(IV) ions and the viscosity of the membrane liquid as shown in Figs. 13 and 14, respectively. Figure 15 shows the effect of TBP concentration on D.C. According to Fig. 12, the flux of Th(IV) ions

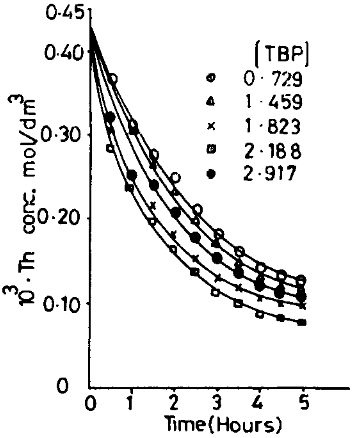

FIG. 10 Th ions transport with TBP concentration variation in the membrane phase.

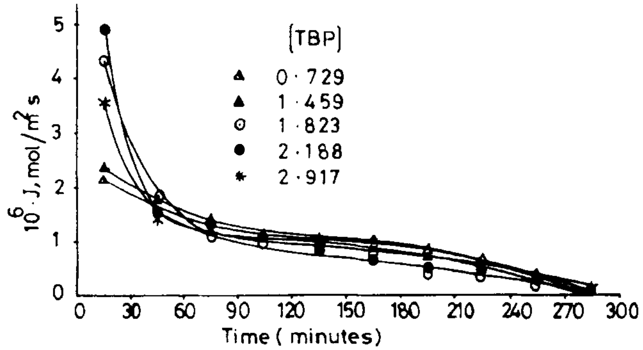

FIG. 11 Th flux as a function of time at various TBP concentrations in the membrane.

increases with an increase in TBP concentration and reaches a maximum at 2.188 mol·dm^{-3} TBP concentration and then decreases gradually with a further increase in TBP concentration. According to Eq. (10), *J* is proportional to [TBP]. The decrease in flux observed is due to an increase in viscosity of the membrane liquid which provides enhanced resistance to diffusion of the Th(IV) complex with TBP. Viscosity and diffusion coefficient are related indirectly. An increase in viscosity will reduce the diffusion coefficient of the diffusing species inside the membrane, and this is to be expected. Actually, this fall in diffusion coefficient results in low flux values beyond 2.188 mol·dm^{-3} TBP concentration.

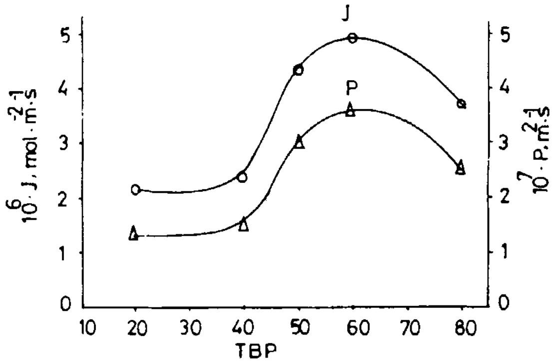

FIG. 12 Flux, *J*, and permeability, *P*, as a function of TBP concentration in the membrane.

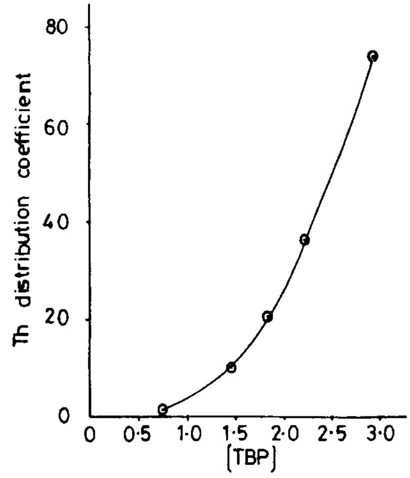

FIG. 13 Effect of TBP concentration on distribution coefficient. Initial [Th] = 0.431 × 10^{-3}, 25°C, $[HNO_3]$ = 6.0.

Data of viscosity and flux variation with TBP concentration helps in estimating the number of extractant (TBP) molecules involved in complex formation with Th ions by using Eq. (11) from the plot of log ηJ against log[TBP] as given in Fig. 16. The value of the slope of the plot varies and has a value of nearly 0.5 for a TBP concentration range of 0.729 to 1.459

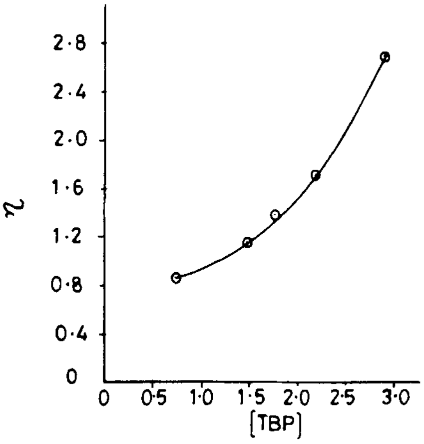

FIG. 14 Effect of TBP concentration on viscosity. Initial [Th(IV)] = 0.431 × 10^{-3}, $[HNO_3]$ = 6, 25°C.

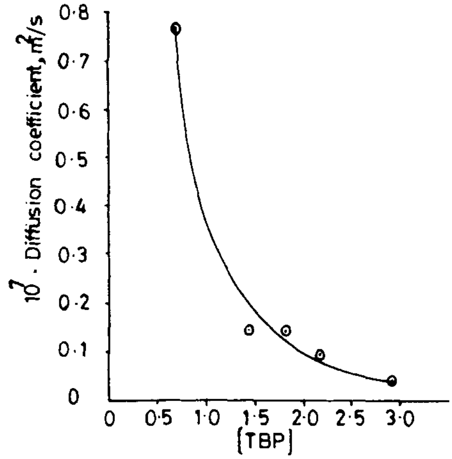

FIG. 15 Effect of TBP concentration on diffusion coefficient. Initial [Th(IV)] = 0.431 × 10^{-3}, 25°C, $[HNO_3]$ = 6.

mol·dm^{-3}. After this TBP concentration the slope range increases to a value of 3.18 and then decreases to a value of nearly 0.5. This indicates that with a change in TBP concentration, the number of extractant TBP molecules changes. The slope value of 3.18 indicates that complexes with 2, 3, or 4 extractant molecules are formed. Below 1.459 mol·dm^{-3} TBP,

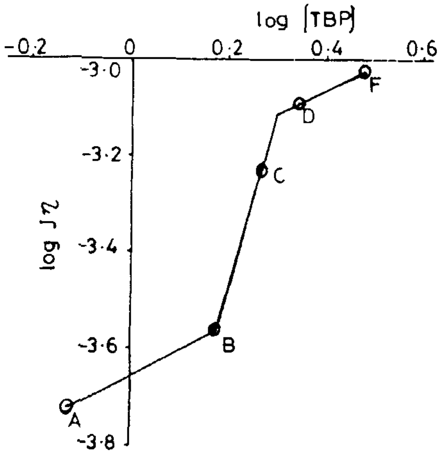

FIG. 16 Plot of log $J\eta$ versus log[TBP].

less than one molecule of extractant is involved in complex formation. Like other actinides, stoichiometric requirements of Th(IV) ions extraction appear to be less straightforward, where it has been demonstrated that 2 molecules of the extractant associate with each actinides atom. This is according to Siddall (11, 13) and Katzin (12), who favored a thorium complex with 3 extractant molecules. Data of Siddall (11) also favor a Th(IV) complex with 3 extractant molecules.

A complex with more extractant molecules will diffuse slowly through a membrane, thereby affecting the flux value of the Th ions. It is probable that at a low concentration of TBP the complexes with a smaller number of extractant molecules will be favored, but at higher concentrations more than 2 extractant molecules are involved. This may be another reason why flux decreases with a rise in TBP concentration. This is also in accordance with the data of McKay and his associates (14) who have shown that only 2 extractant molecules complex with TBP at high dilution.

The permeability coefficient of Th(IV) ions has also been determined as a function of TBP concentration (Fig. 12), with a trend similar to that of Th ions flux variation with TBP concentration change.

EFFECT OF TEMPERATURE

The transport of Th(IV) ions has been indicated at different temperatures (15, 20, 25, 30, and 35°C) in Fig. 17. The concentration of TBP in the membrane liquid phase was kept constant at 2.188 mol·dm^{-3} and the

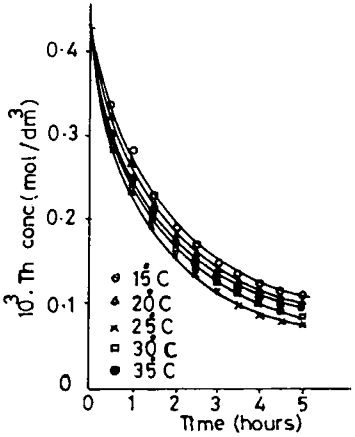

FIG. 17 Plot of Th concentration versus time at various temperatures.

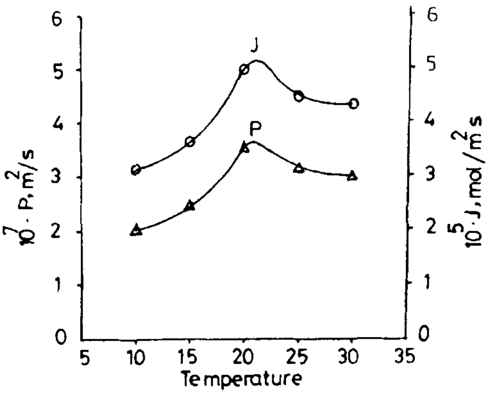

FIG. 18 Flux, *J*, and permeability, *P*, as a function of temperature.

nitric acid concentration in the feed at 6 mol·dm^{-3}. The initial flux, *J*, was evaluated from these plots as shown in Fig. 18. The maximum flux was observed at 25°C.

The decreases in D.C. for a higher initial Th(IV) concentration are due to separation of the organic solvent into two phases, a Th-rich phase and a Th-free phase. For a low initial concentration of Th(IV) ions, this effect does not persist and D.C. increases with a rise in temperature due to an endothermic Th–TBP complex formation. The decrease in D.C. as well as in flux of Th(IV) ions above 25°C may be due to phase separation.

Permeability of Th ions (Fig. 18) has the same trend as does that for flux variation with temperature.

MECHANISM OF TRANSPORT

Figure 19 shows the scheme for Th(IV) ions transport from aqueous HNO_3 solution to aqueous Na_2CO_3 solution across a TBP–benzene based supported liquid membrane. The extraction of Th(IV) ions by TBP is based on the formation of a $Th(NO_3)_4 \cdot n$TBP complex, where *n* has been found to fall in the 0.5–3.18 range with TBP concentration variation. The complex dissociates after contact with Na_2CO_3 from the stripping phase. The released TBP molecules diffuse back to the feed side of the membrane due to the concentration gradient developed for TBP inside the membrane.

It can be seen from Fig. 19 that thorium ions are stripped with carbonate solution as $Na_2 \cdot Th(CO_3)_3$ species. The Th and nitrate ions are transported

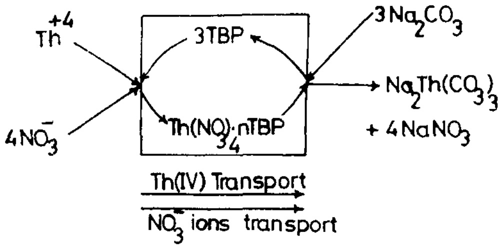

FIG. 19 Mechanism of Th ions transport coupled with nitrate ions from feed acid aqueous phase to alkaline phase with TBP as complexing agent.

in the same direction. Therefore, the Th ions transport follows the coupled co-ions membrane transport phenomenon.

CONCLUSION

It is concluded that the maximum flux of Th(IV) ions through a supported liquid membrane is attained with a TBP concentration of 2.188 mol·dm^{-3} in the membrane liquid, a feed solution acidity of 6 mol·dm^{-3}, and at 25°C for the temperature range studied. The stoichiometry of the Th(IV) complex with TBP in the liquid membrane system has been found to be similar to that of other actinides. The TBP molecules involved in complex formation are found in the 0.5 to 3.18 range. At higher TBP concentrations a mechanism of complex formation with 3 or 4 extractant molecules is possible, and at lower TBP concentrations complexes with 2 molecules of TBP or less may exist. Maximum values of flux and permeability are at 25°C. The value of the distribution coefficient has been found to increase with an increase in HNO_3 concentration in the aqueous feed solution and TBP concentration in the organic membrane phase. The diffusion coefficient of the Th–TBP complex varies with acid concentration.

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