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Coupled Transport of Zr(IV) through Tri-*n*-butylphosphate–Xylene-Based Supported Liquid Membranes

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Abstract

The transport of Zr(IV) through tri-*n*-butylphosphate-xylene-based liquid membranes, supported in a polypropylene hydrophobic microporous film, has been studied. The concentration of HNO_3 in the feed solution and tri-*n*-butylphosphate (TBP) carrier in the membrane were varied, and the flux and permeability coefficients were determined. The optimum conditions found for maximum flux were determined to be 10 mol/dm^3 HNO_3 and 2.93 mol/dm^3 TBP with a flux value of 12.9×10^{-6} mol · m^{-2} · s^{-1}. The solvent extraction study revealed that 1.25 to 3.5 protons are involved in zirconium transport, and that two molecules of TBP are involved in the complex formation. The value of protons involved varies with acid concentration. The zirconium ion transport is coupled with nitrate ions transport.

INTRODUCTION

Zirconium is used in the nuclear industry because of its low neutron cross-section. The metal is invariably associated with its twin hafnium, which has a high neutron absorption coefficient. For its use in nuclear processes, hafnium is required to be reduced to less than 100 ppm in zirconium. This purification was very difficult, particularly on an industrial scale, until the advent of solvent extraction, which allows purification to

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the required extent, but not however, in an absolutely pure form. There are at present three solvent extraction systems used for this purpose. These methods are TBP-HNO_3 (*1, 2*), MIBK-thiocyanate (*3, 4*), and amine sulfate (*5*). The TBP–HNO_3 method is the most exploited method. Liquid membrane separation is a new technique (*6, 7*) and has not been tried for the separation of zirconium from hafnium. The estimation of flux under various conditions for a given membrane system is therefore the basic way to test this separation method. The purpose of the present work is basically therefore to study two parameters, i.e., nitric acid concentration in the feed solution and carrier concentration in a supported liquid membrane, to determine the flux of the zirconium ions. The distribution coefficient for zirconium(IV) ions between the membrane feed aqueous phases and membrane solutions has also been determined in order to study the stoichiometry of the Zr–TBP complex formed and the mechanism of zirconium(IV) transport through the supported liquid membrane.

EXPERIMENTAL

Liquid Membrane Cell

The liquid membrane cell used during this study was fabricated from Prespex and is described elsewhere (*8*). It consisted of two half cells, each having a capacity of 106 cm^3. The membrane, of effective area 12.56 cm^2, was fixed in between these two half cells with two stirrers fixed at the top to agitate the liquid confined in the half cells. The cell was equipped with outlets for draining the liquids and collecting the samples, and with separate feed and stripping agent inlets.

Membranes

The supported liquid membrane (SLM) used consisted of tri-*n*-butylphosphate as the carrier or complexing agent, dissolved in xylene and supported in polypropylene film (Celgard 2400) from Celanese Corporation (USA). The polymer film was soaked in the TBP–xylene solution for more than 24 h before use. It has a pore size of the order of 0.02 μm, a thickness of 25 μm, and a porosity of 38%.

Analytical Instruments

For the analysis of zirconium(IV) in solution form, a UV/visible spectrophotometer Model 634S from Varian, Australia, and a pH meter, Model Metrohm 605, with magnetic stirrer from Metrohm Herisau, Switzerland, were used.

Chemicals and Reagents

The following chemicals and reagents were used in all the experimental work for the zirconium(IV) transport study.

Chemicals. GPR-grade zirconyl chloride ($ZrOCl_2$), tri-*n*-butylphosphate, and 99.99% pure, laboratory reagent-grade xylene were from BDH. 4-(2-Pyridy-azo-resorcinol) (PAR) and sodium hydroxide were of AnalR grade from E. Merck. All chemicals were used without further purification.

Reagents. *Zirconium(IV) Feed Solution.* 0.1221 g zirconyl chloride was dissolved in nitric acid of given molarity in a 250 cm^3 volumetric flask to prepare 250 $\mu g/cm^3$ (250 ppm) solution.

TBP Solution. The required concentrations of TBP solutions for the SLM were prepared by diluting a given volume of this chemical in a known volume of xylene.

PAR Solution. 0.1% PAR solution was prepared by dissolving 250 mg of the monosodium salt of PAR in 250 cm^3 distilled deionized water.

Disodium Tetraborate Solution. 12.7677 g of this chemical were dissolved in distilled deionized water in a 250 cm^3 volumetric flask after adjusting to pH 9 with 0.1 mol/dm^3 sodium hydroxide to prepare 0.25 mol/dm^3 disodium tetraborate solution.

Analytical Method for Zr(IV)

The method used for analysis was derived from Ref. 9. Standard solutions of Zr(IV) (10, 20, 30 40, 50 ppm) were taken in separate beakers.

1 cm^3 of the PAR solution and 10 cm^3 of disodium tetraborate were added, and the solution pH was adjusted to 9. The volume of the solutions was made up to 25 cm^3, and the absorbance was measured against the reagent blank at 530 nm wavelength. A plot of the absorbance against concentration furnished the calibration line. 100 μL of the samples was taken and handled in the same way up to the last step. The concentrations of these samples were read from the calibration line. The relative standard deviation was ±1.0 at 30 μg zirconium.

Solvent Extraction

Equal volumes of the aqueous zirconium(IV) in the various nitric acid concentrations and the organic solution were shaken for 15 min in separatory funnels and allowed to stand for 20 min. The aqueous layer was separated from the organic layer and analyzed spectrophotometrically.

Flux Measurements

The membrane was fixed in the cell. The feed and stripping solutions were placed in the half cells. The solutions in both compartments were kept stirred at a rate greater than 1500 rpm to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. All the experiments were performed at room temperature (26 ± 2°C). Samples (1 cm^3) from the feed and stripping solutions were taken after the given time intervals and analyzed as described above. For zirconium(IV) the pH of the stripping solution was also measured at different time intervals to measure the proton flux in certain cases. The stripping phase used in all the experiments was pure distilled deionized water.

THEORETICAL IDEAS ABOUT Zr(IV) TRANSPORT THROUGH SLM

Zirconium ions in the aqueous acidic solution exist in the form of zirconyl (ZrO^{2+}) ions. These ions in the solvent extraction system may be extracted into the organic phase after their complexation with TBP. The complex formation reaction (*10*) is described as

$$\mathrm{ZrO^{2+}_{aq} + 2H^{+}_{aq} + 4NO^{-}_{3\,aq} + 2TBP_{org} \rightleftharpoons [Zr(NO_3)_4 \cdot 2TBP]_{org} + H_2O_{aq}} \tag{1}$$

This chemical reaction is supposed to take place at the membrane interface on the feed solution side. The coupled transport of the zirconyl ions through the membrane may be represented as given in Fig. 1. Keeping in view Reation (1), the equilibrium constant K_{Zr} for the reaction can be represented as

$$K_{\mathrm{Zr}} = \frac{[\mathrm{Zr(NO_3)_4 \cdot 2TBP}]_{\mathrm{org}}}{[\mathrm{ZrO^{2+}}]_{\mathrm{aq}}\,[\mathrm{H^+}]^2_{\mathrm{aq}}\,[\mathrm{NO_3^-}]^4_{\mathrm{aq}}\,[\mathrm{TBP}]^2_{\mathrm{org}}} \tag{2}$$

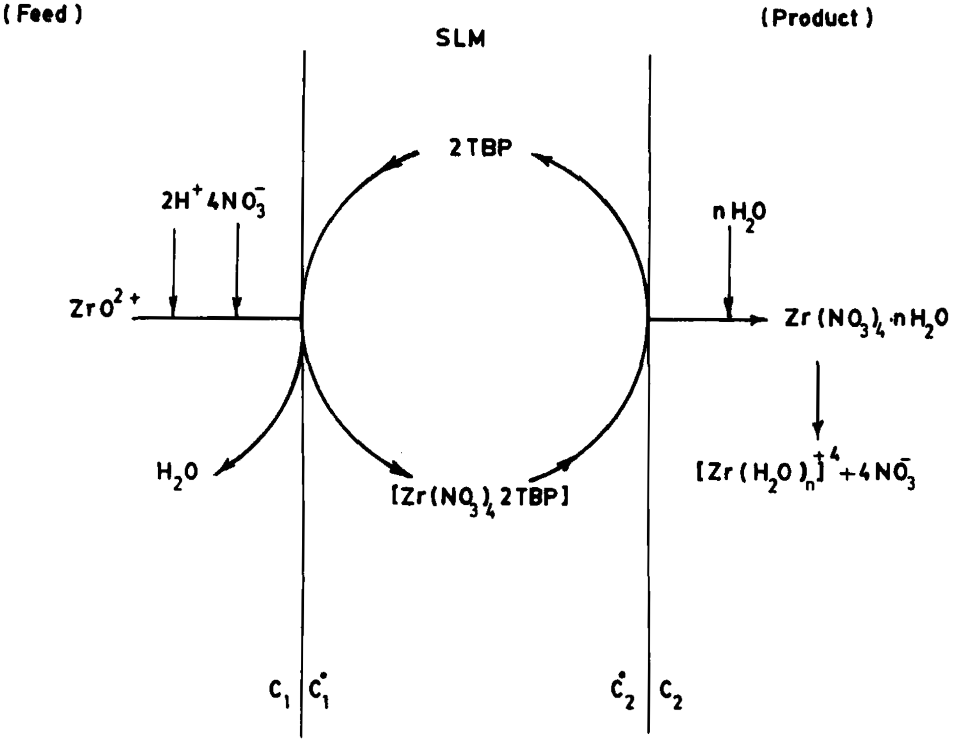

FIG. 1. Possible scheme for zirconium(IV) transport from HNO_3 solution to H_2O through TBP-xylene-based supported liquid membrane.

If the distribution coefficient for zirconium(IV), λ, is introduced into Eq. (2), it becomes

$$K_{\mathrm{Zr}} = \frac{\lambda G}{[\mathrm{H}^+]^2_{\mathrm{aq}}[\mathrm{NO}_3^-]^4_{\mathrm{aq}}[\mathrm{TBP}]^2_{\mathrm{org}}} \tag{3}$$

where G is the factor which collectively represents the activity coefficient for all the species involved.

Equation (3) can be rewritten as

$$\lambda = \frac{K_{\mathrm{Zr}}[\mathrm{H}^+]^2_{\mathrm{aq}}[\mathrm{NO}_3^-]^4_{\mathrm{aq}}[\mathrm{TBP}]^2_{\mathrm{org}}}{G} \tag{4}$$

In dilute solutions the activity of the involved species approaches unity, which gives

$$\lambda_{G\to 1} = K_{\mathrm{Zr}}[\mathrm{H}^+]^2_{\mathrm{aq}}[\mathrm{NO}_3^-]^4_{\mathrm{aq}}[\mathrm{TBP}]^2_{\mathrm{org}} \tag{5}$$

According to Fick's law, the flux of a given species is directly proportional to the concentration gradient, dC/dx, so the flux of ions, J, can be given as

$$\begin{aligned} J &\propto dC/dx \\ &\propto (C_1 - C_2)/l \end{aligned} \tag{6}$$

where x represents the linear distance and C_1 and C_2 are, respectively, the concentrations of zirconium(IV) in the feed and in the stripping sides inside the membrane. l is the membrane thickness.

If D is the difference coefficient of zirconium(IV) in the membrane of the above system, then the proportionality relation can be converted into

$$J = \frac{D(C_1 - C_2)}{l} = \frac{D(C_1\lambda_1 - C_2\lambda_2)}{l} \tag{7}$$

where λ_1 and λ_2 are the distribution coefficients of the given species (metal ions in the present case) between the membrane and the aqueous phase on the feed and stripping sides into the membrane. C_1 and C_2 are the concentrations of the metal ions in the bulk solution on the membrane interface. The permeability coefficient, P, is related to the diffusion coefficient and the distribution coefficient through the relation

$$P = D\lambda \tag{8}$$

Therefore, if $\lambda_1 = \lambda_2 = \lambda$,

$$J = \frac{P(C_1 - C_2)}{l} \tag{9}$$

Taking into consideration the porosity, ε, of the membrane, Eq. (7) can be modified to

$$J = \frac{D\varepsilon\lambda(C_1 - C_2)}{l} \tag{10}$$

If the metal ion carrier complex breaks at the stripping side of the membrane interface and the metal ions transfer to the stripping phase is fast, then $C_2 \rightarrow 0$ and can be neglected in Eq. (10), which gives

$$J = \frac{D\varepsilon\lambda_1 C_1}{l} \tag{11}$$

Combining Eqs. (5) and (11):

$$J = \frac{D\varepsilon[\mathrm{H}^+]^2_{\mathrm{aq}}[\mathrm{NO}_3^-]^4_{\mathrm{aq}}[\mathrm{TBP}]^2_{\mathrm{org}} \cdot C_1 \cdot K_{\mathrm{Zr}}}{l} \tag{12}$$

According to the Wilke-Change relation (*11*),

$$D = \frac{K'T}{\eta} \tag{13}$$

where K' is a constant, T is the temperature (in degrees Kelvin), and η is the viscosity of the liquid in the membrane phase.

From Eqs. (12) and (13):

$$J = \frac{AT[\mathrm{H}^+]^2_{\mathrm{aq}}[\mathrm{NO}_3^-]^4_{\mathrm{aq}}[\mathrm{TBP}]^2_{\mathrm{org}}C_1}{\eta} \qquad (14)$$

where A is a new constant, or

$$\log J = \log AT - \log \eta + 2 \log [\mathrm{H}^+]_{\mathrm{aq}} + 4 \log [\mathrm{NO}_3^-]_{\mathrm{aq}} + 2 \log [\mathrm{TBP}]_{\mathrm{org}} + \log C_1 \qquad (15)$$

In deriving Eq. (15) it has been assumed that there are 2 H^+ ions, 4 nitrate ions, and 2 TBP molecules involved through Reaction (1). If the feed concentration C_1 is kept constant, which is nearly possible for a short time, then the stoichiometry of the complex formation can be determined, provided that the effect of only one variable is studied while keeping the others constant. If this is not true, then the general equation dealing with the flux of Zr(IV) ions will be given by Eq. (15).

$$\log J = \log AT - \log \eta + n \log [\mathrm{H}^+]_{\mathrm{aq}} + m \log [\mathrm{NO}_3^-]_{\mathrm{aq}} + q \log [\mathrm{TBP}]_{\mathrm{org}} + \log C_1 \qquad (16)$$

where n, m, and q represent the actual number of protons, nitrate ions, and TBP molecules taking part in the metal ions transport.

From Eq. (9), when C_2 is neglected:

$$P = \frac{Jl}{C_1} = \frac{dC}{dt}\,\frac{Vl}{AC} \qquad (17)$$

where A and V are the membrane effective area and the volume of the feed, respectively.

Integration of this equation within the limits of time, t, and concentration C, i.e., $t = t_0$ to $t = t$ and $C = C_1$ to C_{1t}, where C_{1t} and C_1 are the concentrations of the metal ions in the feed at a given time t and at the start:

$$-\ln \frac{C_{1t}}{C_1} = \frac{PAt}{Vl} \qquad (18)$$

Value of the permeability coefficient can be determined from the plot of $-\ln C_{1t}/C_1$ against time t, from the slope of the straight line, so that

$$P = \frac{Vl \cdot d(\ln C_{1t}/C_{1}]}{A} \tag{19}$$

If P is known, the diffusion coefficient of the metal ion–carrier complex in the membrane can be calculated by using Eq. (8). λ for the metal ions can be determined by using solvent extraction data. The contribution of λ and D toward the overall transport of metal ions through the membrane can thus be assessed.

RESULTS

The results obtained during this study for Zr(IV) transport through SLM are recorded in Figs. 2 to 11. Basic experimental results indicating Zr(IV) transport against the concentration gradient are shown in Figs. 2 and 3. The effect of nitric acid concentration on the transport of Zr(IV) through a TBP–xylene-based liquid membrane is shown in Figs. 4 and 5, and the results obtained that indicate the effect of TBP concentration in the membrane on the transport of this metal ion are shown in Figs. 6 to 8. The distribution data for this metal ion in the aqueous and organic phases (distribution coefficient and relation between λ and HNO_3 concentration) are shown in Figs. 9–11.

DISCUSSION

Zirconium(IV) Transport Against Concentration Gradient

Curve I in Fig. 2 is based on the absence of zirconium(IV) in the stripping solution initially, and Curve II is the result of a similar experiment with 250 μ/cm^3 zirconium(IV) in both the feed and product solutions at the start. Figure 2 shows that the transport of metal ions is affected to some extent by the presence of zirconium(IV) in the stripping solution and the flux is reduced, but it is clear from Figs. 2 and 3 that the zirconium(IV) ions are transported against their concentration gradient through the supported liquid membrane.

Effect of Nitric Acid Concentration

Figure 4 indicates the variation in the concentration of the feed solution with respect to zirconium as a function of time. The zirconium concentra-

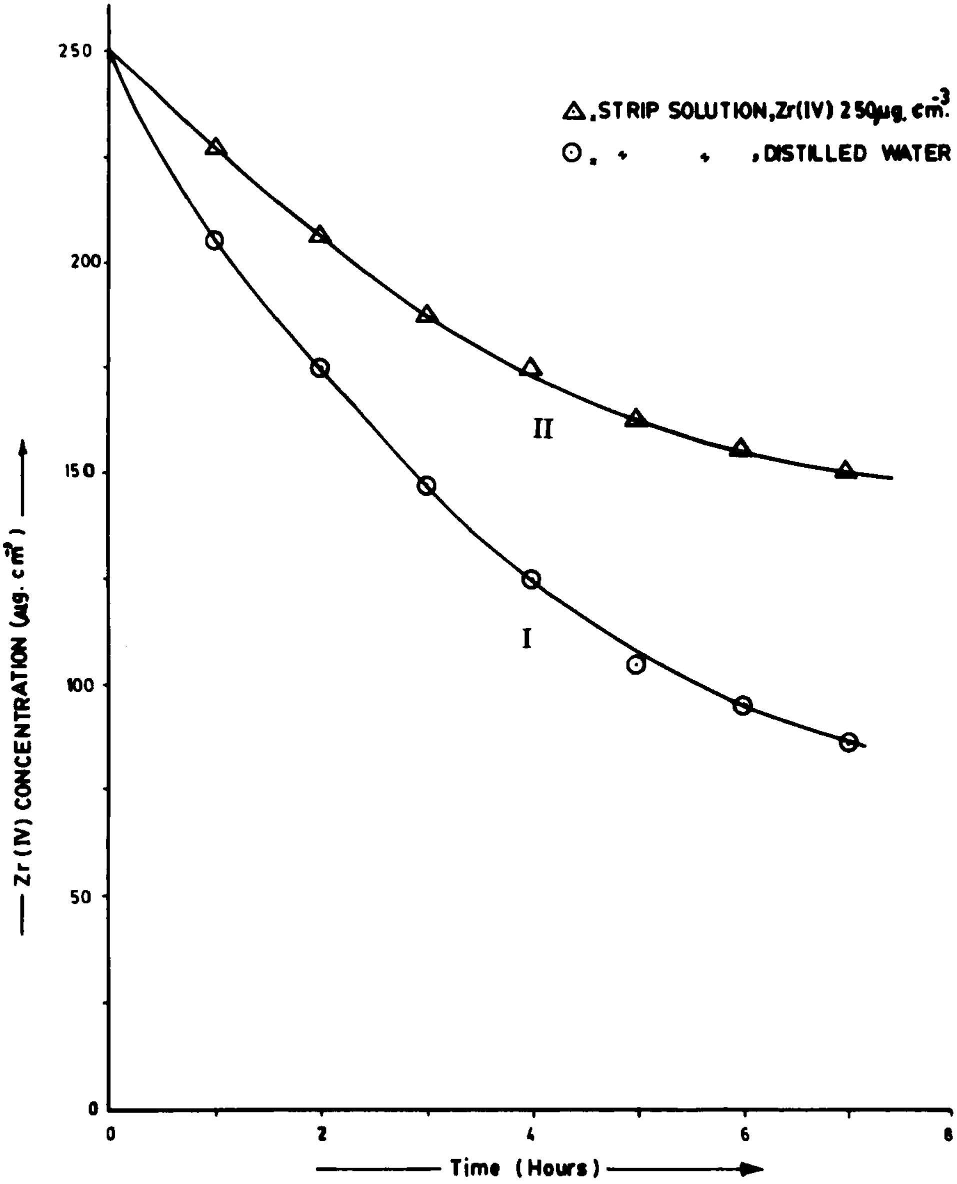

FIG. 2. Zr(IV) concentration as a function of time in the feed solution.

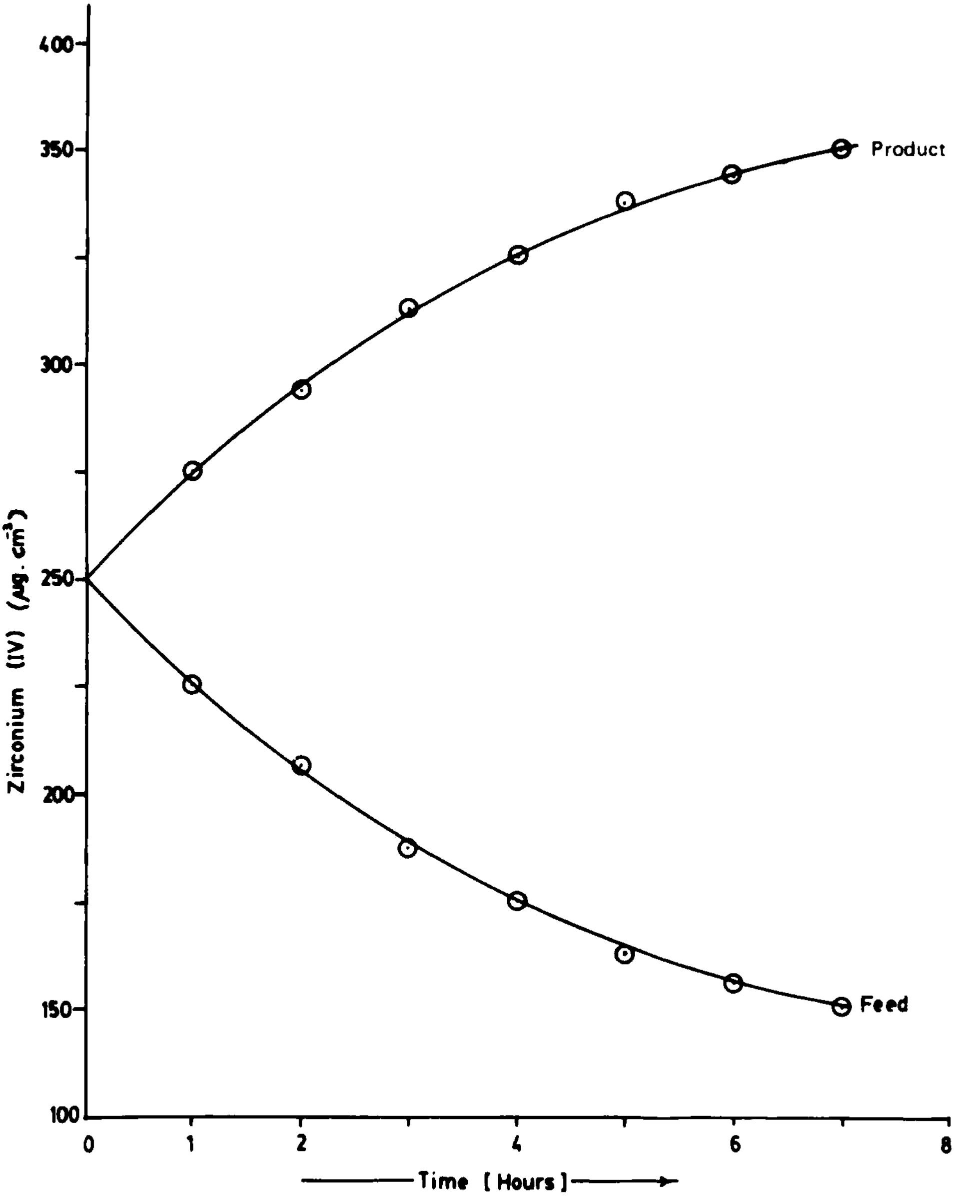

FIG. 3. Zr(IV) concentration in the feed and product solutions as a function of time.

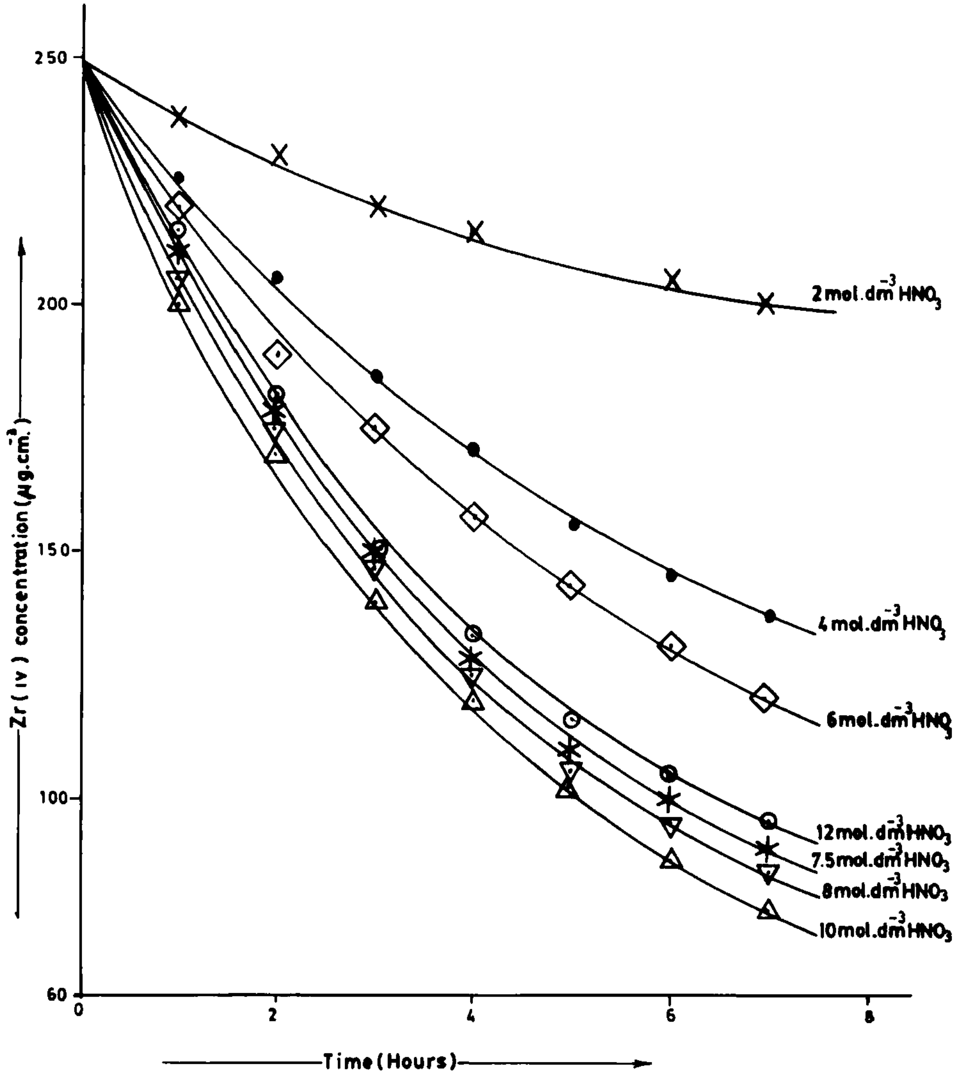

FIG. 4. Concentration versus time for Zr(IV) at varying HNO_3 concentrations in the feed solution.

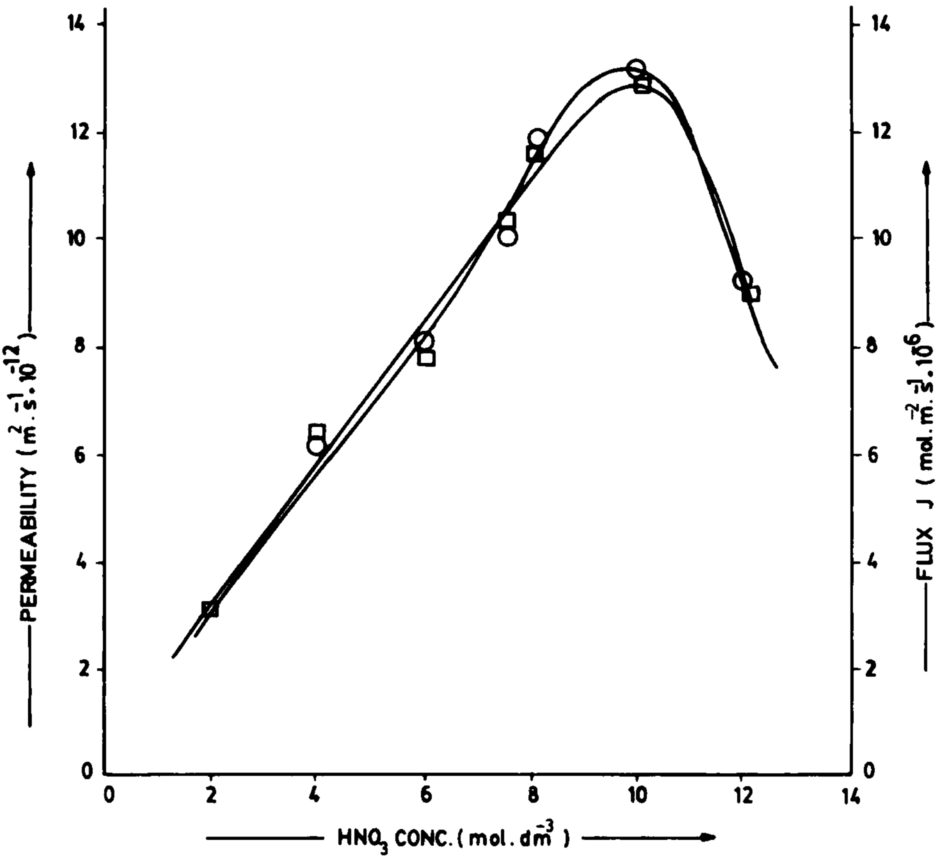

FIG. 5. Permeability and flux versus HNO_3 concentration for Zr(IV) transport: (○) permeability, (□) flux.

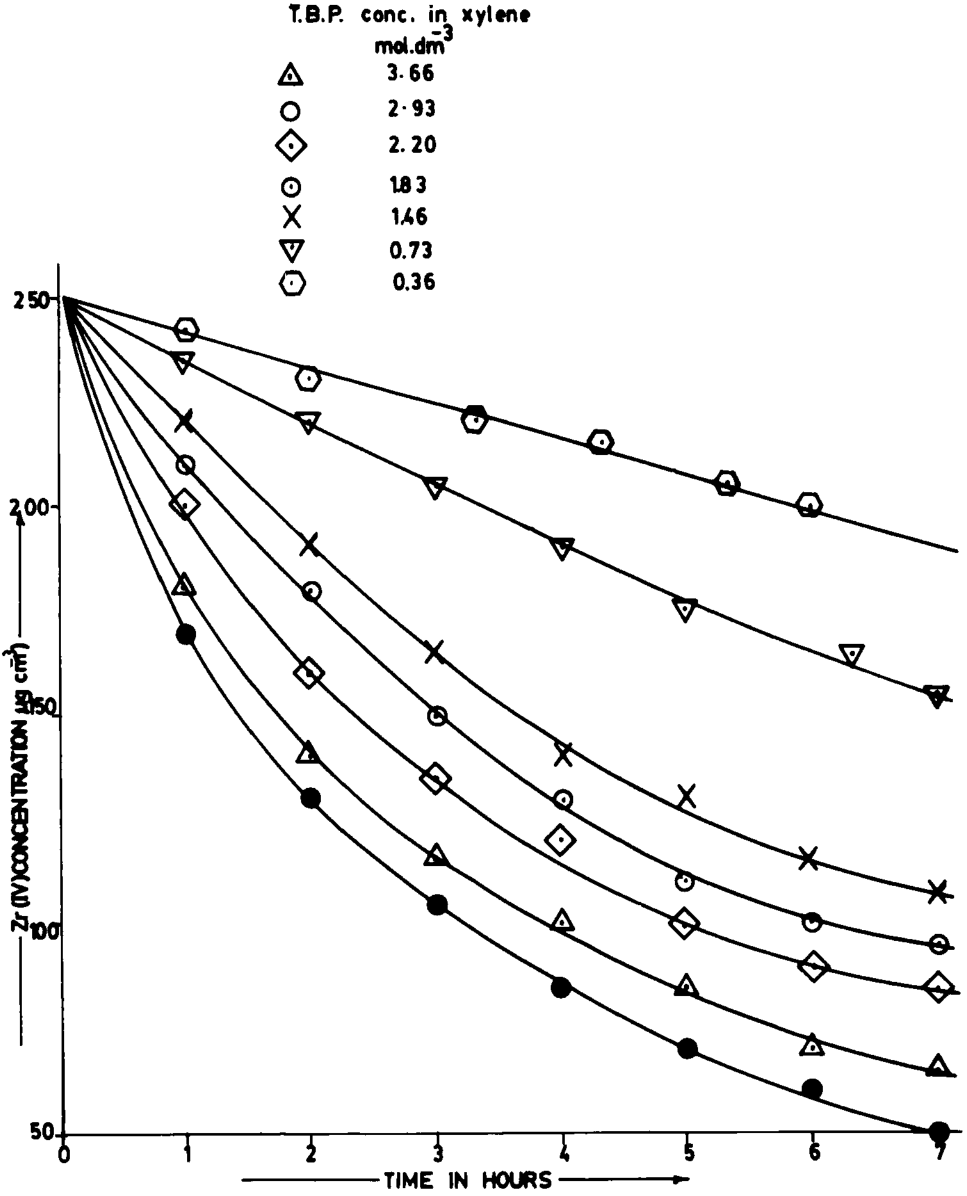

FIG. 6. Concentration versus time for Zr(IV) at different TBP concentrations in xylene.

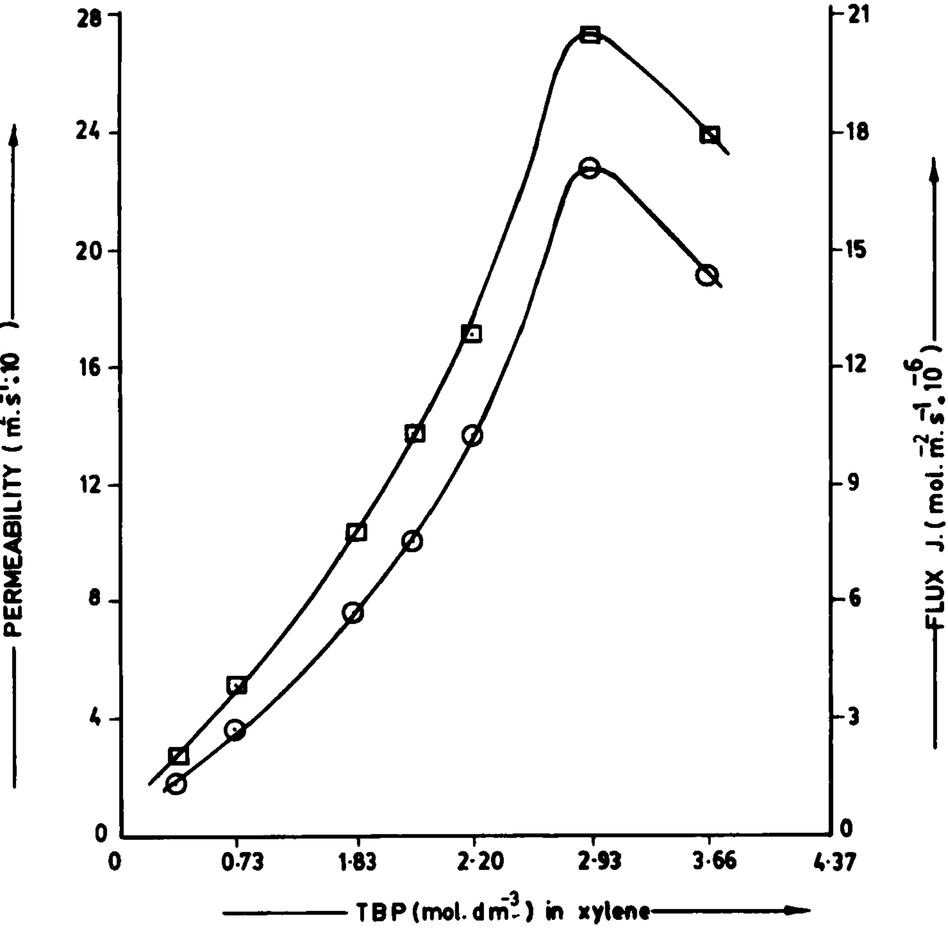

FIG. 7. Permeability and flux versus TBP concentration in xylene for Zr(IV) transport: (O) permeability, (□) flux.

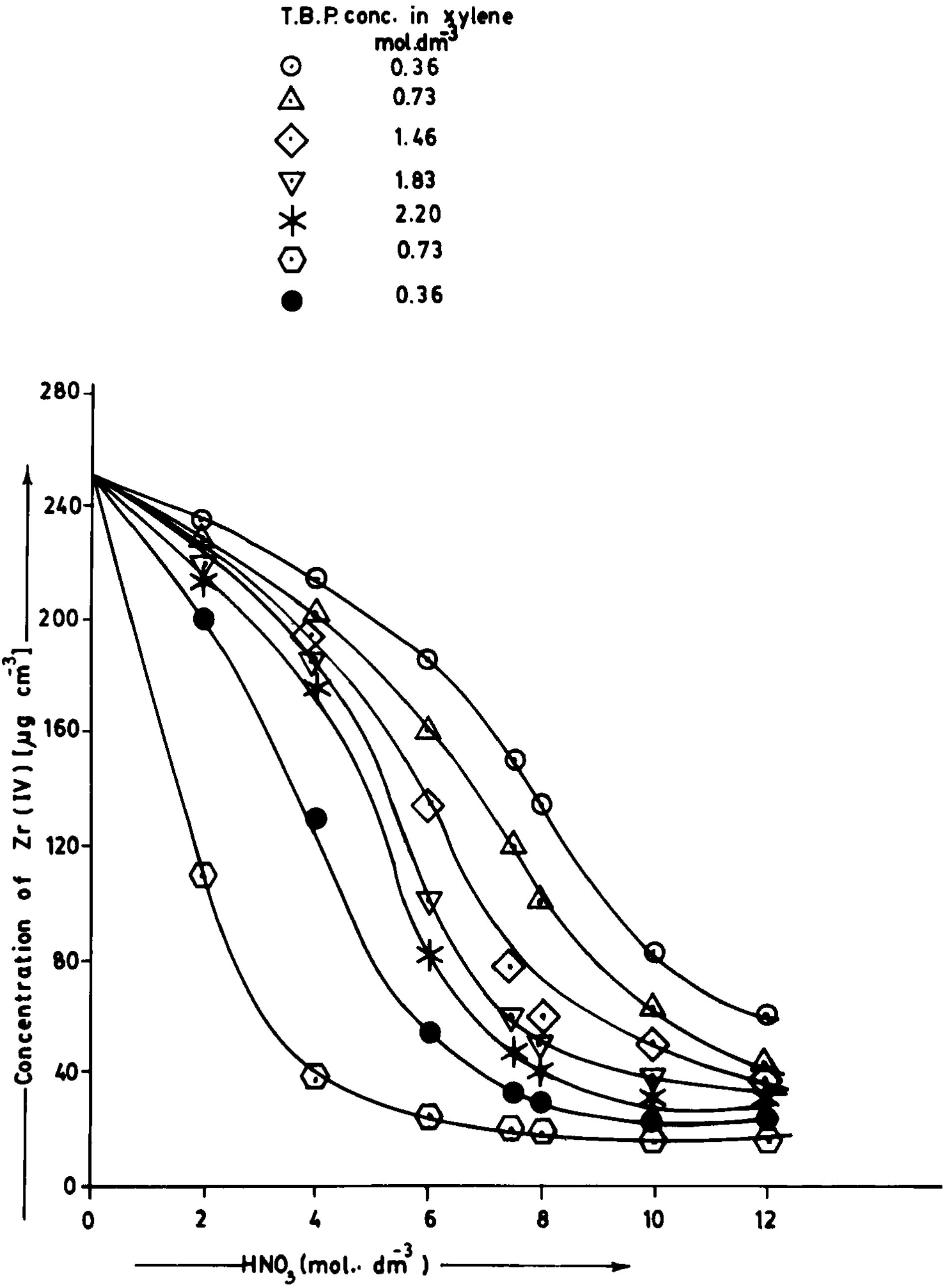

FIG. 8. Zr(IV) concentration in the organic phase as a function of HNO$_3$ concentration.

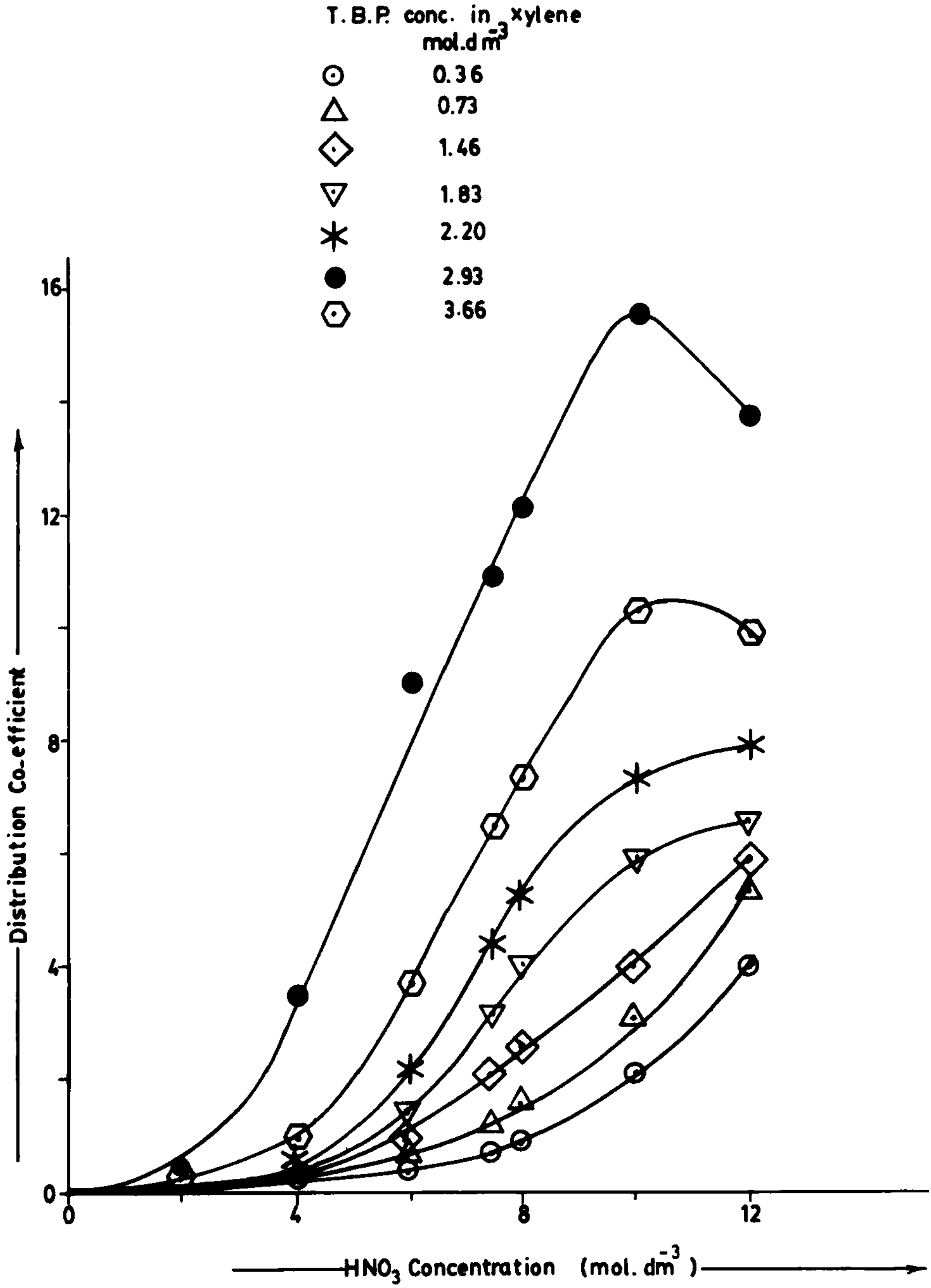

FIG. 9. Distribution coefficient versus HNO_3 concentration at different TBP concentrations in xylene. Initial Zr(IV) concentration: 250 μm/cm^3.

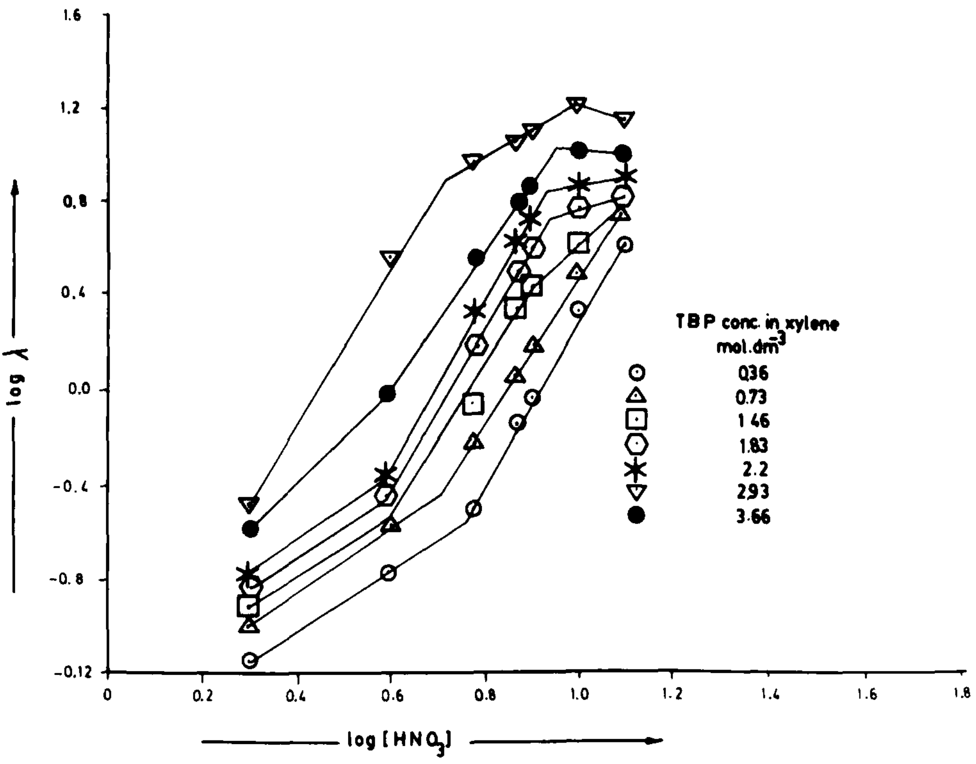

FIG. 10. Log λ versus log [HNO_3].

tion in the feed compartments decreases with time from 250 μg/cm^3 to less than 50 μg/cm^3 in 6 h through an overall membrane effective area of 12.56 cm^2. The figure also shows that up to 10 mol/dm^3 HNO_3 in the feed, the amount transferred within a given time interval increases, but beyond that it decreases. The same effect is shown in Fig. 5 by a plot of flux and permeability versus HNO_3 concentration in the feed at a fixed concentration of TBP in the membrane. The reasons for low flux at these acid concentrations may be the higher viscosity of TBP at higher acid concentrations and increases in the flux of the protons at faster rates at such concentrations.

Another reason for this may be the formation of a species like [$H_nZrO(NO_3)_{2+n}$] which causes the flux of acid transfer to increase. The study of the transport of acid through such membranes is not reported here. It does take place and it does affect the transport of zirconium.

From a plot of log λ versus log [HNO_3] (Fig. 10) (data for λ taken from a solvent extraction study), it is clear that the slope of the curves increases with an increase in concentration, indicating more nitric acid molecules

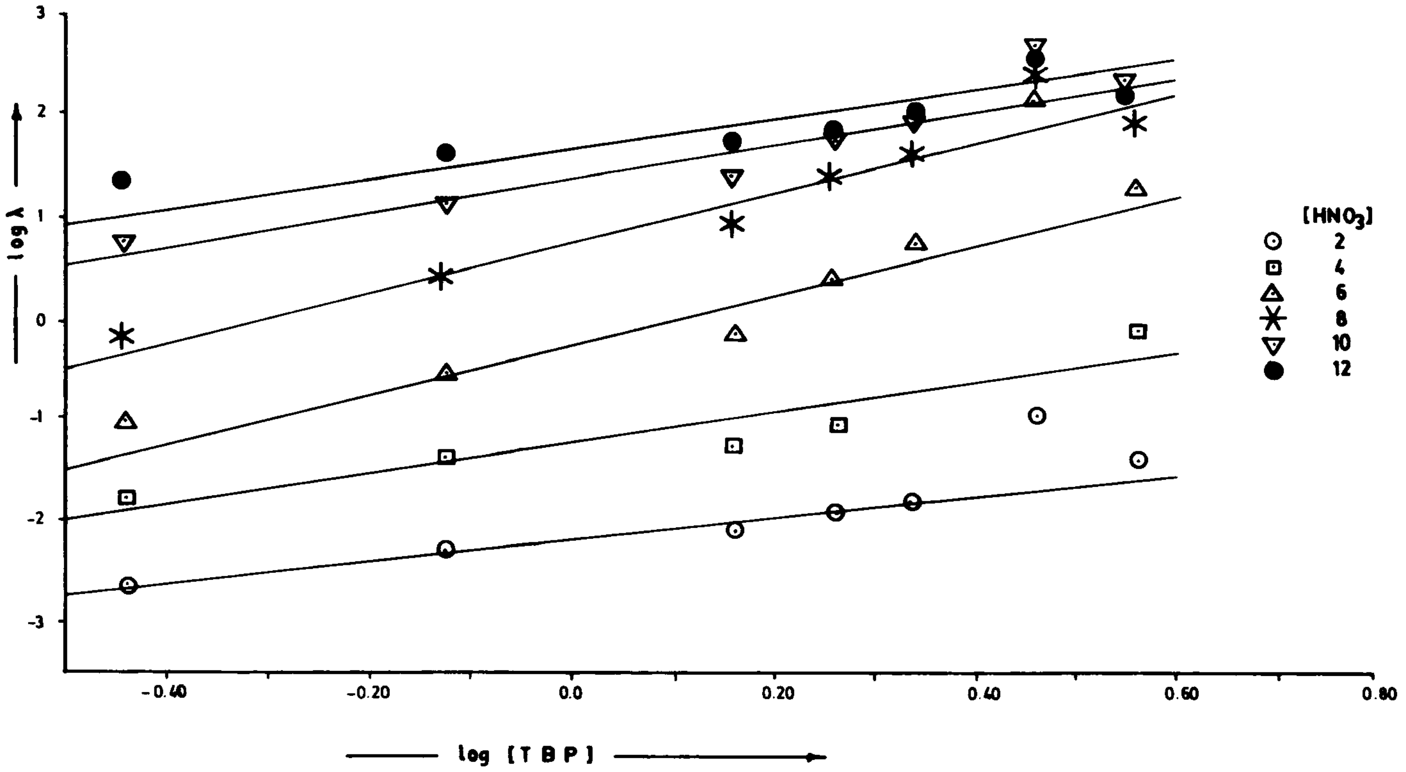

FIG. 11. Log [TBP] versus log λ at different HNO$_3$ concentrations.

or protons are involved at higher acid concentrations in the feed. The species described above and $HNO_3 \cdot TBP$ are therefore expected. The value of the slope of the line up to 7–8 *M* nitric acid concentration is 1.25 at all TBP concentrations in the organic phase, while the value of the slope increases to 3.5 above this concentration level of HNO_3, indicating that at lower acid concentrations the protons involved are fewer compared to their values at higher acid concentrations in the complex formation of zirconium ions with TBP.

Effect of TBP Concentration

Zr(IV) transport through a liquid membrane is enhanced by increasing TBP concentration in the supported liquid membrane (Fig. 6). The same results are depicted in Fig. 7, which indicates there is an increase in the flux and permeability of zirconium(IV) ions with an increasing concentration of TBP in the liquid membrane up to 2.93 mol/dm^3. After that, the flux and the permeability decrease with increasing TBP concentration in the liquid membrane. A similar behavior is observed in Fig. 9, based on data from a solvent extraction study, where increasing the TBP concentration increases λ, reaching a maximum value at a TBP concentration of 2.93 mol/dm^3 in xylene as in the case of flux and the permeability coefficient. Above this concentration its value decreases (Fig. 7). This may be explained on the basis of the rate of complex formation of zirconium(IV) with TBP and its extraction into the organic membrane phase at the feed–solution interface. An increase in TBP concentration gives rise to more Zr(IV)–TBP complex formation, and hence an increase in its concentration gradient within the membrane along the membrane thickness. The decrease in the flux of Zr(IV) with increased TBP concentration beyond 2.93 mol/dm^3 may be explained as due to an organic phase viscosity increase. This parameter is still to be studied. Similar behavior has been indicated during UO_2^{2-} transport through a TBP–kerosene oil-based liquid membrane (*8*). An increase in viscosity means more friction or resistance to Zr(IV)–TBP complex transport.

In a plot of log λ versus log [TBP] (Fig. 11), the slope of the straight lines varies from 0.45 to 2.25, indicating that up to two molecules are involved in the complex formation reaction during the solvent extraction process.

The flux data can be used to study the stoichiometry of the complex formed if the viscosity of the membrane phase constituting the liquid is known and the initial concentration of the metal ions present in the feed solution are sufficiently large that the feed solution concentration is not greatly affected during a short time interval. This is possible by using Eq. (15).

Values of the permeability coefficient P and the distribution coefficient λ are given in Table 1 and Fig. 7. By using Eq. (8), values of D, the diffusion coefficient, have been calculated, and they are listed in Table 1. Here the value of λ is greater than that of D, hence the distribution coefficient makes a larger contribution toward the permeability or flux of metal ions. To improve the flux, both these parameters have to be increased. For this purpose, carriers having higher distribution coefficient values must be used. The feed solution chemical conditions must also be improved.

TABLE 1
Diffusion Coefficient as a Function of HNO_3 in the Feed and TBP Concentration in the Membrane

a) Effect of HNO_3 on D with 1.83 mol/dm^3 TBP in the Membrane

HNO_3 concentration (mol/dm^3)	λ	P [(cm^2/s) × 10^{-8}]	$D = P/\lambda$ [(cm^2/s) × 10^{-8}]
2	0.14	2.99	21.35
4	0.34	6.12	18.00
6	1.48	8.12	5.48
8	3.17	11.90	3.75
10	5.94	13.19	2.22
12	6.58	9.26	1.40

b) Effect of TBP on D with 8 mol/dm^3 HNO_3 Concentration in Feed

HNO_3 concentration (mol/dm^3)	λ	P [(cm^2/s) × 10^{-8}]	$D = P/\lambda$ [(cm^2/s) × 10^{-8}]
0.36	0.85	1.90	2.23
0.73	1.50	3.60	2.40
1.45	2.62	7.76	2.96
1.83	3.17	11.90	3.75
2.20	5.25	13.60	2.59
2.33	12.16	22.70	1.87

Mechanism of Zr(IV) Transport

When the zironyl ions (ZrO^{2+}) in the feed solution compartment come in contact with TBP supported in the liquid membrane in the presence of H^+ and NO_3^- ions (present in the feed), the following reaction takes place:

$$ZrO^{2+} + nH^+ + mNO_3^- + q\text{TBP} \rightarrow Zr(NO_3)_m \cdot q\text{TBP} + nH_2O$$

As revealed by this study, the numbers of protons and TBP molecules associated in the complex are greater than 3 and 2, respectively, depending on the nitric acid or TBP concentrations. The effect of nitrate ions on zirconium transport is still to be studied. If stoichiometric conditions are followed, there should be four associated nitrate ions in this complex.

As the $Zr(NO_3)_4 \cdot q\text{TBP}$ complex is formed on the membrane interface on the feed side, its concentration within the membrane on that side increases. This complex moves toward the stripping solution within the membrane under the concentration gradient. As the complex reaches the stripping solution side of the membrane, the following reaction takes place:

$$Zr(NO_3)_4 \cdot 2\text{TBP} + nH_2O \rightarrow Zr(NO_3)_4 \cdot nH_2O + 2\text{TBP}$$

The TBP molecules are left in the organic membrane phase, and the $Zr(NO_3)_4 \cdot nH_2O$ species enters the stripping solution. The concentration of the $Zr(NO_3)_4 \cdot 2\text{TBP}$ complex in the liquid membrane remains high on the feed side because the complex is continuously being formed on that side and its concentration remains very low on the stripping side. Then this complex breaks, releasing $Zr(NO_3)_4$ into the stripping solution. This complex thus moves continuously from the feed to the stripping solution side within the liquid membrane under its concentration gradient. The TBP molecules become free on the stripping solution side of the membrane, resulting in a TBP concentration gradient in a direction opposite to that of the metal ions, thus returning the TBP molecules from the stripping to the feed solution side within the membrane. As the nitrate ions move in the direction of zirconium ions, there is a coupled cotransport process. The acid concentration decrease on the feed side is due to the association of protons in the complex formation. The protons are neutralized (Fig. 1) in the stripping solution. As $Zr(NO_3)_4$ comes in contact with water on the strip solution side, it may again be converted into ZrO^{2+} ions as indicated in Fig. 1. This means that the protons consumed on the feed side are furnished to the stripping phase. Apart from that, at high acid concentrations the TBP–HNO_3-type complex may also be formed, thus ending acid transport at such nitric acid concentrations.

CONCLUSION

The coupled transport of Zr(IV) ions by using the tri-*n*-butylphosphate carrier in xylene, supported on microporous films, has been carried out. Basic parameters like acid concentration in the feed and carrier concentration in the membrane, which influence separation by liquid membranes, have been studied. Solvent extraction data for Zr(IV) ions under the given feed–solution conditions have also been obtained. It has been found that the flux of Zr(IV) ions increases with an increase in nitric acid in the feed and with the tri-*n*-butylphosphate concentration in the membrane. Maximum flux has been observed for these ions at 10 mol/dm^3 HNO_3 and 2.93 mol/dm^3 TBP concentration in the membrane (12.8×10^{-6} $mol/m^2 \cdot s$). The maximum distribution coefficient for Zr(IV) ions has been observed at similar acid and TBP concentrations, thus providing an explanation for the maximum flux of these ions under the liquid membrane conditions. The permeability and diffusion coefficients, which characterize the membrane in the case of Zr(IV) ions, have also been determined by using the mathematical equations and expermental data to conclude that the distribution coefficient value is greater than that of the diffusion coefficient, and hence the distribution coefficient contribution to the membrane performance is larger.

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