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Transport Study of Hafnium(IV) and Zirconium(IV) Ions Mutual Separation by Using Tri-*n*-butyl Phosphate–Xylene-Based Supported Liquid Membranes

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Abstract

A Hf transport study through supported liquid membranes has been carried out to determine flux and permeability data for this metal ion. Tri-*n*-butyl phosphate (TBP)–xylene-based liquid membranes supported in polypropylene hydrophobic microporous film have been used. These data for hafnium and the previous data for zirconium have furnished the Zr to Hf flux ratio (*S*) as a function of nitric acid and TBP concentrations of the order of 12 in a single stage at room temperature. Optimum conditions for the separation of these two metal ions appear to be 5–6 TBP mol/dm^3 HNO_3, concentrations $\leq$ 2.93 mol/dm^3, and 10°C. The value of *S* from an aqueous solution containing 2.4% Hf with respect to Zr has been found to be >125 at 10°C and 1.78 mol/dm^3 TBP concentration in the membrane. The technique appears to be feasible for purification of Zr with respect to Hf or vice versa.

1. INTRODUCTION

The separation of hafnium from zirconium is difficult due to the close chemical properties of these metal ions (*1*). Flux measurement and permeability determination studies have been performed and were reported in a previous paper for Zr(IV) ions using tri-*n*-butylphosphate (TBP)–xylene-based supported liquid membranes (SLM) (*2*). Similar work has been performed during the present study by using the same type of TBP–xylene liquid membranes supported in polypropylene film. Studies using ion-exchange resin separation have revealed that the two metal ions can be separated to the required extent (*3–5*). There are many other methods in which the solvent extraction technique has also been used successfully to

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obtain nuclear-grade purity of the zirconium metal, but the liquid membrane separation process has not previously been studied or applied for the purpose. In the present paper, data have been evolved with respect to hafnium, and experiments have been made for flux measurements. Permeability coefficients have been determined and compared to the same for zirconium. The separation factors that can be achieved by using this technique as a function of nitric acid concentration in the feed and TBP concentration in the membrane have also been determined.

The objective behind this work was to find the optimum conditions for separation of Hf from Zr ions. Hence, a scheme for the purification of these two metal ions was devised. The stripping phase in the present case is distilled, deionized water. The stripping solution can be used as the feed for the next stage.

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2. EXPERIMENTAL

2.1. Membranes

The membranes were made from tri-*n*-butylphosphate (TBP) dissolved in xylene in various concentrations, washing the solution with HNO_3 of given concentrations, and keeping the Celgard 2400 hydrophobic film in these solutions for more than 48 h.

2.2. Liquid Membranes Cell

The two compartment cell was made of Perspex. Its details were described previously (*6*). The volume of each cell compartment was 106 cm^3.

2.3. Chemicals

The following chemicals were used without further purification. TBP, 98% pure of GPR grade from BDH; xylene, 95% pure LG from BDH; hafnium oxide, 99% pure from Johnson & Matthey, England; zirconyl chloride GPR grade from BDH.

2.4. Reagents

The TBP–xylene solution was made by dissolving TBP in xylene to the required concentration. HfO_2 was first dissolved in HCl with a few drops of HF, heated to dryness, and finally dissolved in the required HNO_3 concentration.

2.5. Flux Measurements

The procedure for hafnium flux measurement was similar to that described in Ref. *2*. The hafnium ions were complexed with 4-(2-pyridylazo)-resorcinol and analyzed spectrophotometrically by using the method described in Ref. *2*. Inductively coupled plasma spectrometry was used to analyze Hf and Zr in mixed Hf and Zr solution samples.

3. THEORETICAL

It is assumed that the following chemical reaction, similar to that of zirconium, takes place when hafnium ions are extracted with TBP from nitric acid solutions:

$$HfO^{2+} + 2H^+ + 4NO_3^- + 2TBP \rightarrow Hf(NO_3)_4{\cdot}2TBP + H_2O \qquad (1)$$

This is a picture of the extraction process in the absence of knowledge about the different Hf species involved. In mass terms, the extraction

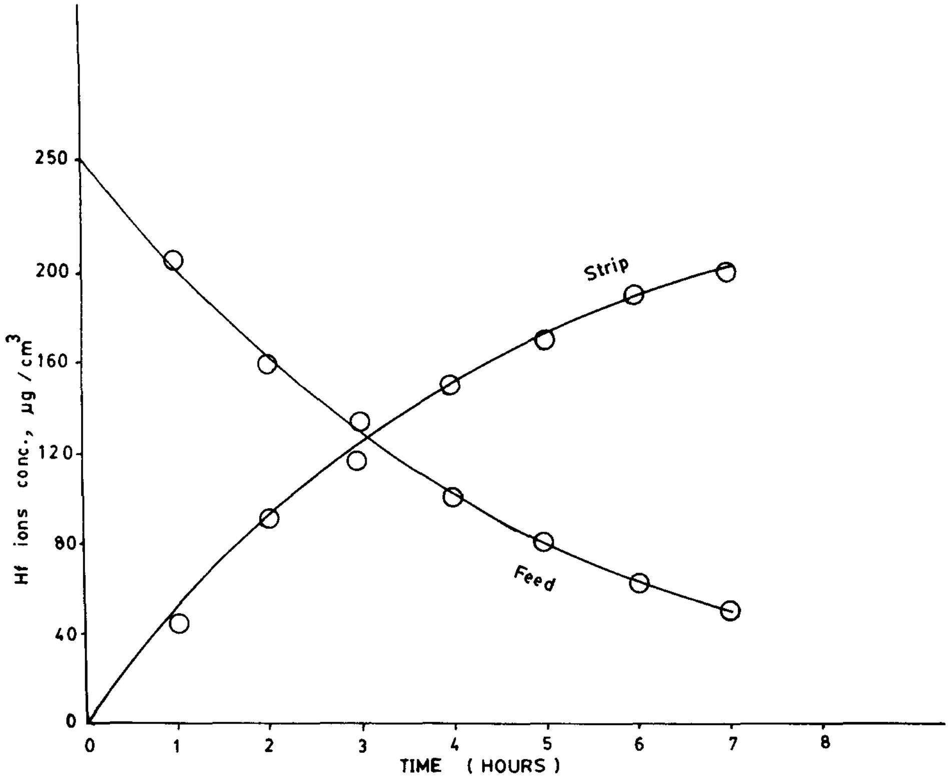

FIG. 1. Hf concentration in the feed and strip solution as a function of time.

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constant can be written as

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

G is a term based on the activity coefficients of the species involved. Because the chemical reaction is believed to be similar to that of zirconium,

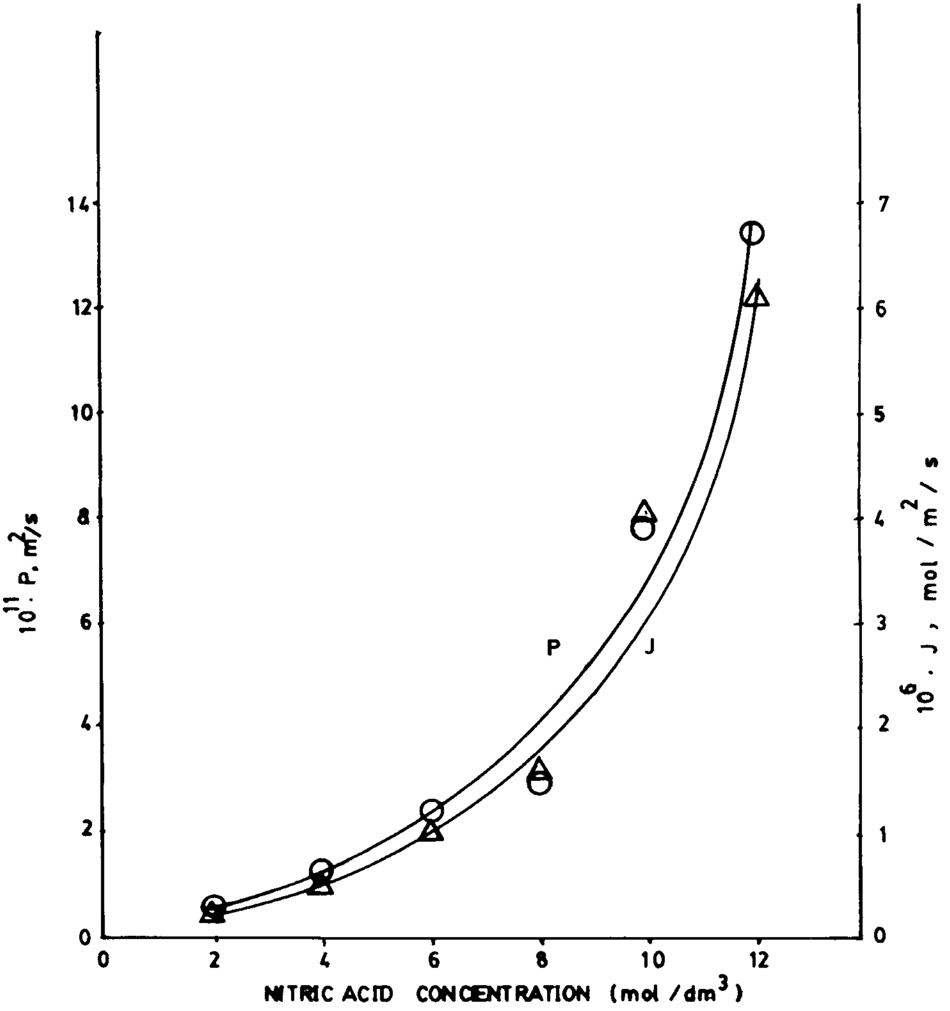

FIG. 2. Plots of J and P for Hf(IV) versus HNO_3 concentration.

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the equations derived in Ref. *2* may hold for hafnium transport studies as well. The following equation has therefore been derived:

$$\log J = \log At - \log \eta + n \log [\mathrm{H}^+] + m \log [\mathrm{NO}_3^-] + q \log [\mathrm{TBP}] + \log C_1 \quad (3)$$

where J is the flux of metal ions across the membrane, T and η the absolute temperature and viscosity of the membrane liquid phase, respectively, and C_1 is the membrane phase concentration of the feed compartment. Using this equation, if viscosity, temperature, nitrate ion concentration in the feed, and TBP concentration in the membrane phase are known, then one can determine the flux at a given feed solution concentration of metal ions, which allows the membrane area for a given plant to be fixed. The studies made here were under turbulent conditions, so in a plant the velocities

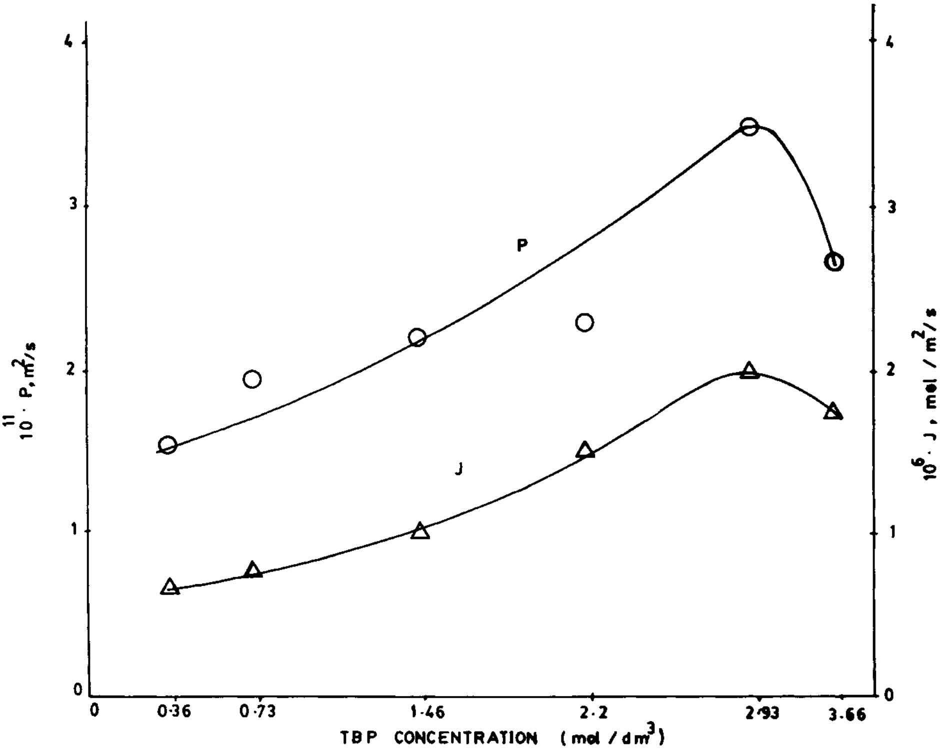

FIG. 3. Plots of J and P for Hf(IV) ions versus TBP concentration.

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should be fixed so that concentration polarization in the membrane phase is not allowed.

The relation between permeability and concentration in the feed solution as a function of time is described by

$$\ln (C_{1t}/C_1) = PAt/Vl \tag{4}$$

where C_1 and C_{1t} are the feed solution concentrations with respect to metal ions at times 0 and t, P is the permeability coefficient, V and A are the volumes of the feed compartment and the membrane area, respectively, and l is the membrane thickness. It is also known that

$$P = D\lambda \tag{5}$$

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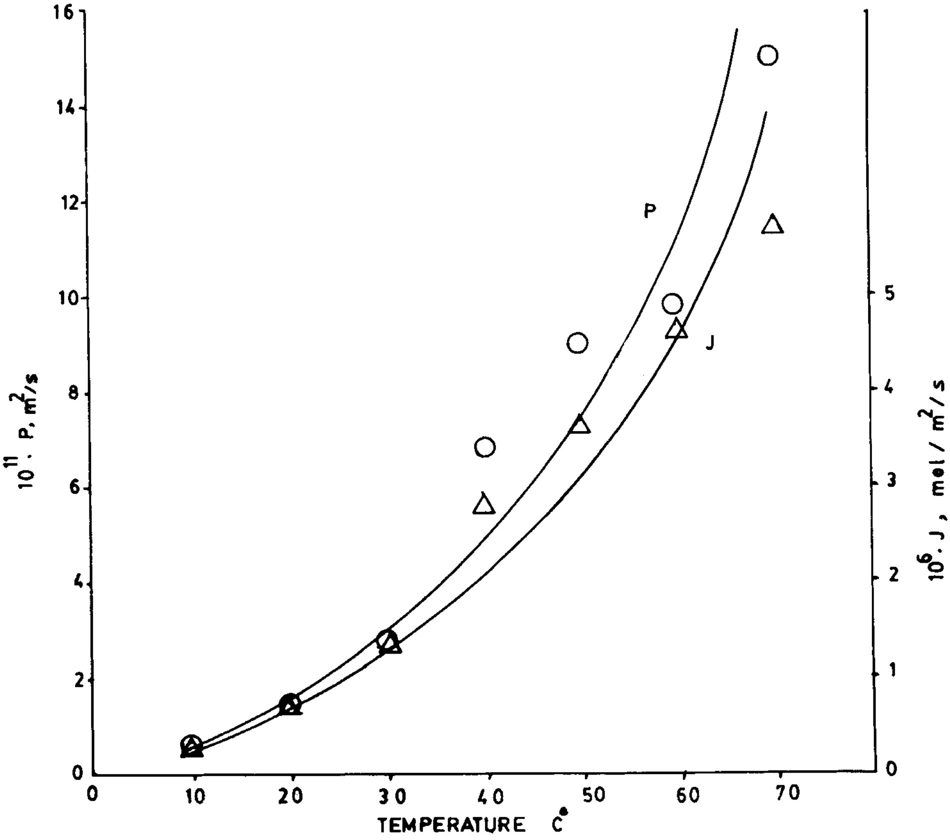

FIG. 4. Plots of J and P for Hf(IV) ions versus temperature.

where λ is the distribution coefficient from a solvent extraction study and D is the diffusion coefficient. So the value of D can be determined if λ is known, and P can be determined from the slope of the plot of ln C_{1t}/C_1 versus t by using Eq. (4).

Separation factor S, the ratio of Zr to Hf flux, can be determined from

$$S = J_{\mathrm{Zr}}/J_{\mathrm{Hf}} \tag{6}$$

where J_{Zr} and J_{Hf} represent Zr and Hf flux values.

4. RESULTS

The results for Hf transport from the present work are recorded in Figs. 1–10. Figure 1 is a plot of Hf ions concentration in the feed and strip

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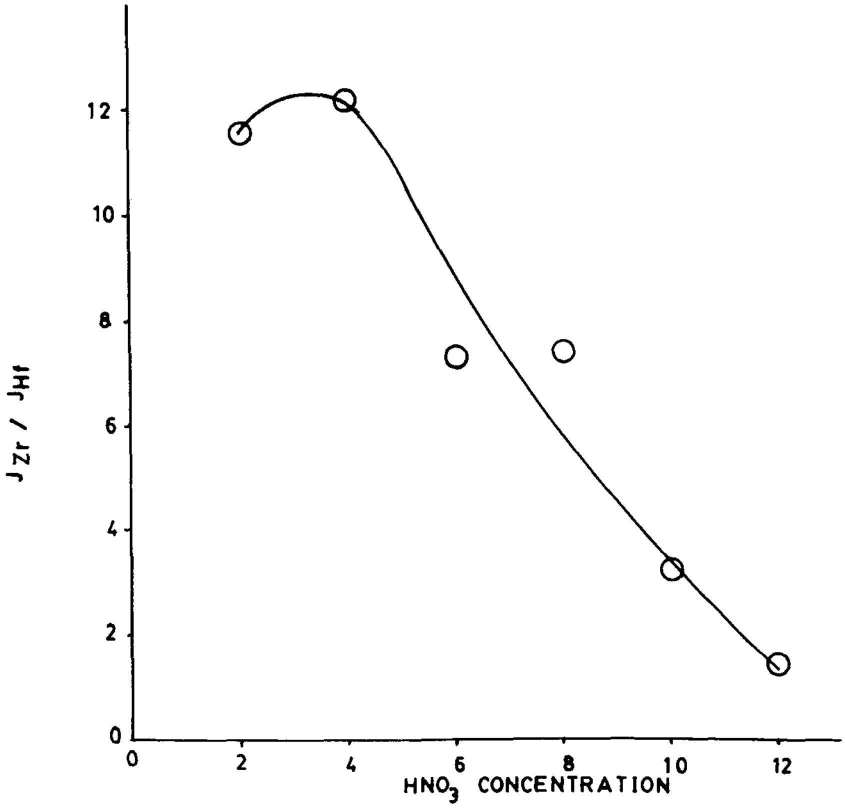

FIG. 5. Plot of $J_{\mathrm{Zr}}/J_{\mathrm{Hf}}$ at room temperature as a function of HNO$_3$ concentration.

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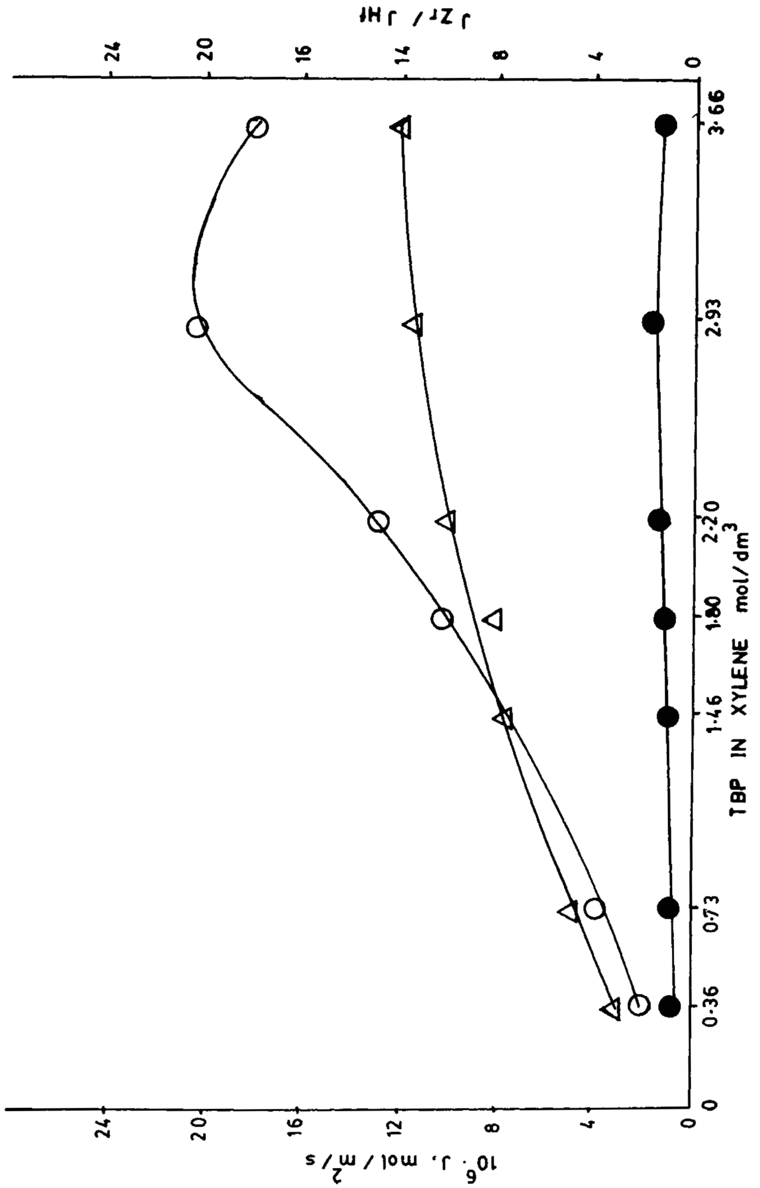

FIG. 6. Plots of *J* and *S* (separation factor) for Zr and Hf as a function of TBP concentration.

solutions against time to show that these ions can be transported across the membrane by using the coupled transport SLM technique. Plots of *P* and *J* versus HNO_3 concentrations in the feed solution are given in Fig. 2. Figure 3 shows plots of *J* and *P* against TBP concentration. Figure 4 presents plots of *J* and *P* versus temperature at various TBP concentrations. Figures 5 and 6 present the separation factors for Zr and Hf versus HNO_3 and TBP concentrations, respectively. In Fig. 7 the effect of temperature on flux of Hf and Zr and their separation factor have been recorded. Figure

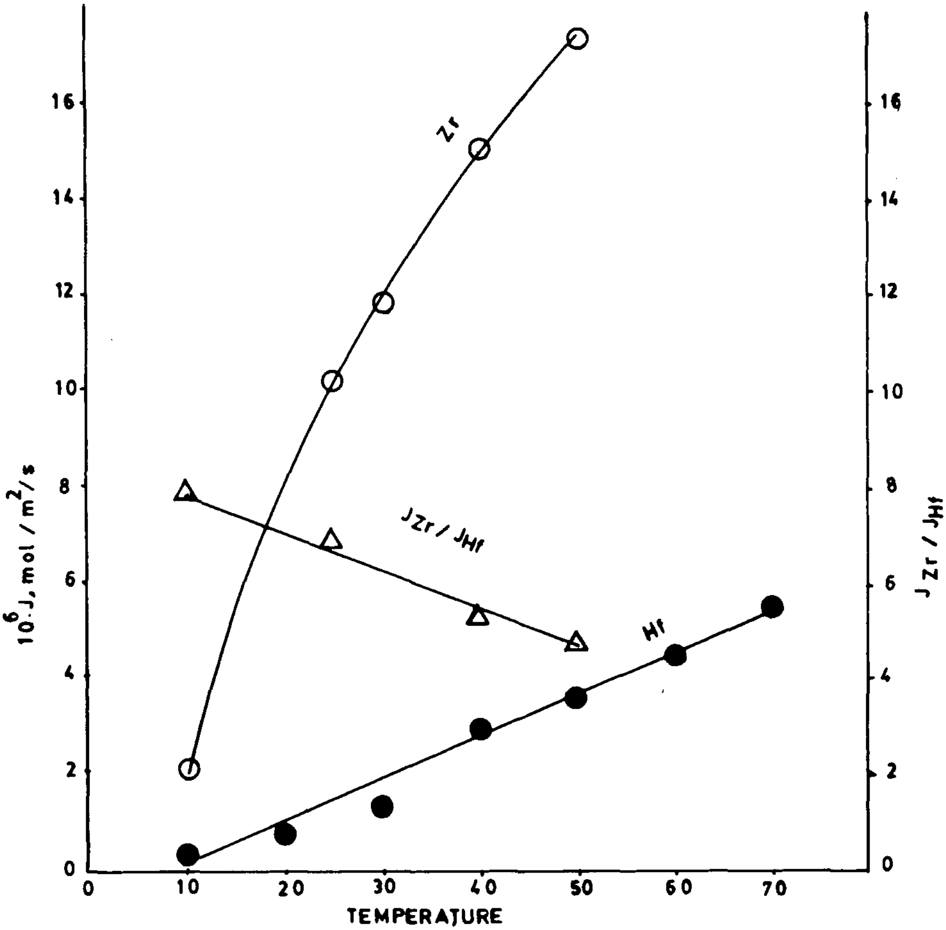

FIG. 7. Plots of J and J_{Zr}/J_{Hf} as a function of temperature at a TBP concentration of 1.83 mol/dm^3, a Zr concentration of 250 μg/cm^3, an Hf concentration of 250 μg/cm^3, and an HNO_3 concentration of 5 mol/dm^3.

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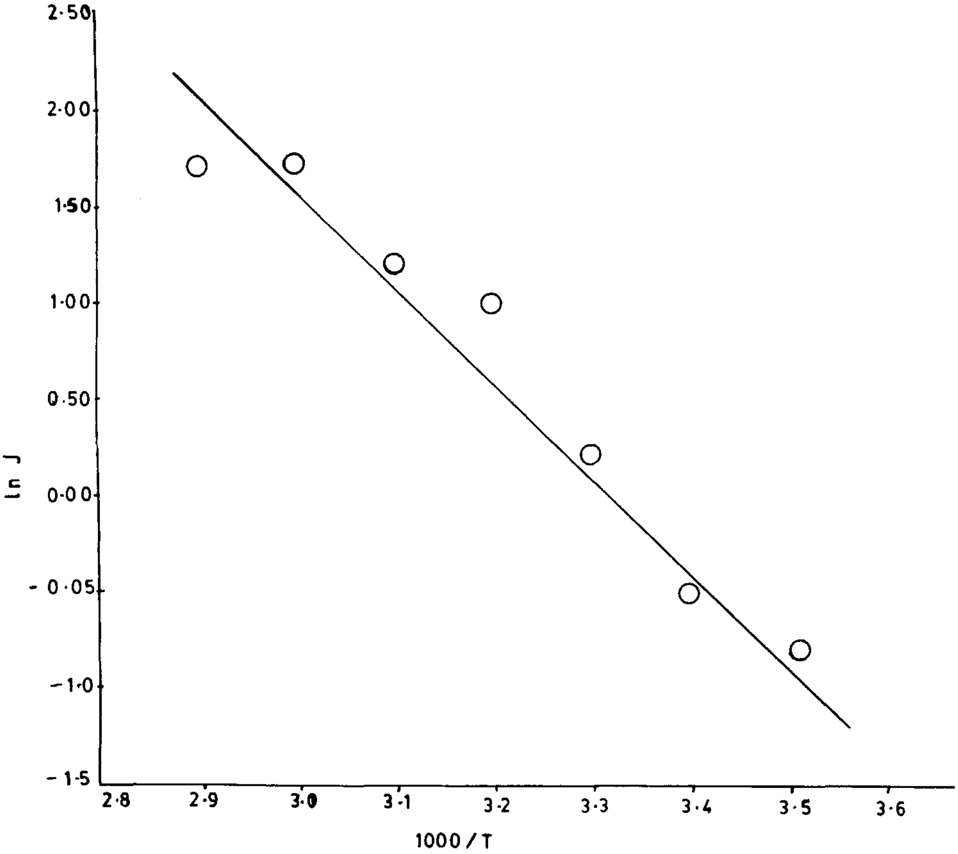

FIG. 8. Plot of ln J versus $1/T$ for Hf transport through TBP kerosene oil supported liquid membrane.

8 is a plot of ln J versus $1/T$, the absolute temperature. Figure 9 presents plots of Hf and Zr concentrations in the strip solution as a function of time at 10 and 15°C and 5.5 mol/dm^3 HNO_3 feed solution concentration. The same figure has plots of Hf and Zr concentrations in the feed as a function of time at 10°C and 10 mol/dm^3 HNO_3. Figure 10 contains J_{Zr}/J_{Hf} plots as a function of time.

5. DISCUSSION

It can be seen from Fig. 1 that Hf ions can be transported through a TBP–xylene-based supported liquid membrane, no doubt at a slower rate than the zirconium ions.

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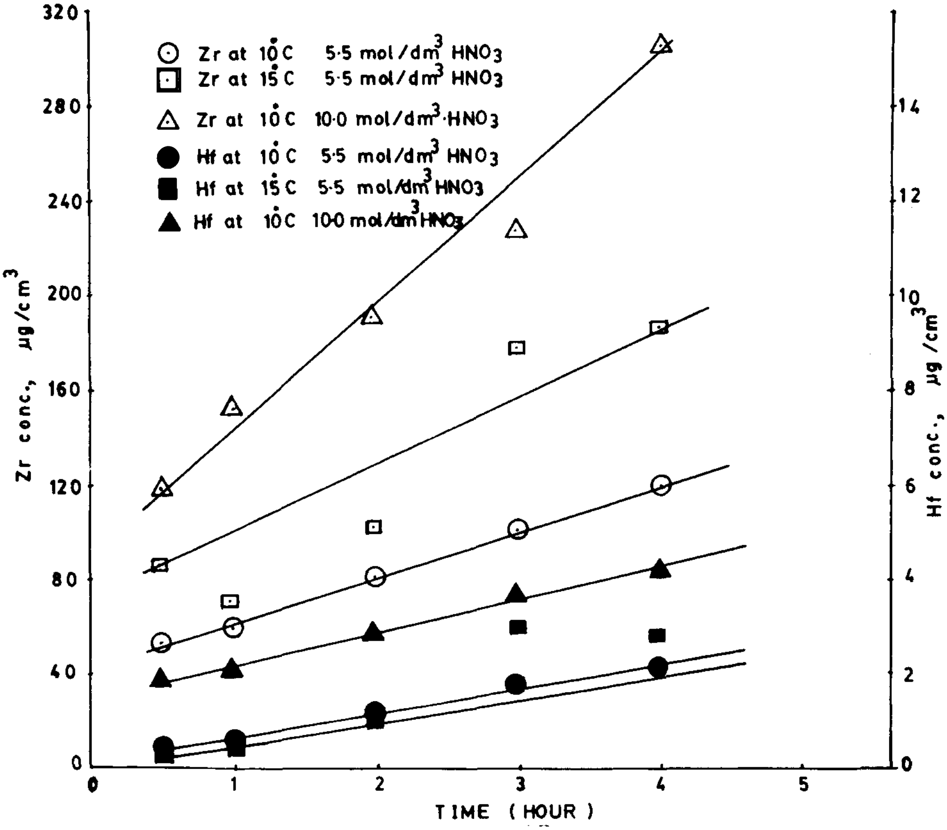

FIG. 9. Plots of Zr and Hf concentration in the feed versus time.

It can be seen from Fig. 2 that in the range of HNO_3 concentrations studied, flux and permeability of Hf ions increase with HNO_3 concentration, in agreement with Eq. (3). *J* is directly proportional to $[H^+]$ because both protons and nitrate ions increase with increasing HNO_3 concentration, so they affect the flux value positively. Actually, these ions help form a $Hf(NO_3)_4 \cdot q$TBP-type complex, which then diffuses through the membrane.

Figure 3 depicts *J* and *P* as a function of TBP concentration increase, which helps increase these parameters up to 2.93 mol/dm³ TBP concentration, after which there is a slight variation. The effect can be explained by keeping in mind the increased viscosity of the membrane liquid and the tendency of HNO_3 to complex directly with TBP molecules at higher concentrations, just as in the case of zirconium (*2*).

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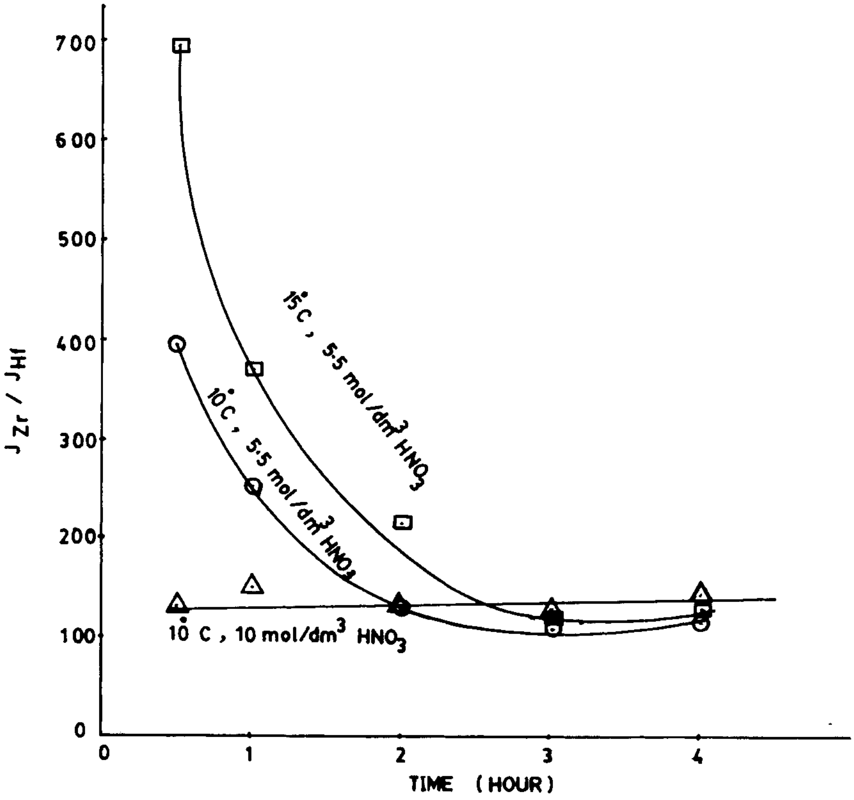

FIG. 10. Plots of J_{Zr}/J_{Hf} versus time at different temperatures and HNO_3 molarities in the feed.

The separation factor determined for Zr and Hf as a function of HNO_3 concentration in the feed and TBP concentration in the membrane are shown in Figs. 5 and 6. It is clear that there is an increase in the value of J for Hf with an increase in these two parameters, and therefore an effect on the separation factor. Apart from that, at higher HNO_3 concentrations there is the problem of acid transport from the feed to the strip solution. The optimum value of flux is at 6 mol/dm^3 HNO_3, so the feed solution HNO_3 concentration has to be restricted to a concentration below this value. Zr flux has been found to be a maximum at 2.93 mol/dm^3 TBP concentration, so this value may be adopted to prepare membranes. In the plot of J versus TBP concentration, the flux of Hf is a maximum of 2.93 mol/dm^3 TBP concentration, and after that it starts decreasing because of the reasons mentioned above. Its flux remains nearly constant from 2.2 to

2.93 mol/dm^3 TBP concentration. In an actual plant the TBP concentration should be fixed at 2.93 mol/dm^3 or less to keep the flux of Hf to a minimum value.

It has also been seen that J increases with temperature. This may be due to the decrease in viscosity of the membrane liquid with an increase in temperature and relaxation of the membrane matrix which becomes more flexible to the transport of diffusing species.

The plot of flux and permeability data in Fig. 4 represent a positive effect of temperature on these parameters. This indicates that the reaction involved is endothermic. The separation factor of Hf and Zr and their flux as a function of temperature in condensed form are shown in Fig. 7, which indicates that the separation factor deteriorates with an increase in temperature. Supposing that the transport of Hf ions is diffusive in nature and that there are no coupling effects, it can be shown that

$$\ln J = \ln M\,(E_a/RT) \tag{7}$$

where M is a constant, E_a is the energy of activation, and R and T have their usual meanings. Value of E_a have been calculated from the slope of Eq. (6):

$$E_a = R\frac{d \ln J}{d \ln (1/T)} \tag{8}$$

and has been found to be of the order of 40 kJ/mol. The plot of ln J versus $1/T$ is given in Fig. 8.

Figure 9 presents a record of Hf and Zr concentration in the strip solution as a function of time. The feed solution was prepared for a $ZrOCl_2$ salt containing 2.4% Hf with respect to Zr. The Zr concentration in the solution was 1100 μg/cm^3. The TBP concentration was 1.78 mol/dm^3, with HNO_3, 5.5 M at 10 and 15°C and also with 10 M HNO_3 feed at 10°C. It can be seen from this figure that Hf concentration in the product solution is quite low compared to the Zr concentration. The flux ratio of Zr and Hf is recorded in Fig. 10 from these experiments. It can be seen that the J_{Zr}/J_{Hf} value at 10 and 15°C is of the order of 400 at the start and then reduces to ~125 after about 3 h. This means that Zr ions are initially picked up faster by the membrane than Hf ions, as expected, and so their flux is higher. After equilibrium is reached, this reduces to a lower value. J_{Zr}/J_{Hf} is defined as separation factor S in Eq. (6). In individual Hf and Zr flux measurement experiments, this separation factor was found to be of the order of 12. This means that this value is enhanced in mixed Hf and Zr solution experiments, and the results are better than expected.

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It can further be seen in Fig. 10 that at 10 *M* HNO_3 in the feed, J_{Zr}/J_{Hf} is >125 and constant within 4 h, while at 5.5 *M* HNO_3 concentration in the feed, J_{Zr}/J_{Hf} is much higher within the first two hours at both 10 and 15°C.

This means that a HNO_3 concentration near 5.5 mol/dm^3 should be maintained in the feed. The temperature should be below 15°C for maximum separation, but higher acid concentrations may be selected for faster Zr fluxes, but then the number of stages should be increased. Zr flux is maximum at 2.93 mol/dm^3 TBP concentration, which should be used for its purification.

6. CONCLUSION

From the present study on Hf transport and a previous study on Zr transport, it has been shown that liquid membranes can be used for separation of Hf and Zr. The optimum conditions for separation of Hf from Zr ions are

TBP concentration	<2.93 mol/dm^3
HNO_3 concentration	5–6 mol/dm^3
Temperature	10°C

Because the strip solution in the present study was always distilled, deionized water, the solution from one stage can be fed to the next stage after HNO_3 dosing to achieve the required HNO_3 concentration in the solution. The process is preferred over solvent extraction because of the low membrane or extracting liquid use and the reduction in the overall number of stages. If the porous membranes are similar in configuration to those in ultrafiltration and reverse osmosis systems and have similar membrane area to volume ratios, the technique can be made economical and faster.

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