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Tri-*n*-octylamine–Xylene-Based Supported Liquid Membranes and Transport of Ce(IV) Ions

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ABSTRACT

An extraction and stripping study of Ce(IV) ions by using supported liquid membranes has been performed. Tri-*n*-octylamine has been used as a carrier diluted in xylene. Sodium carbonate, ascorbic acid (AA), and mandelic acid (MA) have been used in the stripping phase. AA and MA reduce the Ce(IV) ions by their anion transport to the feed solution containing Ce(IV) ions and sulfuric acid. Transport of cerium ions has been observed with sodium carbonate as the strippant. The flux of these ions increases with an increase in the system operating temperature. Optimal conditions for the transport of cerium ions have been found to be 0.4 M H_2SO_4 in the feed and 0.2 M TOA in the membrane.

INTRODUCTION

Supported liquid membrane (SLM) extraction and stripping on a simultaneous basis has attracted worldwide attention, and much work has been directed toward developing methods for the separation of various metal ions (1–4).

Cerium ions are present in the fission fragments of uranium (5). Their removal from waste is therefore of great importance. For the present paper

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various parameters responsible for the extraction of Ce(IV) ions from bulk aqueous solutions have been studied for the same purpose. The parameters studied are the effect of tri-*n*-octylamine (TOA) concentration in the membrane, sulfuric acid concentration in the feed, and the reducing effect of ascorbic and mandelic acids in the stripping phase. The optimum conditions of extraction and stripping for Ce(IV) ions have been determined. The mechanism of Ce(IV) ions reduction by the α-hydroxy acids mentioned above have also been considered and discussed to explain the results obtained.

THEORETICAL IDEAS

Reaction on the Feed Side

$(NH_4)_2Ce(NO_3)_6$ salt has been used in this study. It will ionize in the aqueous phase to furnish $Ce(NO_3)_6^{2-}$ ions:

$$(NH_4)_2Ce(NO_3)_6 \rightleftharpoons 2NH_4^+ + Ce(NO_3)_6^{2-} \tag{1}$$

The $Ce(NO_3)_6$ will further react with sulfuric acid present in the aqueous phase:

$$Ce(NO_3)_6^{2-} + H_2SO_4 \rightleftharpoons Ce(SO_4)_2 + 6NO_3^- + 2H^+ \tag{2}$$

$Ce(SO_4)_2$ in the presence of a higher sulfuric acid concentration will result in $Ce(SO_4)_3^{2-}$-type species:

$$Ce(SO_4)_2 + H_2SO_4 \rightleftharpoons H_2Ce(SO_4)_3 \rightarrow Ce(SO_4)_3^{2-} + 2H^+ \tag{3}$$

Amine molecules in an acidic aqueous solution will form a neutral species, **I**, which is extractable into the organic phase:

$$\underset{aq}{2H^+} + \underset{aq}{Ce(SO_4)_3^{2-}} + \underset{org}{2R_3N} \rightarrow \underset{\substack{org\\ \mathbf{I}}}{[Ce(SO_4)_3(R_3NH)_2]} \tag{4}$$

Reaction on the Stripping Side

In the presence of sodium carbonate in the stripping phase the reaction on the stripping side membrane face will be

$$\underset{org}{(R_3NH)_2Ce(SO_4)_3} + \underset{aq}{Na_2CO_3} \rightarrow \underset{aq}{Na_2Ce(SO_4)_3} + \underset{org}{2R_3N} + H_2O + CO_2 \tag{5}$$

$$Na_2Ce(SO_4)_3 + 3CO_3^{2-} \rightarrow Ce(CO_3)_3^{2-} + 2Na^+ + 3SO_4^{2-} \tag{6}$$

i.e., sulfate ions as well as protons diffuse into the stripping phase.

Ce(IV) ions in sulfuric acid can be extracted as $(R_3NH)_2Ce(SO_4)_3$. The overall reaction on the feed side is

$$\underset{aq}{Ce(IV)} + 2R_3N + \underset{aq}{2H^+} + 3SO_4^{2-} \rightleftharpoons (R_3NH)_2Ce(SO_4)_3 \qquad (7)$$

Therefore, K_e, the extraction coefficient for Ce, is given by

$$K_e = \frac{\underset{org}{[(R_3NH)_2Ce(SO_4)_3]}}{\underset{org}{[R_3N]^2}\ \underset{aq}{[H^+]^2}\ \underset{aq}{[Ce^{4+}]}\ \underset{aq}{[SO_4^{2-}]^3}} \qquad (8)$$

D, the distribution coefficient for Ce, is given by

$$D = \frac{\underset{org}{[(R_3NH)_2Ce(SO_4)_3]}}{\underset{aq}{[Ce(SO_4)^{2-}]}} \qquad (9)$$

$$J = \frac{A_1 T}{\eta} \underset{org}{[R_3N]^2}\ \underset{aq}{[H^+]^2}\ \underset{aq}{[SO_4]^3} C_f^0 \qquad (10)$$

or

$$\log \eta J = \text{constant} + \log T + 2 \log\underset{org}{[R_3N]} + 2 \log\underset{aq}{[H^+]} + 3 \log\underset{aq}{[SO_4^{2-}]} + \log C_f^0 \qquad (11)$$

Here η, T, and C_f^0 refer to the viscosity of the organic membrane phase, the absolute temperature of the operation, and the Ce(IV) concentration in the bulk feed. J is the Ce(IV) flux across the membrane and A_1 is a constant.

Equation (11) may also reveal the stoichiometry of the chemical reactions involved. If b, m, and n represent the number of moles of R_3N, H^+, and sulfate ions involved per mole of cerium ions, then the general form of Eq. (11) will be

$$\log \eta J = \text{constant} + \log T + b \log[R_3N] + m \log[H^+] + n \log[SO_4] + \log C_f^0 \qquad (12)$$

Equation (12) also indicates that flux is reduced as a result of membrane phase liquid viscosity and is enhanced by increasing the cerium ions concentration, C_f^0, in the feed solution. If C_{ft}^0 represents the feed solution Ce concentration in the feed at time t, and C_f is the initial Ce(IV) concentration in the feed, the membrane permeability, p, for the Ce(IV)–TOA diffusing species is given by

$$-\ln \frac{C_{ft}^0}{C_f^0} = \frac{apt}{Vd} \qquad (13)$$

where a and V refer to the membrane effective area and the total volume of the feed liquid, respectively, and d represents the membrane thickness.

Equation (13) furnishes the value of p from the slope of the plot of $-\ln C_{ft}^0/C_f^0$ versus t.

EXPERIMENTAL

Apparatus

The liquid membrane cell used for this study was fabricated from Perspex material. It consisted of two compartments, each having a volume of 106 cm^3. Membranes with an effective area of 12.56 cm^2 could be fixed within the two compartments. Each compartment was equipped with an agitator which was rotated by an electric motor, and an inlet and an outlet for filling and draining the strip and feed solutions, respectively.

Membranes

The porous film used for this study had a pore size of the order of 0.02 μm, a thickness of 25 μm, and a porosity of 38%. The film was obtained from Celanese Corporation USA under the trade name Celgard 2400.

In the case of Ce(IV), TOA dissolved in xylene and supported on the polymeric film was used as the carrier. The membrane was soaked in the carrier solution for more than 24 hours before use.

Analytical Instruments

The instruments used for the analysis of Ce(IV) ions were

1. A UV-160A Shimadzu spectrophotometer
2. A Waters high performance liquid chromatograph (HPLC) consisting of an IC-PAC anion-exchange column, a Solvent Delivery System 590, a WISP 710B injector, a Conductivity Detector 430, a System Controller 721, a Data Module 730, and a UV Visible Detector 481
3. An ICP (inductively coupled plasma) Spectrometer, Model JY-38, with a Durr Plasma Generator.

Chemicals

The following chemicals and reagents were used for the analysis of Ce(IV): H_2SO_4, HCl, Na_2CO_3, ascorbic acid (AA) mandelic acid (MA), and tri-*n*-octylamine (TOA), all AnalaR grade from B.D.H.

Reagents

Ce(IV) Stock Solution. A stock solution of 1000 ppm Ce(IV) was prepared by dissolving 0.3949 g ammonium ceric nitrate in 100 mL ultrapure water.

Ce(IV) Feed Solution. A known amount of the 1000 ppm stock solution was diluted with water to a given extent after adding a calculated amount of the desired acid.

Ce(IV) Stripping Solution. The stripping solution consisted of various acids of different concentrations. It was prepared by taking the required amount of an acid and diluting it with deionzed water to a known volume.

TOA Solution. TOA solutions of different concentrations were prepared by diluting with xylene.

N-Benzoyl-n-phenyl-hydroxylamine (BPHA) Solution. BPHA (0.2 g) was dissolved in a 100-mL volumetric flask in ethanol and diluted up to the mark to prepare a 0.2% solution of BPHA in ethanol.

10% Ammonium Nitrate Solution. Ammonium nitrate (10 g) was dissolved in 100 mL deionzed water.

Ce(IV) Analysis

For the analysis of Ce(IV), 1 cm^3 of the sample solution was taken and diluted to 20 mL with deionized water. To this solution were added 5 mL each of 0.2% *N*-benzoyl-*n*-phenyl-hydroxylamine and 10% ammonium nitrate solutions, and the pH was adjusted to 8 with dilute ammonia solution. The solution was stirred occasionally and, after 30 minutes, transferred to a separating funnel. The solution was shaken with chloroform (two 5 mL volumes) for 3 minutes. The organic phase was separated (in a 25-mL volumetric flask). The aqueous phase was washed twice with 3 mL volumes of chloroform and added to the previously collected organic extract and diluted to 25 mL with chloroform. Absorbance was measured at 460 nm against a reagent blank. The concentrations of the Ce solution samples were read from the calibration curve for Ce(IV) ions, which was prepared by repeating the above steps with known concentrations, and measuring the absorbance and its plot versus concentration. The method was derived from Ref. 6. The results were further confirmed by ICP or HPLC analyses.

Flux Measurements

The membrane was fixed between the two compartments of the Perspex cell. The cell compartments were filled with feed and the stripping solutions and kept stirred at a rate greater than 1500 rpm to avoid concentration polarization at the membrane surface. All the experiments were performed at room temperature (25 ± 2°C) except for the experiments in which the temperature effect was studied. Samples were taken at regular time intervals and analyzed as mentioned above.

RESULTS AND DISCUSSION

Ce(IV) Study

Effect of TOA Concentration as Carrier

Figure 1 indicates the decrease in the concentration of cerium ions in the feed. Figure 2 represents the variation in flux with time. According to Eq. (12), *J* is proportional to C_f^0, i.e., the concentration of cerium ions in the feed. C_f^0 decreases and so *J* decreases. As shown in Fig. 2, in the case of 0.8 and 0.9 M TOA the flux is low even at the start and so there is less variation in the concentration of Ce with time and a very slight decrease in *J*. Figure 3 indicates that the flux and permeability increase with an increase in concentration up to 0.2 M TOA in the membrane.

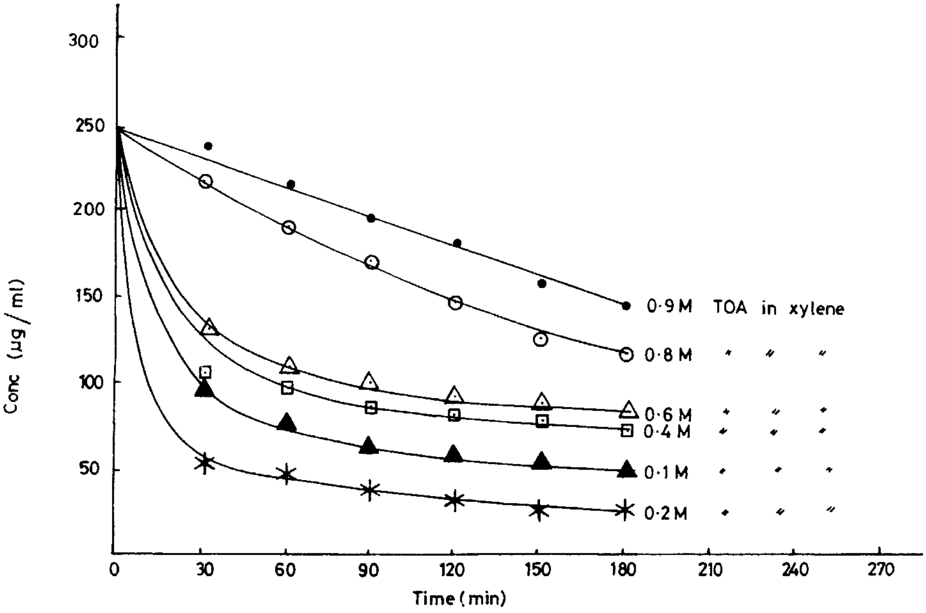


FIG. 1 Plot of Ce(IV) concentration versus time at different concentrations of TOA–xylene as the SLM.

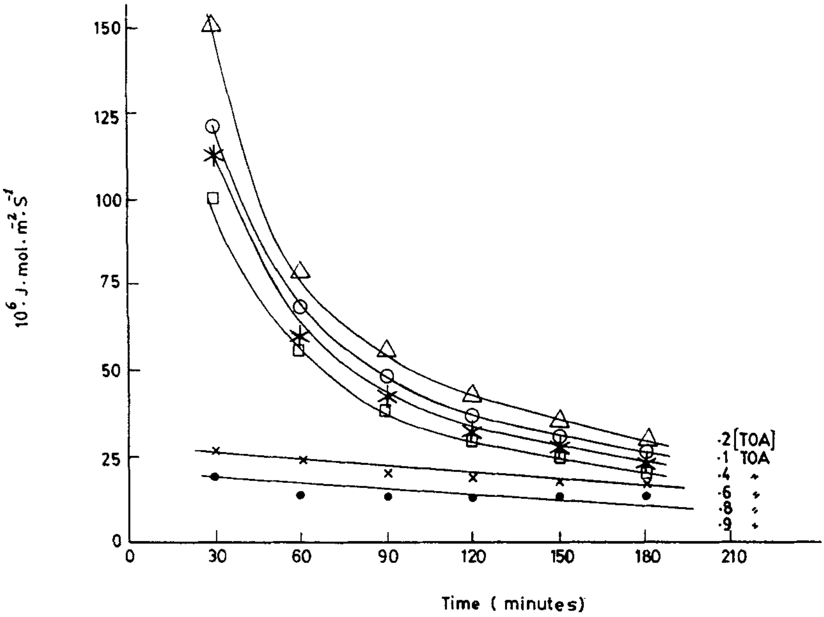


FIG. 2 Plot of flux of Ce(IV) versus time at different concentrations of TOA as the supported liquid membrane.

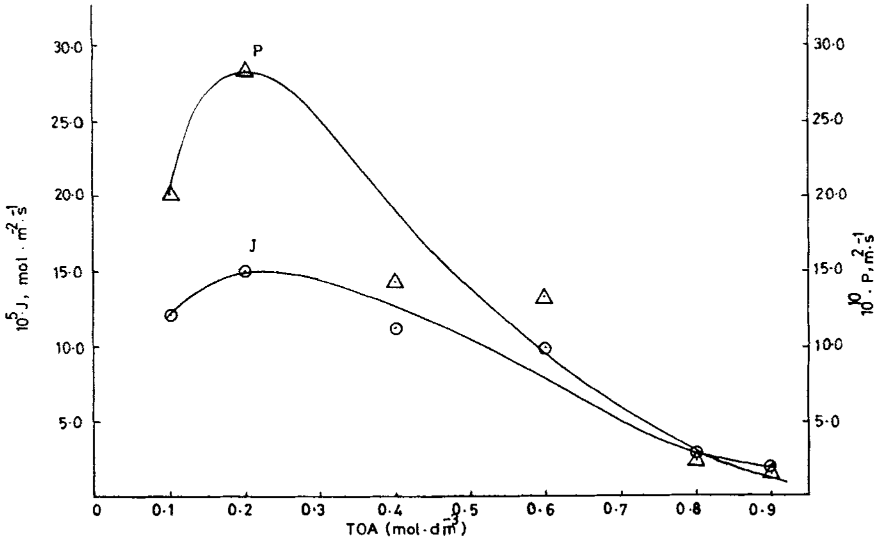


FIG. 3 Plot of flux (J) and permeability (p) of Ce(IV) versus different TOA–xylene concentrations as the supported liquid membrane.

Beyond that, the values of permeability and flux decrease continuously. 0.4 M H_2SO_4 was used in the feed solution, so it is believed that protons furnished by H_2SO_4 are utilized to protonate such species as $Ce(SO_4)_2$, $H_2Ce(SO_4)_3^-$, $Ce(SO_4)_3^{2-}$, and $H_2Ce(SO_4)_4^{2-}$. It was observed in our previous study that the viscosity of TOA (7) in xylene increases with an increase in TOA concentration. The same situation occurs here with the flux of Ce ions. This has been observed previously in the cases of uranium, hafnium, and strontium (7–9).

On the low concentration side, only two points have been studied, at 0.1 and 0.2 mol/dm^3 TOA concentrations, which are not sufficient to provide information about the stoichiometry of the chemical reactions involved in using SLM. The optimum condition with respect to TOA concentration for Ce(IV) metal ions transport is 0.2 mol/dm^3.

Effect of H_2SO_4 Concentration in the Aqueous Feed Solution

It is quite clear from Figs. 4–6 that the flux and the permeability values increase up to 0.4 M concentration in the feed solution. Beyond that, a

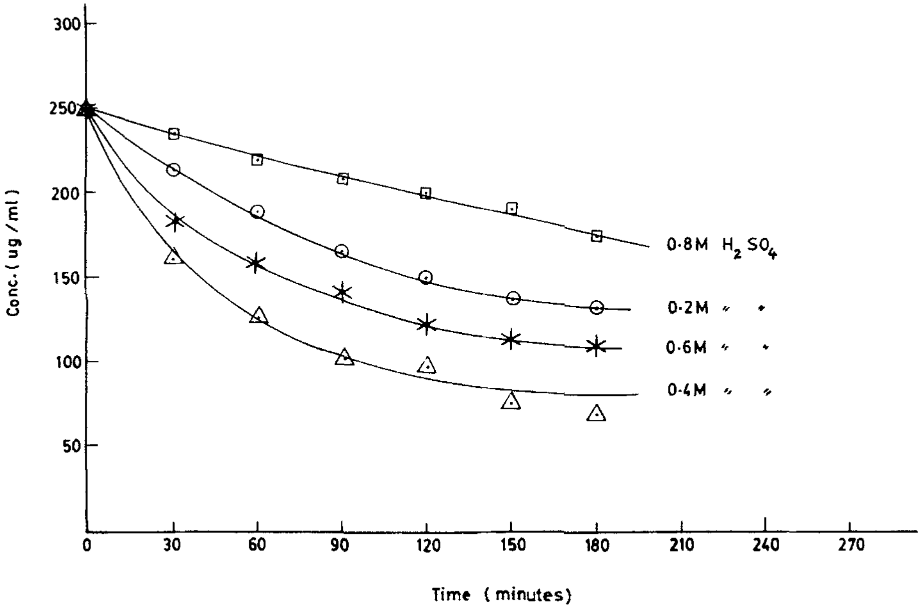


FIG. 4 Plot of Zr(IV) concentration versus time at different concentrations of H_2SO_4 (mol·dm^{-3}) in the feed solution.

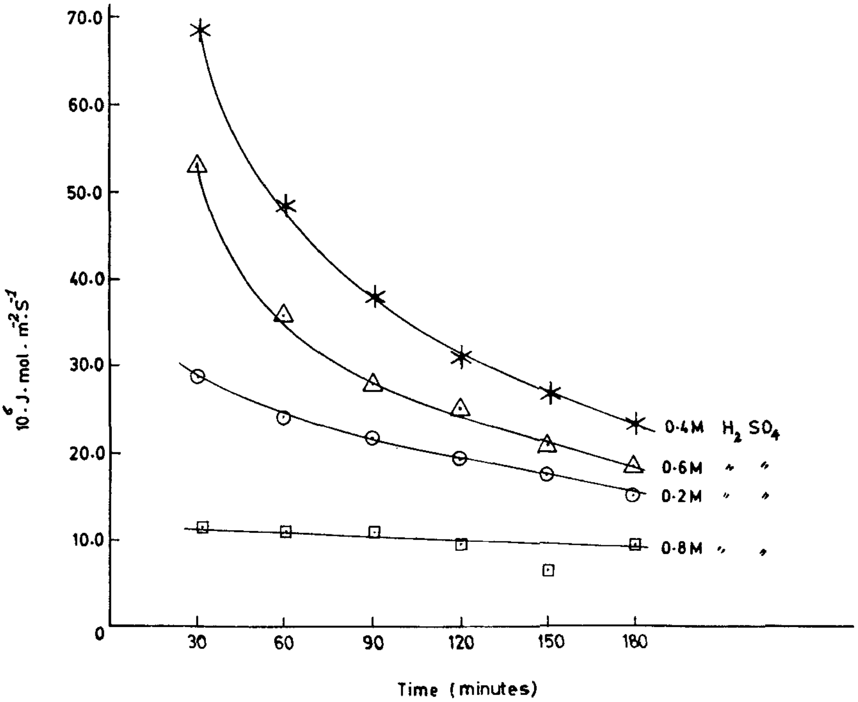


FIG. 5 Plot of flux (J) of Ce(IV) versus time at different concentrations of H_2SO_4 in the feed solution.

decrease in their value has been observed. The values of J and p are given in Fig. 6. The permeability increases up to 0.80×10^{-9} m^2/s and flux to 15.2×10^{-5} mol/dm^3 at 0.4 M. The values of J and p at 0.8 M decrease to 1.16×10^{-5} mol/m^2·s and 1.13×10^{-10} m^2/s respectively, which indicates the importance of sulfate ions and protons in the aqueous phase. If we suppose the Ce(IV) species present is only $H_2Ce(SO_4)_3$, then it is quite obvious from Reaction (7) and Eq. (2) that the flux is proportional to both the protons and the sulfate ions concentrations in the aqueous feed. This can also be seen from the following ionization reaction of $H_2Ce(SO_4)_3$:

$$H_2Ce(SO_4)_3 \rightleftharpoons 2H^+ + Ce^{4+} + 3SO_4^{2-} \qquad (14)$$

If the amounts of protons and sulfate ions increase, the reaction will shift backward and there may be difficulties in dissociating the ceric ions from the R_3NH^+ cation. The results are shown experimentally in Fig. 6. It is evident that beyond 0.4 mol/dm^3, the J value decreases continuously.

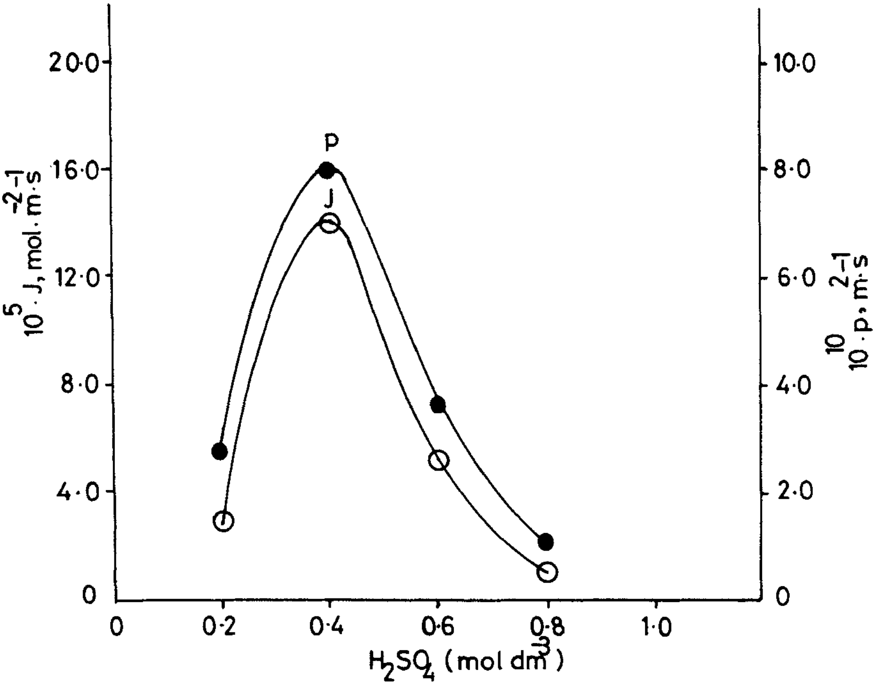


FIG. 6 Plot of flux (*J*) and permeability (*p*) of Ce(IV) versus different concentrations of H_2SO_4.

Another reason may be the increase in hindrance to diffusion as a result of an increase in the size of the extractable species.

Figure 5 indicates a decrease in the flux of Ce(IV) with time. This is again attributed to a decrease in C_f^0 as a result of the transport of the given ions through the membrane.

Effect of Temperature

The effect of temperature on the transport of Ce(IV) ions across the TOA–xylene-based SLM is shown in Figs. 7–10. Figure 7 shows Ce(IV) concentration vs time in the feed, which clearly appears to decrease with time. It is quite obvious that the flux and permeability of the given membrane increase with an increase in temperature (Figs. 9 and 10). The *J* value obtained varies from 0.482×10^{-4} to 6.8×10^{-4} mol/m^2·s, and *p* varies from 0.56×10^{-9} to 6.85×10^{-9} m^2/s. According to kinetic theory,

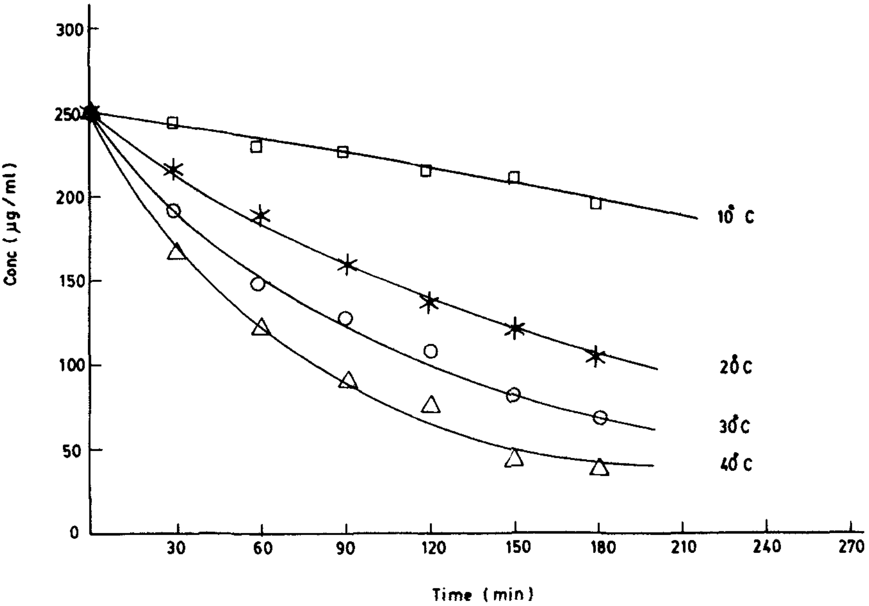


FIG. 7 Plot of Ce(IV) concentration versus time at different temperatures.

molecules move faster with an increase in temperature, and so the chances of diffusion through the membrane will increase with an increase in temperature.

The results agree with Eq. (12), which shows that the flux increases with an increase in temperature. If *T* is constant, then the term involving *T* will become part of the constant provided in Eq. (12).

The results are in accord with the derived equation and the Wilke-Chang equation in which temperature has a similar relationship to the diffusion coefficient. However, it has been observed that the membranes are stable at all temperatures.

The mechanism of Ce(IV) ions transport from H_2SO_4 to the sodium carbonate stripping phase is shown in Fig. 11.

Effect of Ascorbic Acid and Mandelic Acid

Ascorbic acid and mandelic acids are α-hydroxy acids, and they have been used as stripping agents in the aqueous phase in contact with TOA in the membrane. The concentration effect of these acids in the stripping

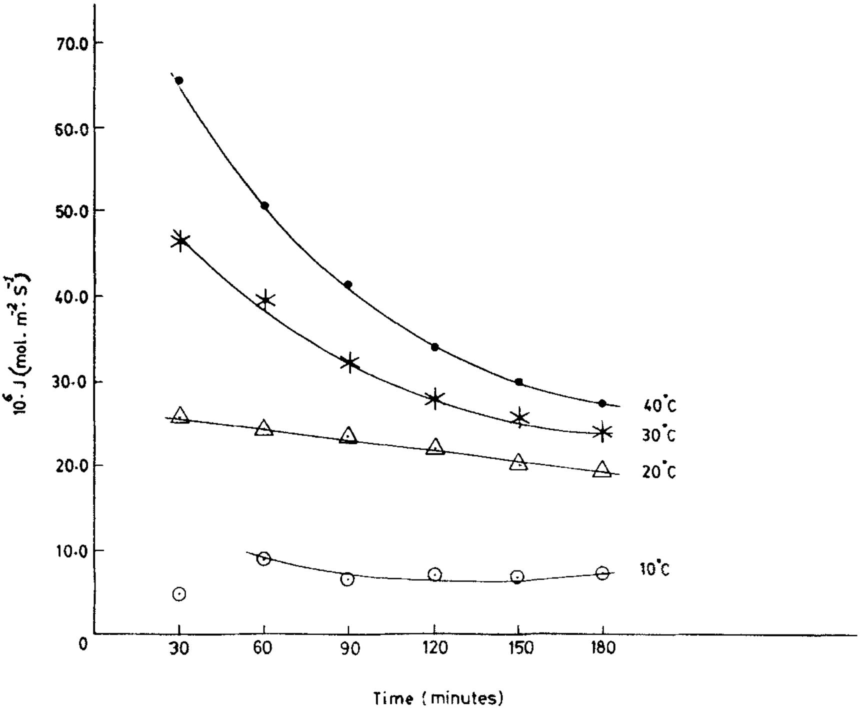


FIG. 8 Plot of flux (J) of Ce(IV) versus time at different temperatures.

phase has been studied. The absorbance of the feed solution samples, after following the analytical procedure provided for Ce(IV) ions in the Experimental Section, indicated a very rapid decrease (Fig. 12). It was at first felt that Ce ions were transporting to the stripping phase. To confirm this result, analysis of strip and feed solution samples taken at different time intervals were done by using HPLC and ICP, and it was found that a very small amount of Ce ions transported to the stripping phase. A possible explanation of these results is that Ce(IV) ions present in the feed are very slowly extracted to the organic phase, while at the same time α-hydroxy acid anions coupled with R_3NH^+ cations are transferred from the strip to the feed solution and reduce Ce(IV) to Ce(III) according to a mechanism involving a free radical reaction. There is an intermediate species (**I**) of cerium sulfate with α-hydroxy acids which further decomposes to a free radical (**II**) which reacts with Ce(IV) to reduce it to Ce(III) as shown in Ref. 10. The mechanism is:

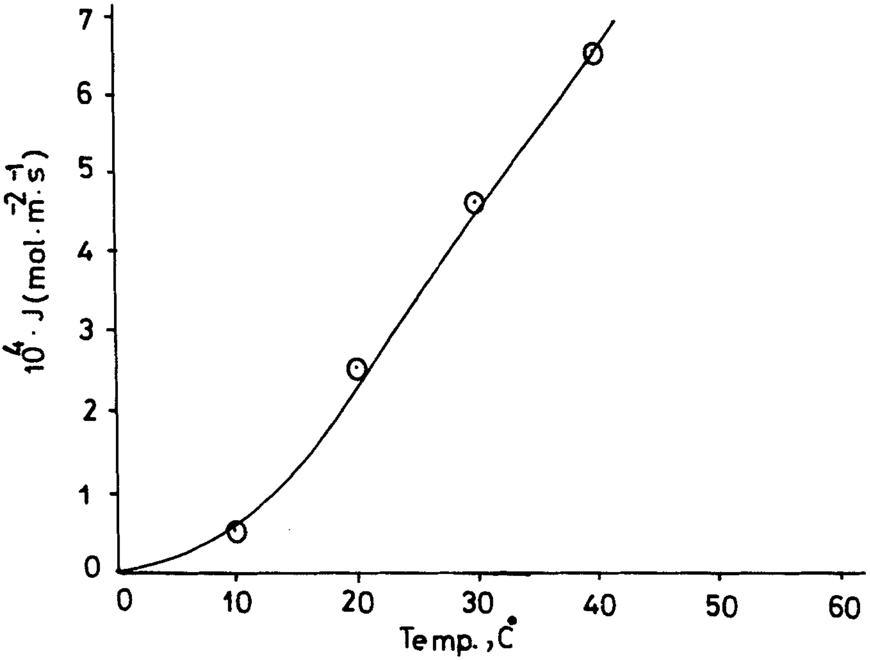
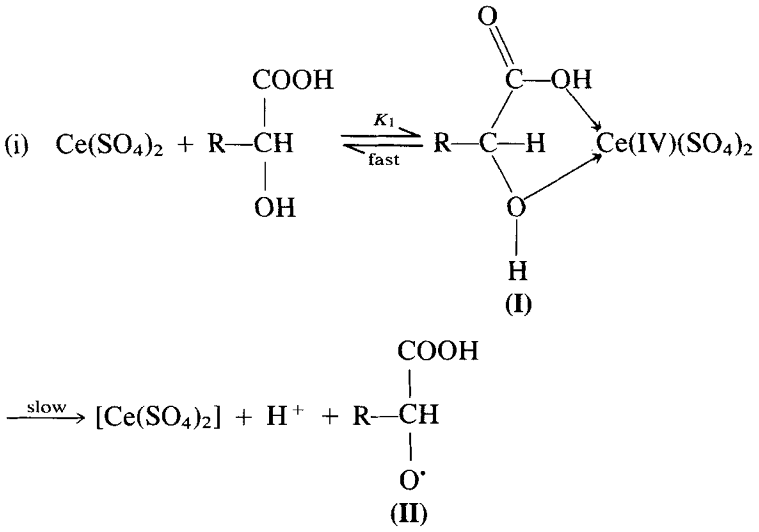


FIG. 9 Plot of flux (J) of Ce(IV) versus temperature through SLM at constant time.



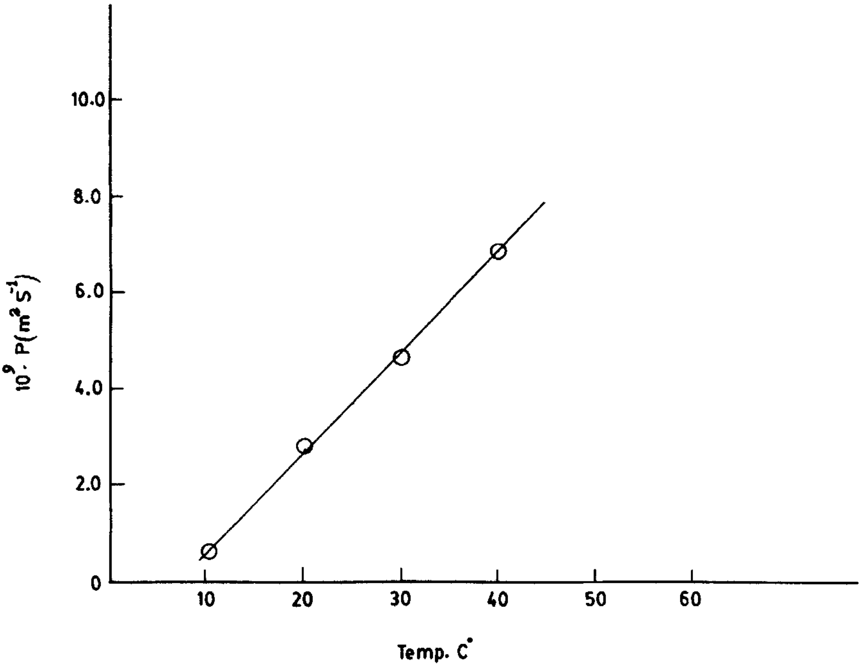
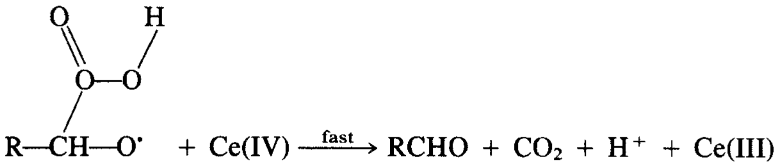


FIG. 10 Plot of permeability of Ce(IV) versus temperature.

(ii)



$$\mathrm{R{-}CH(O{-}O{-}C(=O)H){-}O^{\bullet}} + \mathrm{Ce(IV)} \xrightarrow{\text{fast}} \mathrm{RCHO} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{Ce(III)}$$

The intermediate species of Ce with α-hydroxy acid are formed very quickly. They decompose comparatively slowly to free radical species, and then the reduction of Ce(IV) to Ce(III) is a very fast reaction, so the overall reduction process is very fast as indicated by the absorption data obtained at 460 nm in the analytical procedure. The absorption decrease is due to a decrease in Ce(IV) ions concentration. The amount of α-hydroxy acid anions diffusing through the membrane to the feed solution from the stripping phase with the passage of time is still to be determined using HPLC (this work has not been completed).

Further evidence of Ce(IV) to Ce(III) reduction is provided in the absorption spectrum of Ce feed solution at various time intervals. Ce(III)

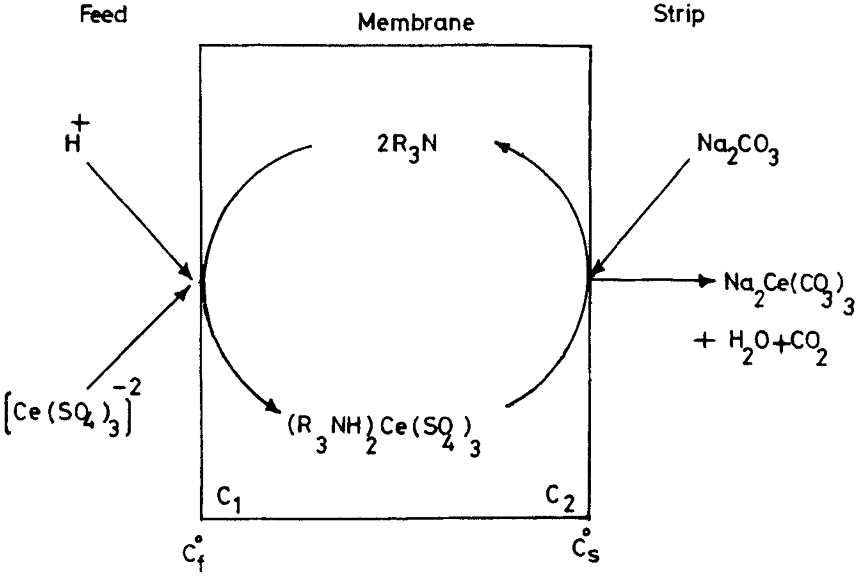


FIG. 11 Possible scheme for the transport of Ce(IV) ions from sulfuric acid solution to sodium carbonate through a TOA–xylene-based supported liquid membrane.

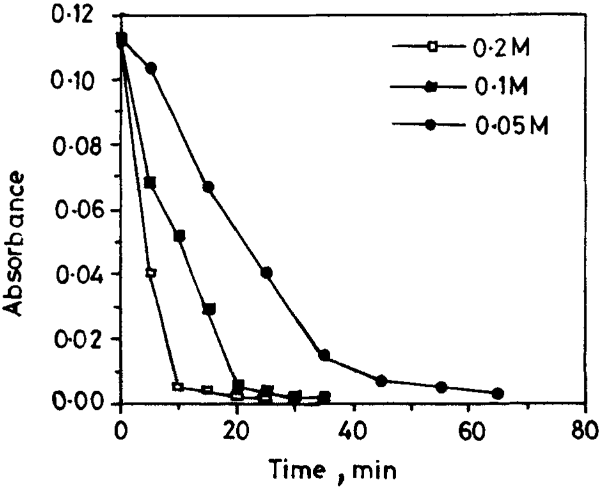


FIG. 12 Absorbance of feed side analytical samples for Ce(IV) as a function of time. Conditions: Ascorbic acid = 0.05, 0.1, and 0.2 M; TOA = 0.2 M.

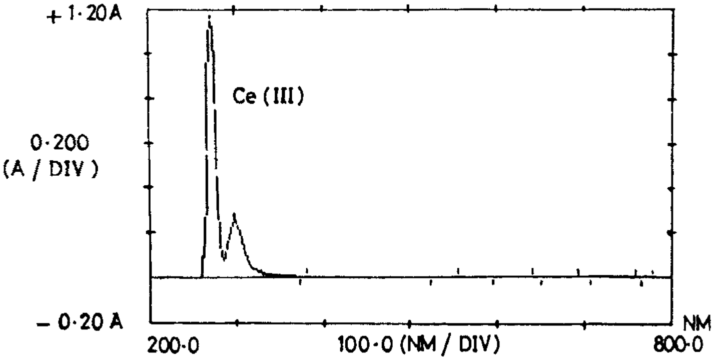


FIG. 13 Absorption spectrum of Ce(III).

absorbs at 275 nm from the feed solution (Fig. 13), while Ce(IV) species have absorption maxima at 400 nm as shown in Fig. 14. The absence of Ce(IV) species absorption at 400 nm and the appearance of Ce(III) absorption at 275 nm in the feed solution is indicated in Fig. 13. This is clear evidence of the reduction of Ce(IV) to Ce(III) by the feed solution. In Fig. 15 there is only one peak shown for absorption at 302 nm, which is a mixed peak of Ce(III) and a peak of Ce(IV). This indicates that even if a very small amount of Ce(IV) is transferred to the stripping phase, it is as Ce(III).

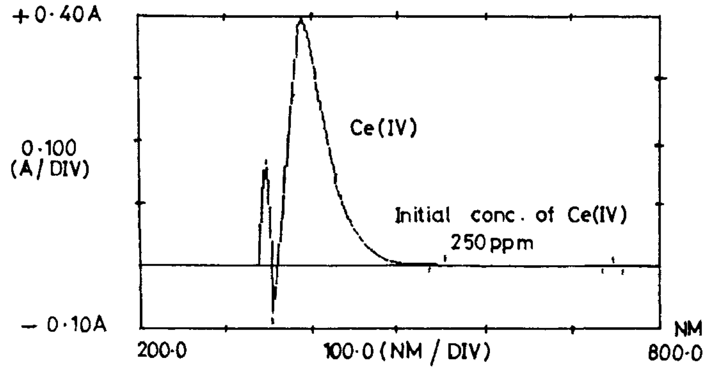


FIG. 14 Absorption spectrum of Ce(IV).

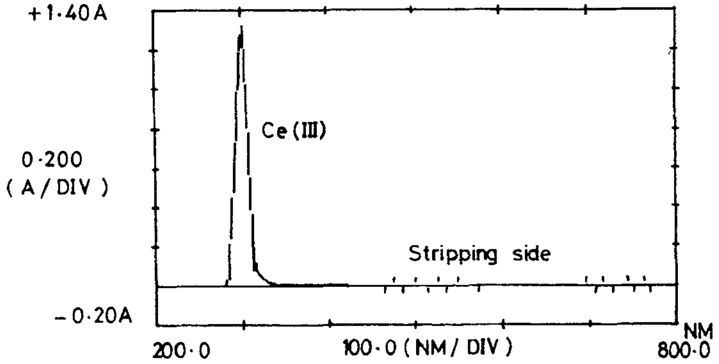


FIG. 15 Absorption spectrum of Ce(III).

CONCLUSION

Ce(IV) ions can be transported across a TOA–xylene-based SLM, with the optimum conditions of 0.2 M TOA membrane, 0.4 M sulfuric acid in the feed, 0.25 M sodium carbonate in the stripping phase, and a temperature of 40°C. The α-hydroxy acids do not strip Ce(IV) ions. The Ce(IV) ions are reduced by MA and AA by the transport of their respective anions. Transport studies of other metal ion isotopes present in nuclear waste will also to be studied before conclusions are reached about their separation from other fragments present in the waste.

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