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Transport of Mo(VI) Ions through Tri-*n*-octylamine-Xylene Based Supported Liquid Membranes

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Abstract

The study of Mo(VI) ions transport through tri-*n*-octylamine (TOA)-xylene liquid membranes supported in polypropylene hydrophobic microporous film has been performed with varying concentrations of HCl, TOA, and NaOH in the feed membrane, strip solution, and temperature. Maximum flux of the order of 1.62×10^{-4} mol · m^{-2} · s^{-1} and permeability of 2.51×10^{-10} m^2/s at 1.35 mol/dm^3 TOA and 0.1 mol/dm^3 NaOH at 35 ± 2°C have been observed. The flux of metal ions increases with an increase in temperature. Decomposition of $[Mo_7O_{24}]^{6-}$ ions into lower species appears to occur, and a pH decrease in the feed with the passage of time during transport of these metal ions is an indication of this effect. Mixed polymetal anions appear to be responsible for complexing with TOA molecules and the transport through the membrane. The transport mechanism of this metal ion through the membrane is based on the association of metal anions with protonated tri-*n*-octylamine (TOA) molecules on the feed-side interface, diffusion through the membrane, decomposition of the complex on the strip/solution-side membrane interface in alkaline conditions, and backdiffusion of TOA molecules. Transport with the membrane is dependent on the concentration gradient but in the surrounding solutions it is inversely related to the concentration gradient.

INTRODUCTION

The separation of molybdenum ions is important in ^{99}Mo and ^{99m}Tc isolation from reactor coolant water (*1*) and in the ^{99}Mo and ^{99}Tc generator

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(*2*). Molybdenum also has well-established industrial applications. The liquid membrane separation technique employing coupled transport phenomenon has not been applied for its separation from other metal ions, and no transport studies have been made. Tri-*n*-octylamine (TOA) is an important extractant and can complex with molybdenum anions.

In this work, TOA diluted in xylene is used to effect transport of $(Mo_7O_{24})^{6-}$ ions across a liquid membrane of the liquid supported in polypropylene film. Various parameters influencing the flux of these ions across the membrane, including TOA and HCl concentration variations in the feed, NaOH concentration in the strip solution, and operating temperature effects, have been optimized to determine the process parameters and to study the mechanism of this metal ions transport in using this technique.

EXPERIMENTAL

Appparatus

Liquid Membrane Cell

The liquid membrane cell used for this study was fabricated from Perspex. It consists of two half cells (compartments) having equal capacities of 106 cm^3. A membrane with an effective area of 12.56 cm^2 was fixed between these two half cells with two stirrers fixed at the top to agitate the confined liquids. The cell was equipped with outlets for driving the liquids and for collecting samples, with separate feed and stripping agent inlets. More details about the cell are available in Ref. *3*.

Membrane

Tri-*n*-octylamine was used as the complexing agent with xylene as a diluent in the Celgard 2400 polypropylene film. The film was kept soaked in TOA–xylene solution for more than 24 h before use. The film has a pore diameter of 0.02 μm, a thickness of 25 μm, and a porosity of 30%.

Analytical Instruments

Spectrophotometer model UV-120-01 from Shimadzu and pH meter model 701A digital from Orion Research were used for analysis.

Chemicals and Reagents

Chemicals

Ammonium-*p*-molybdate $(NH_4)_6 \cdot Mo_7O_{24}.4H_2O$, AnalR grade, 99% pure from BDH; tri-*n*-octylamine, 95% pure, Proanalysi grade; xylene, laboratory grade, NaOH, extra pure grade; Eriochrome Black-T, AnalR grade; sodium acetate, Extra Pure grade; and oxalic acid, Proanalysis grade, all from E. Merck, were used during this work. The other chemicals used were AnalR grade or better. Deionized double distilled water was used throughout.

Reagents

i) Mo(VI) Feed Solution. 0.1150 grams ammonium molybdate was placed in a 250-cm^3 volumetic flask and made up to volume with hydrochloric acid of the required molarity to prepare a 250-µg/cm^3 molybdenum(VI) solution.

ii) Tri-n-octylamine Solution. The required concentration of TOA for SLM was prepared by diluting a given volume of this chemical in known volumes of xylene.

iii) Buffer Solution. 0.2 mol/dm^3 sodium acetate solution was prepared, and the pH of this solution was adjusted to 5 by slowly adding a 0.2-mol/dm^3 acetic acid solution.

iv) Eriochrome Black T Solution. 0.04 grams of this chemical was dissolved in 100 cm^3 methanol to prepare a 0.04% solution.

Analytical Procedure

1 cm^3 of molybdenum(VI) standard solutions of 10, 20, 30, 40, and 50 μg/cm^3 concentration were placed in 10 cm^3 volumetric flasks. 1 cm^3 of Eriochrome Black T solution and 2 cm^3 of buffer solution were added to each flask, and the volume were made up to 10 cm^3 with distilled, deionized water. The absorbance was read at 380 nm against the reagent blank on the spectrophotometer and plotted against concentration to determine the calibration line. The samples were treated in the same way by using the same steps as described above, and concentrations of molybdenum were read from the calibration line.

Flux Measurements

The membrane was fixed in the cell. Feed and strip solutions were filled in the half cells and stirred at a rate greater than 1500 rpm to avoid concentration polarization conditions at the membrane interface. All the experiments were performed at 35 ± 2°C. Samples of 1 cm^3 volume from the feed solution were taken after definite time intervals and analyzed as described above.

Solvent Extraction

Equal volumes of aqueous molybdenum(VI) solution (in different hydrochloric acid concentrations) and organic solution were shaken for 15 min in separatory funnels and allowed to stand for about 24 h. The aqueous layer was separated from the organic layer and analyzed.

THEORETICAL

The salt used for this study was $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. In solution it ionizes:

$$(NH_4)_6Mo_7O_{24} \rightleftharpoons 6NH_4^+ + [Mo_7O_{24}]^{6-} \qquad (1)$$

In the membrane phase, tri-*n*-octylamine in the presence of HCl will be in the following form:

$$Cl^- + H^+ + R_3N \rightleftharpoons R_3N \cdot HCl \qquad (2)$$

R respresents the tri-*n*-octyl group. The expected mechanism of Mo-metal anions transport in the present case may be as shown in Fig. 1. At the liquid membrane surface, the complex formed may be

$$[Mo_7O_{24}]^{6-} + 6R_3NH \rightleftharpoons [R_3NH]_6 \cdot Mo_7O_{24} \qquad (3)$$

The overall reaction which is supposed to occur at the membrane phase in the acid side of solution will be

$$\underset{aq}{6H^+} + \underset{org}{6NR_3} + \underset{aq}{[Mo_7O_{24}]^{6-}} \rightleftharpoons \underset{org}{[R_3NH]_6 \cdot Mo_7O_{24}} \qquad (4)$$

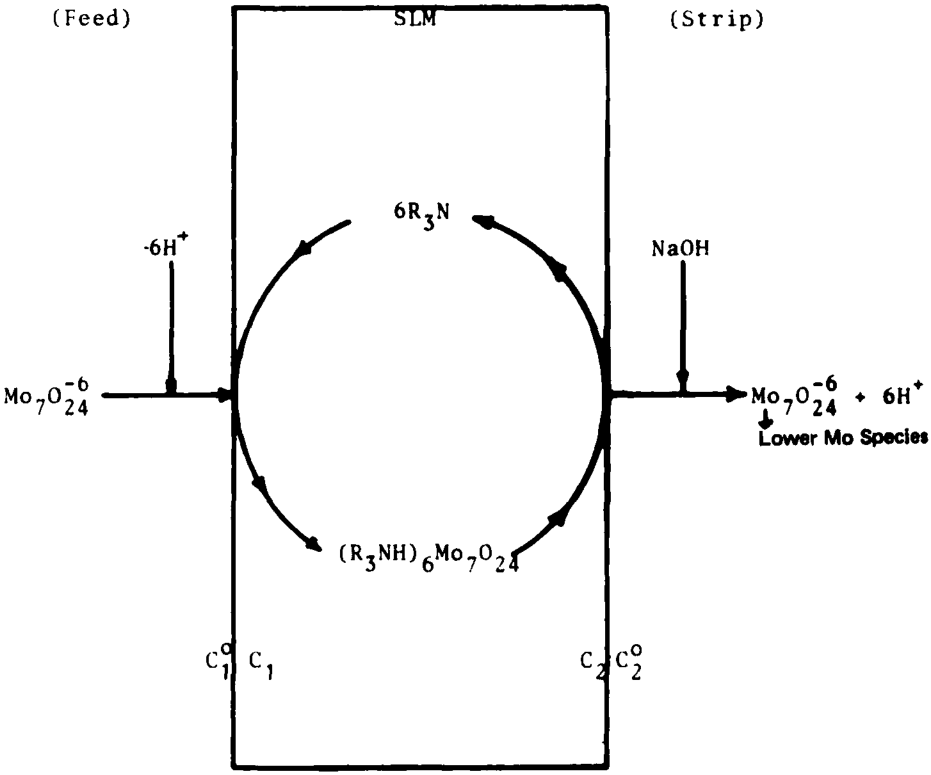


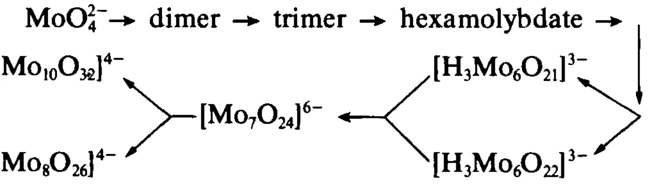
Fig. 1. Possible scheme for molybdenum(VI) transport from HCl solution to NaOH solution through TOA-xylene based supported liquid membrane.

The mechanism of Mo(VI) ion transport through the membrane may therefore be movement of Mo(VI) ions in the feed side bulk solution under diffusion or the stirred condition to the membrane interface, association with the tertiary amine ions from the membrane organic phase, and then dissociation at the other side of the membrane to release Mo(VI) ions into the stripping phase. The amine molecules released will also then travel back in the direction controlled by their concentration gradient in the membrane, i.e., in the reverse direction to that of their complex with Mo(VI) ions.

When the stripping solution is alkaline, the following reaction may be expected:

$$(R_3NH)_6 \cdot Mo_7O_{24} \rightleftharpoons 6R_3N + 6H^+ + (Mo_7O_{24})^{6-} \qquad (5)$$

It has been stated (*4, 6–8*) that monomolybdate ion $(MoO_4)^{2-}$ is present above pH 6.5. Condensation of this species takes place in more acidic solutions, to form trimolybdate ion $(Mo_3O_{11})^{4-}$ at pH 6.5 to 5, hexamolybdate ion $(Mo_6O_{21})^{6-}$ at pH 4.5 to 2, and dodecamolybdate ion $(Mo_{12}O_{41})^{10-}$ at pH 1.5 to 1. It was concluded by Ali Rusheed (*4*) that the scheme for the formation of isopolymolybdate ions in solution is



From the above description it is clear that $[Mo_7O_{24}]^{6-}$ ions, after being released, will travel from the membrane phase to the aqueous NaOH solution, and then species of the $(MoO_4]^{2-}$ type may be formed. Immediate conversion of the higher molybdenum species into a lower species takes place as a result, and because the amine molecules become neutral due to the pH of the solution, the extraction of the given species of molybdenum should be very poor. Hence, the overall transport of polymolybdate ions from a low pH solution to a higher pH solution takes place. The protons also move in the same direction as the metal anion species transport through the membrane, so the transport will be a coupled Co-ion transport. As such, $(Mo_7O_{24})^{6-}$ transport is coupled with proton transport, as shown in Fig. 1. Keeping Reaction (4) in mind, the equilibrium constant K_{Mo} for molybdenum can be represented as

$$K_{Mo} = \frac{\underset{\text{org}}{[(R_3NH)_6 \cdot Mo_7O_{24}] \cdot G}}{\underset{\text{aq}}{[H^+]^6}\ \underset{\text{org}}{[NR_3]^6}\ \underset{\text{aq}}{[Mo_7O_{24}^{-6}]}} \tag{6}$$

where *G* is a factor introduced because of the activity coefficient of all the species involved. If λ represents the ratio of the distribution coefficient of Mo-ion concentration in the organic phase to that in the aqueous phase, then from Eqs. (5) and (6), and using the relation for λ:

$$\lambda = \frac{K_{Mo}}{G}\ \underset{\text{aq}}{[H^+]^6} \cdot \underset{\text{org}}{[NR_3]^6} \tag{7}$$

Subscripts "org" and "aq" refer to the organic and aqueous phases, respectively. For dilute solutions the activities of the involved solutions may approach unity and G → 1. Hence

$$\lambda = K_{Mo}\underset{\text{aq}}{[H^+]^6} \cdot \underset{\text{org}}{[NR_3]^6} \tag{8}$$

According to Fick's law, the flux, *J* of a species under transport is proportional to the concentration gradient, *dc*/*dx*, and so

$$\begin{aligned} J &\propto dc/dx \\ &= \frac{C_1 - C_2}{\delta} \end{aligned} \tag{9}$$

where *G* is the molar concentration of the ionic species, *x* is the position coordinate (the *x*-axis runs perpendicular to the phase boundaries of the membrane; the left boundary then has coordinate *x* as zero and the right boundary is $x = \delta$, the membrane thickness), and C_1 and C_2 are the concentrations of Mo(VI) in the feed and stripping side inside the membrane, i.e., at $x = 0$ and $x = \delta$. Equation (9) can be written as

$$J = \frac{D(C_1 - C_2)}{\delta} = \frac{D\lambda_1 C_1^{\circ} - \lambda_2 C_2^{\circ}}{\delta} \tag{10}$$

where λ_1 and λ_2 are the distribution coefficients of the Mo(VI) ions extracted from the feed and stripping sides in the bulk of the aqueous phases into the organic membrane phase. Superscript "°" in Eq. (10) refers to bulk conditions. D represents the diffusion coefficient of Mo(VI) ions in the membrane. When permeability coefficient $P = D\lambda$ and also if $\lambda_2 \rightarrow 0$:

$$J = \frac{D\lambda_1 C_1}{\delta} \quad \frac{PC_1^\circ}{\delta} \tag{11}$$

Taking into consideration porosity ε of the membrane, and combining Eqs. (8) and (11):

$$J = \frac{D\varepsilon C_1}{\delta} \underset{\text{aq}}{[\mathrm{H}^+]} \underset{\text{org}}{[\mathrm{NR}_3]^6} \tag{12}$$

It can be seen from Eq. (12) that the flux of metal ions is proportional to the concentration of protons present in the aqueous phase and the amine molecules present in the membrane or the organic phase, and the concentration of the metal ions present in the bulk of solution. The main assumptions for the validity of the Eq. (12) are:

1. The concentrations of all components of the medium within the membrane pores are only functions of the coordinate of position x.
2. The medium within the pores and the outside solutions are dilute.
3. The exchange of momentum between the dissolved components is neglected, but the exchange of momentum between the dissolved components and the matrix of the membrane is taken into account. This effect is included in the diffusion coefficient D, which is actually the effective diffusion coefficient.

By using the Wilke-Change relation $D = \bar{K}T/\eta$ from Ref. 5, where $\bar{K}$ is a constant, T is the absolute temperature, and η is the viscosity of the liquid in the membrane phase:

$$J = \frac{\bar{A}T \underset{\text{aq}}{[\mathrm{H}^+]^6} \underset{\text{org}}{[\mathrm{NR}_3]^6} \cdot C_1^\circ}{\eta} \tag{13}$$

$$\text{or } \log J = \log \bar{A}T - \log \eta + 6 \log ([H^+] + 6 \log [NR_3] + \log C_1^\circ \quad (14)$$

where $\bar{A}$ is another constant.

If the reaction indicated by Eq. (4) is true, then Eq. (14) will hold. If not, a general equation for the flux of Mo(VI) ions will be

$$\log J = \log \bar{A}T - \log \eta + n \log \underset{\text{aq}}{[H^+]} + m \log \underset{\text{org}}{[NR_3]} + \log C_1^\circ \quad (15)$$

It was shown in Ref. *3* that if ln C_{1t}/C_1 is plotted against time, then a straight line will be obtained with a slope

$$\frac{d[-\ln C_{1t}/C_1]}{dt} = \frac{\bar{A}P}{V\delta} \quad (16)$$

From Eq. (16), P, the permeability of the membrane under given conditions, can be determined. If λ is known from solvent extraction data, then the value of D can be determined from $P = \lambda D$.

RESULTS

The results obtained from this study for Mo(VI) transport through SLM are recorded in Figs. 2 to 14. The initial results showing Mo(VI) transport against a concentration gradient are shown in Fig. 2. The results related to the transport of this metal, indicating the effects of HCl concentration in the feed, TOA concentration in the membrane, NaOH concentration in the strip solution, and temperature, are shown in Figs. 3 and 4, 5 and 6, 7 and 8, and 9–11, respectively. The results related to solvent extraction of the metal ions are given in Figs. 12 and 13. The variations in pH and the concentration of the feed solution are shown in Fig. 14.

DISCUSSION

(i) It can be seen from Fig. 2 that Mo(VI) ions can be transported by the coupled transport phenomenon, according to the scheme indicated in Fig. 1, following Reactions (1) to (5). At higher pH, $(Mo_7O_{24})^{6-}$ ions are decomposed into simple MoO_4^{2-} ions as explained in Refs. *4* and *6–8*, so

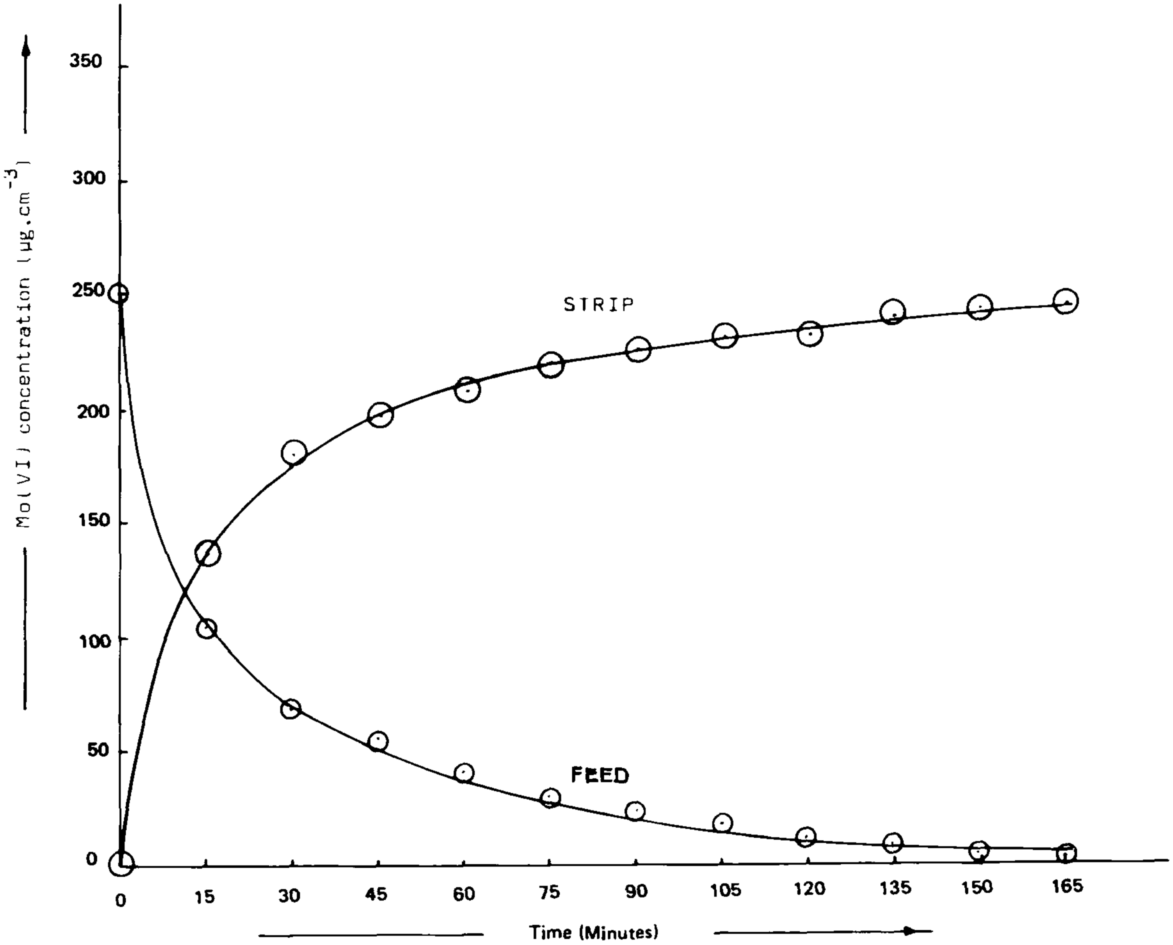


FIG. 2. Mo(VI) concentration as a function of time in feed and stripping solutions: 250 µg/cm^3 in 0.005 mol/dm^3 HCl and 0.1 *N* NaOH as strip solution.

the molybdenum anions become associated with the tri-*n*-octylamine ions in the presence of protons to form a $(R_3NH)_6Mo_7O_{24}$-type complex, which diffuses toward the other side of the membrane. Here six amine molecules associated with molybdenum(VI) ions have been considered, keeping stoichiometric ideas in mind. If there is any decomposition or association of the molybdenum anions in the solution as indicated in the literature (*4*), then the number of amine ions taking part in the transport of metal ions through the liquid membrane can be determined. One may do that through the use of Eqs. (12)–(14), but for that the viscosity of the liquid membrane solution phase must be known. Plots of log $J\eta/C_1^\circ$ versus log $[H^+]$ and log $[NR_3]$ will furnish the number of protons and the number of amine molecules taking part in the extraction and during transport process. Unfortunately, data for the viscosity of the liquid membrane phase are not available at present, and so the stoichiometry of the exact chemical reaction taking place in complex formation cannot be established.

(ii) In Figs. 3 and 4 the effect of HCl concentration on the transport of molybdenum(VI) anions is shown. It has been observed that the flux of metal ions increases up to 0.005 mol/dm³ HCl concentration but then suddenly falls at higher concentrations of HCl. As the concentrations of HCl selected for these experiments were not very high (from 0.001 to 0.1 mol/dm³), the preferred association of HCl with the amine molecules compared to that of the Mo(VI) ions under consideration is ruled out for the following reasons. References *4* and *6–8* state that different species of Mo(VI) with from one to more than ten metal atoms having different charges may be present in the solution as a function of pH. At different HCl concentrations, different species will be present in the solution. A more negative charge will be attracted by the protonated amine ions into the membrane, resulting in higher flux values, while species having lower charges may act oppositely. At pH 1–2.5, the $(Mo_{12}O_{41})^{10-}$ type of species has been reported (*4*), and it has a larger charge than any other species of molybdenum, even at still lower acid concentrations and higher pH values, so it must have a higher transport rate of metal ions at pH values between 1 and 2.5, as observed in the present study. The maximum flux is at pH 2.3 (0.005 mol/dm³ HCl), which conforms to the ideas indicated above. The permeability coefficient values as determined by using Eq. (16) and the flux are plotted in Fig. 4. It can be seen that the flux and permeability vary in the same pattern. The diffusion coefficient D has been calculated from $P = D\lambda$ (Table 1). The value of D varies from 1.8×10^{-12} to 26.8×10^{-11} m²/s while the value of λ varies from 81.8 to 7.77 as a function of HCl concentration, which explains the reason for low flux at higher HCl concentrations.

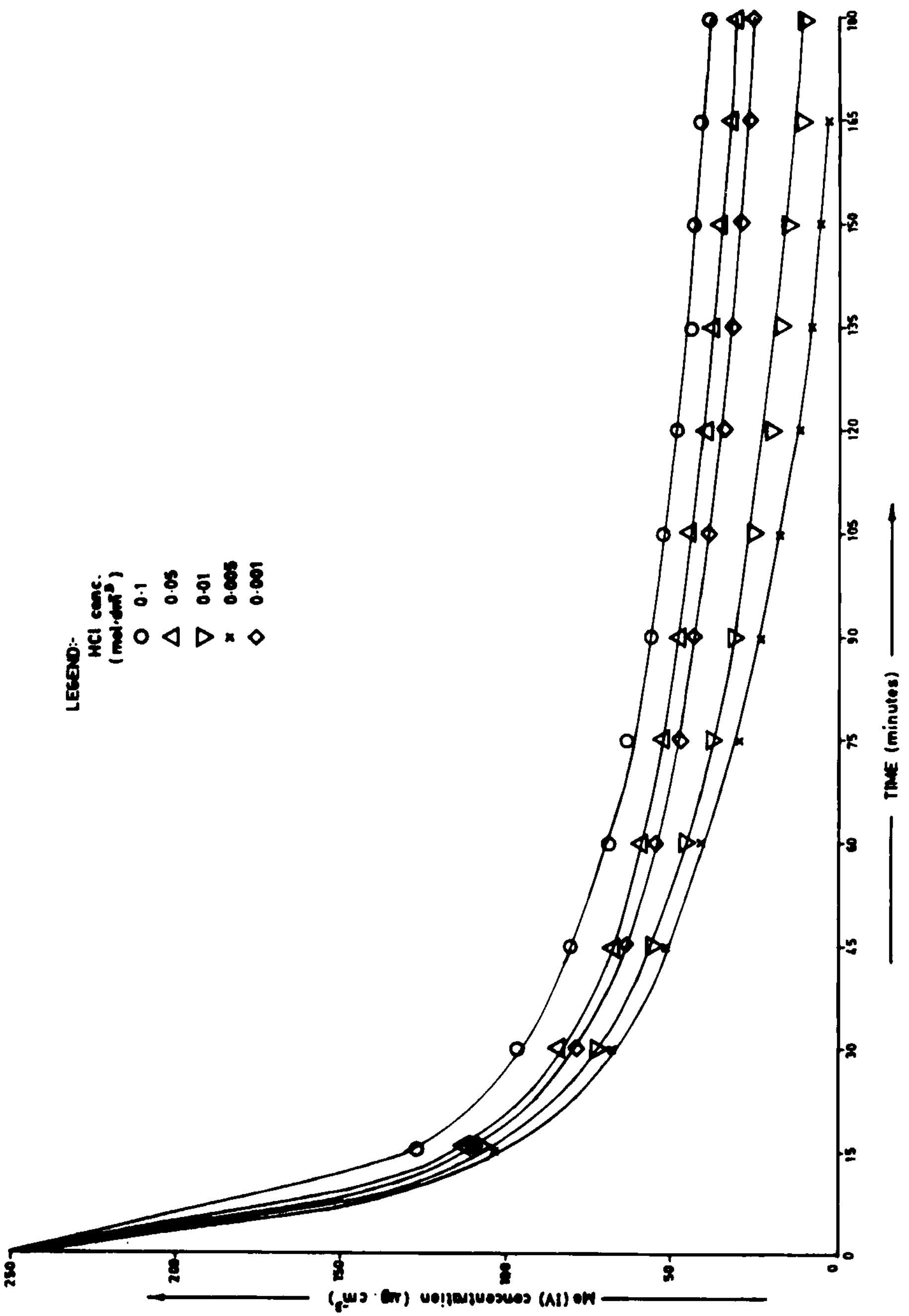


FIG. 3. Mo(VI) concentration versus time at various HCl concentrations in the feed solution.

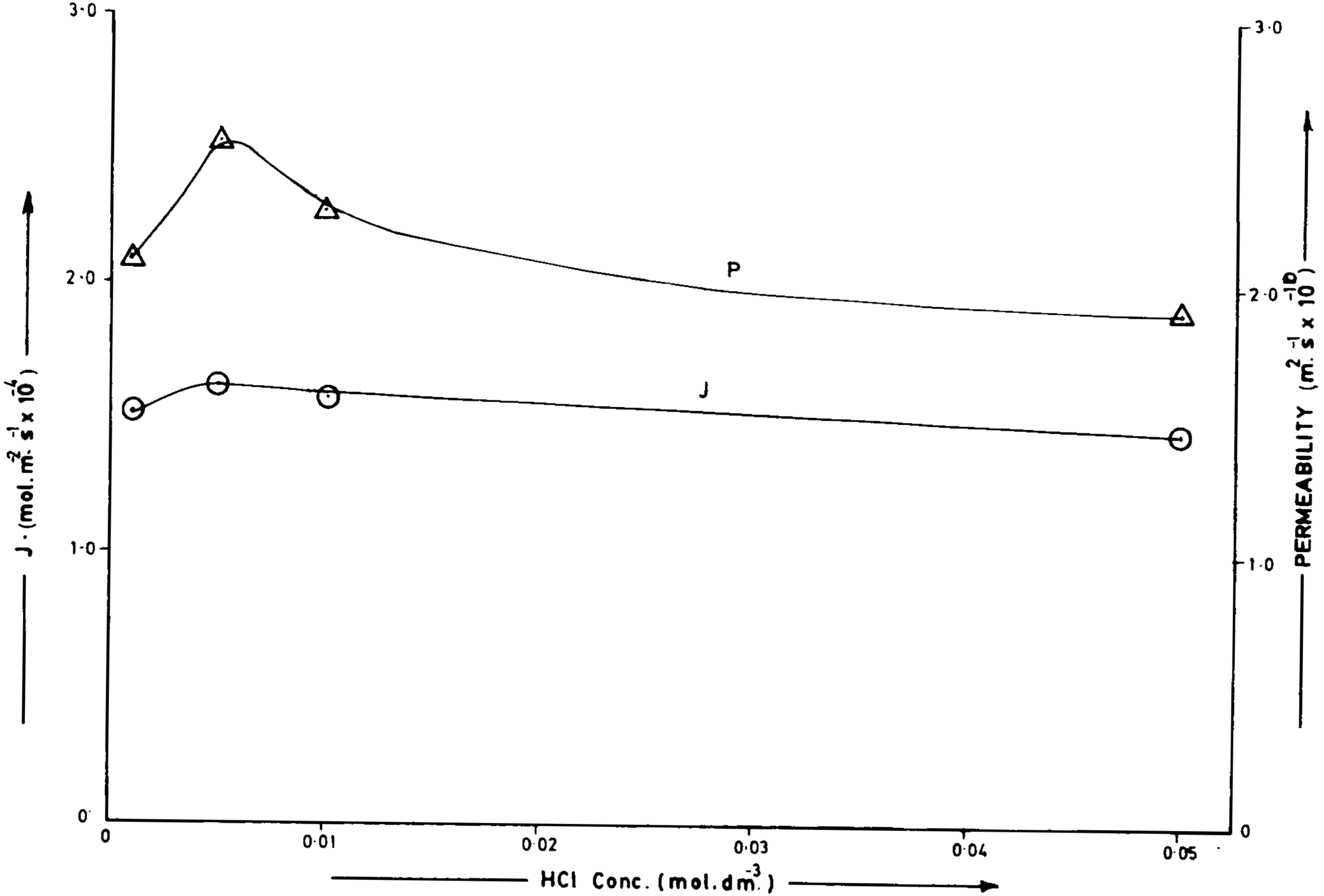


FIG. 4. Mo(VI) ions flux *J* and permeability *P* versus HCl concentration.

TABLE 1

Distribution Coefficient and Permeability of the Mo(VI) Ions through TOA–Xylene/Based Supported Liquid Membranes as a Function of HCl Concentration in the Feed (TOA concentration = 1.3-5 mol/dm^3; 35 ± 2°C

HCl concentration (mol/dm^3)	λ	P (m$^2 \cdot$ s$^{-1} \cdot 10^{-9}$)	D (m$^2 \cdot$ s$^{-1} \cdot 10^{-11}$)
0.001	81.80	1.47	1.80
0.005	62.09	1.91	3.08
0.010	16.67	2.26	13.50
0.150	8.85	2.51	28.40
0.100	7.77	2.08	26.80

(iii) The effect of TOA concentration in the membrane is shown in Figs. 5 and 6. It can be seen from Fig. 6 that the values of flux and permeability increase up to 1.35 mol/dm^3 TOA concentration and then it starts decreasing. This is expected, as reported in the literature for uranium (9) and chromium (*10*) transport through a liquid membrane using TOA, that viscosity has an adverse effect on the values of flux and permeability. Increasing TOA concentration results in more extraction and hence increases in flux and permeability values, but beyond that the opposite forces arising from more viscous liquids act in the opposite direction and reduce the flux and permeability values, as indicated in Fig. 6.

(iv) The effect of stripping solution concentration on the extraction of Mo(VI) ions is indicated in Figs. 7 and 8. The flux and permeability values increase with NaOH concentration up to 0.1 eq/dm^3 and after that start decreasing. The reason for the increase in flux and permeability values is quite obvious if we consider Reaction (2) and (5). An increase in hydroxyl ions results into faster decomposition of the Mo(VI) anion complex and removal of protons from the amine molecules, resulting in a higher stripping rate. But it has been observed that beyond a 0.1 eq/dm^3 NaOH concentration, the flux value decreases. This may be because the hydrated Mo-anionic species formed at higher NaOH concentrations has low extraction in a NaOH solution. The maximum values of flux and permeability values observed at 0.1 eq/dm^3 NaOH are 16.2×10^{-5} mol $\cdot$ m$^{-2} \cdot$ s^{-1} and 2.51×10^{-10} m^2/s, respectively.

(v) The effect of temperature on the transport of Mo(VI) ions is indicated in Figs. 9 and 10. As can be seen from Fig. 10, the flux and permeability values increase with an increase in temperature. There is about a 20-fold increase in the flux value as the temperature is increased from 10

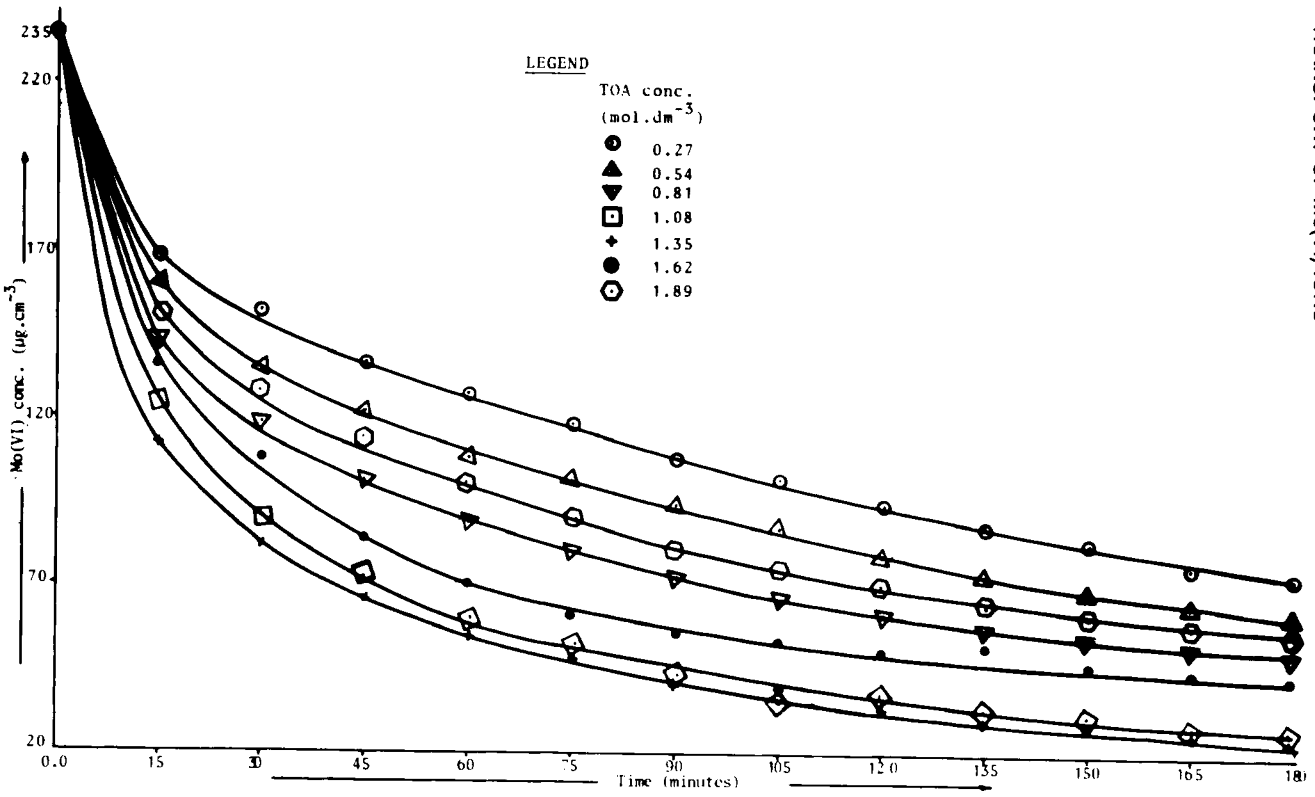


FIG. 5. Mo(VI) concentration versus time at various TOA concentrations.

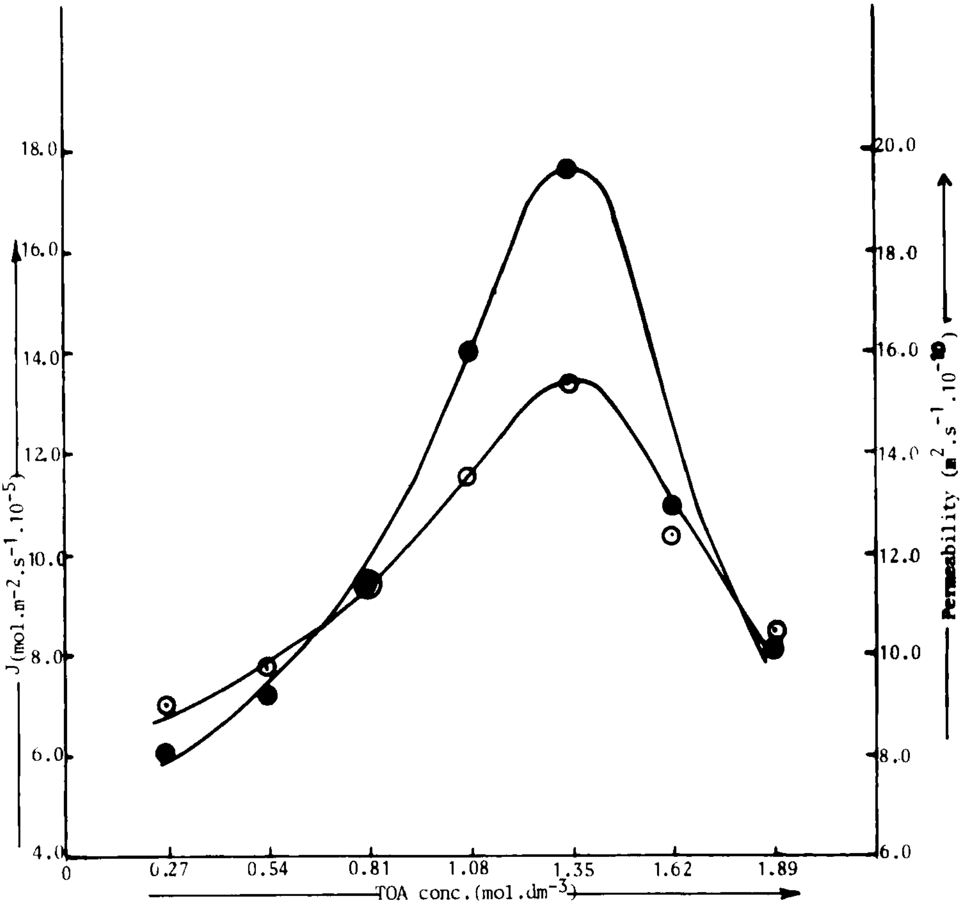


FIG. 6. Flux (O) and permeability (●) versus TOA concentration for Mo(VI) ions transport.

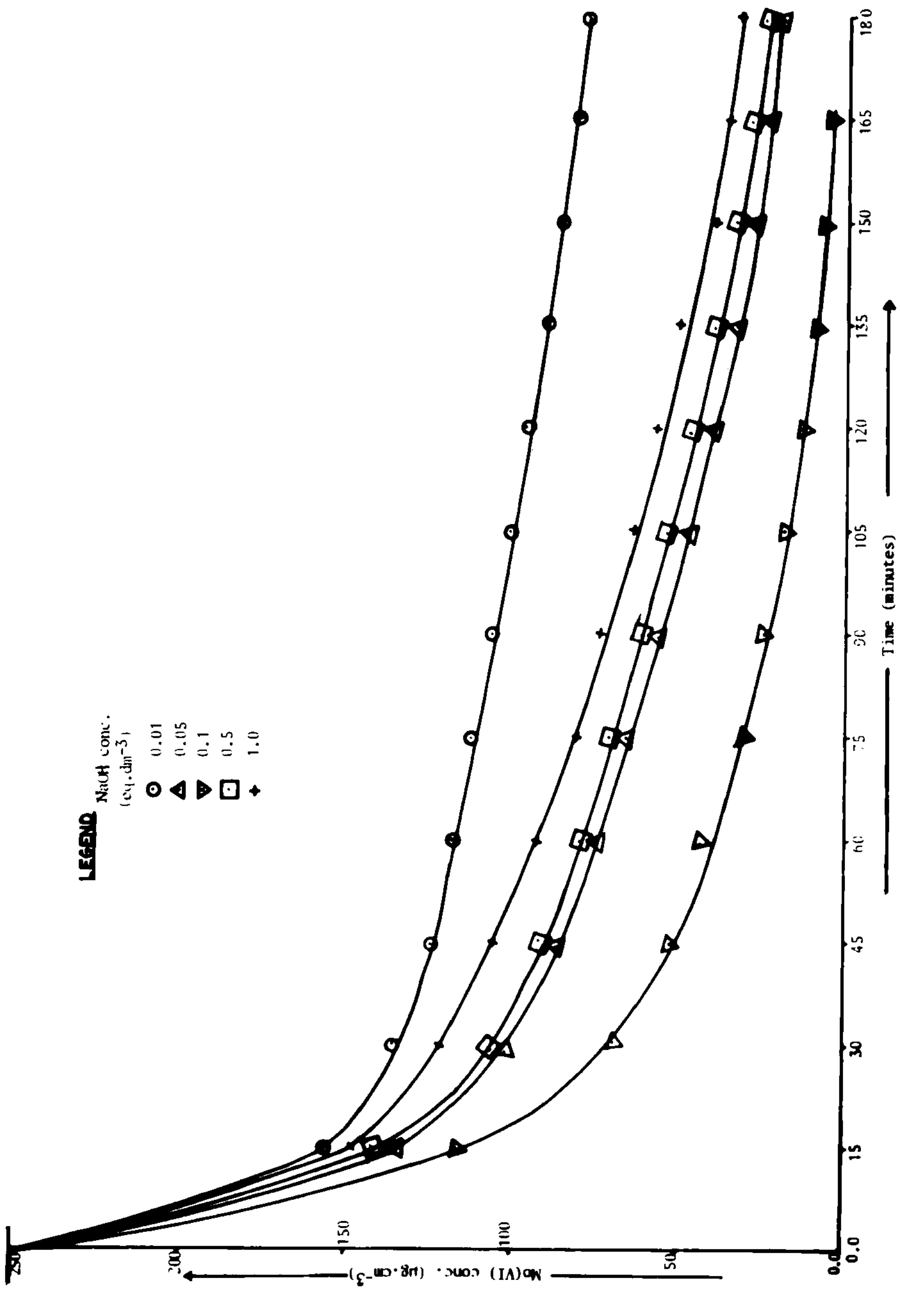


FIG. 7. Mo(VI) concentration versus time as a function of NaOH concentration in stripping solution.

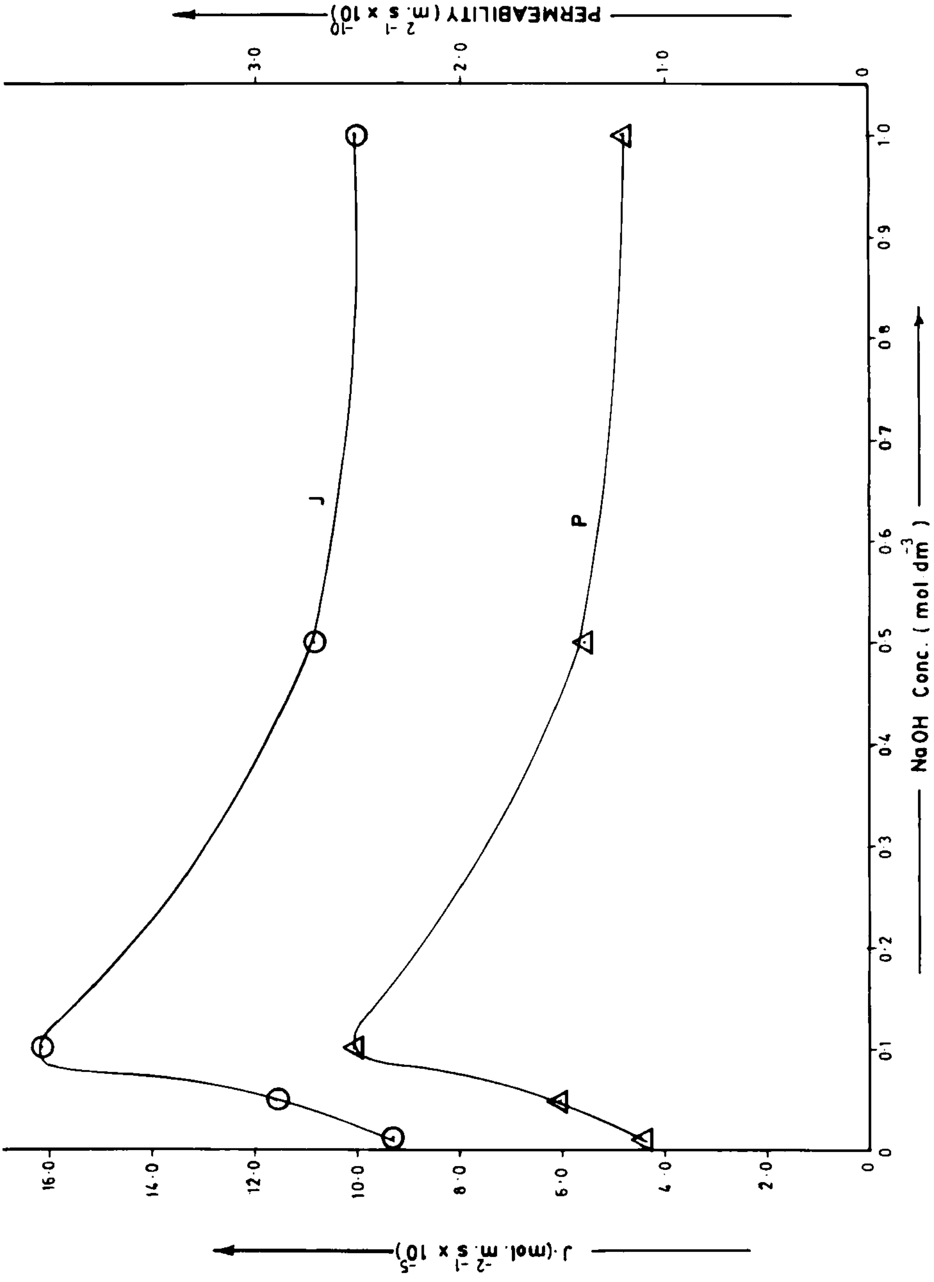


FIG. 8. Mo(VI) ions flux *J* and permeability *P* versus NaOH concentration in stripping solution.

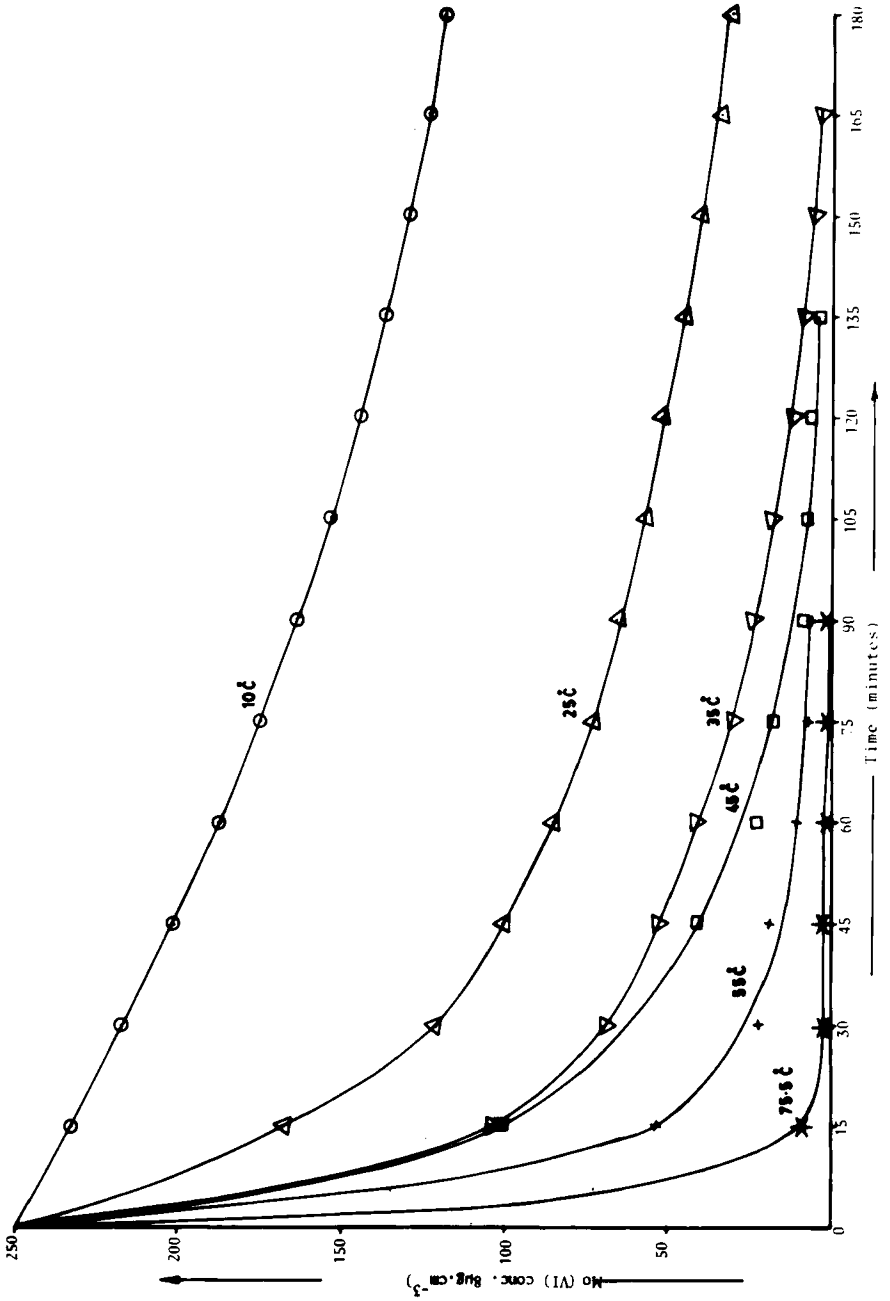


FIG. 9. Mo(VI) concentration versus time as a function of temperature.

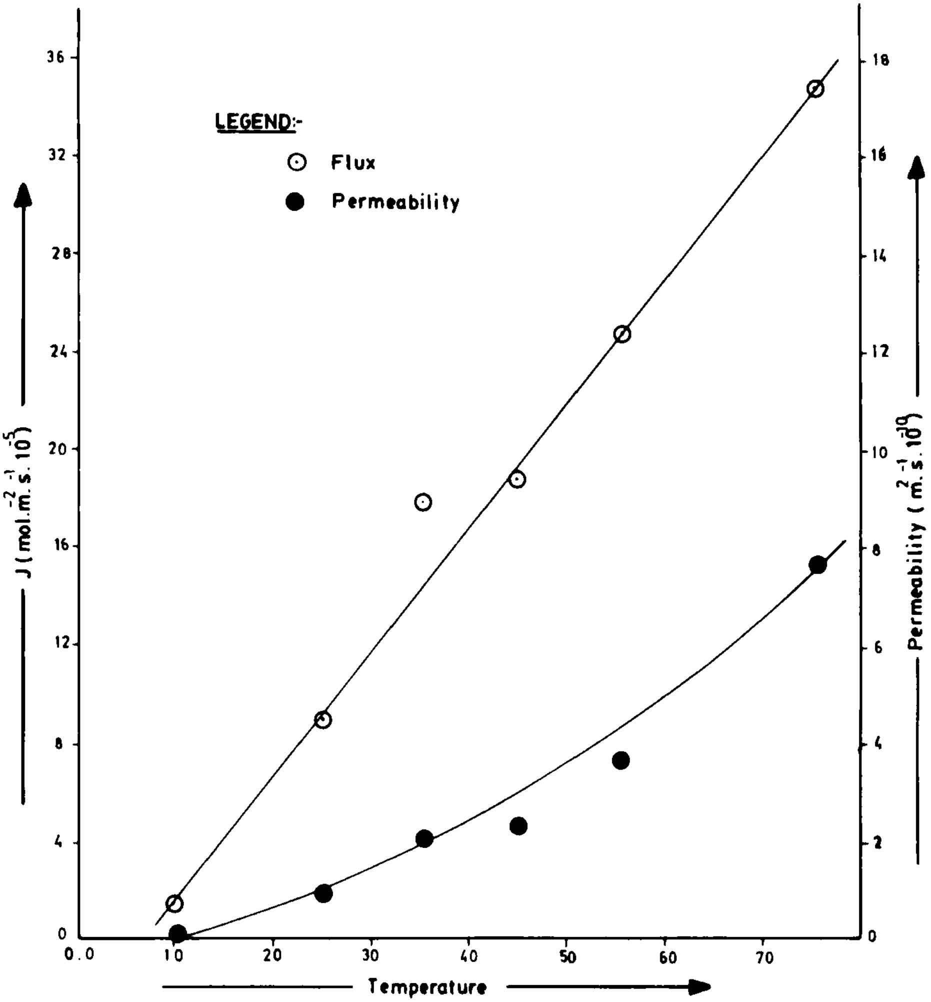


FIG. 10. Flux and permeability versus temperature for Mo(VI).

to 75°C. Plots of log *J* and log *P* versus 1/*T* are given in Fig. 11. The energy of activation value determined from the plot is 16 kJ/mol, while the value determined from the log *P* and 1/*T* plot is 15.92 kJ/mol. The activation energy is nearly the same in both cases. This means that only the diffusion phenomenon is responsible for the transport of Mo(VI) ions through the membrane after complexation of the metal and amine molecules at the feed-side-membrane interface.

(vi) The values of λ as a function of HCl concentration are recorded in Figs. 12 and 13 and Table 2 for different concentrations of TOA. It can be seen that there is a decrease in λ with an increase in HCl molarity; this is why a decrease in flux has been observed at higher HCl concentrations, as reported above.

(vii) In Fig. 14, changes in the concentration of Mo(VI) ions and the pH of the feed solution as monitored experimently are recorded. The pH of the solution increases with time up to 15 min, and then it starts decreasing continuously. It is clear that as the concentration of Mo(VI) ions decreases in the solution due to its transport into the stripping phase, there is a decrease in proton concentration in the solution, after which the $(Mo_7O_{24})^{6-}$ ions start decomposing and produce more protons in the solution, resulting in a decrease in pH. This reaction is (*4*)

$$(Mo_7O_{24})^{6-} + 4H_2O \rightleftharpoons 7(MoO_4)^{2-} + 8H^+ \qquad (17)$$

It is quite clear from this reaction that with the decomposition of one heptamolybdenum anion into a monomolybdenum anion, eight protons are produced. This is why the pH continuously decreases with the transport of molybdenum ions. Mo(VI) ions transport through the liquid membrane is coupled with protons. With a decrease in acid concentration in the feed,

TABLE 2

Distribution Coefficient (λ) as a Function of HCl and TOA Concentrations for Solvent Extraction of Mo(VI) Ions

TOA concentration (mol/dm^3)	λ at HCl (mol/dm^3) concentration				
	0.001	0.005	0.01	0.05	0.10
0.81	18.46	8.04	6.64	5.83	4.98
1.08	21.08	10.83	6.83	6.34	5.31
1.35	81.80	62.09	16.67	8.85	7.71
1.62	27.80	15.26	10.72	8.33	6.50
1.89	24.2	11.86	9.00	7.05	6.20

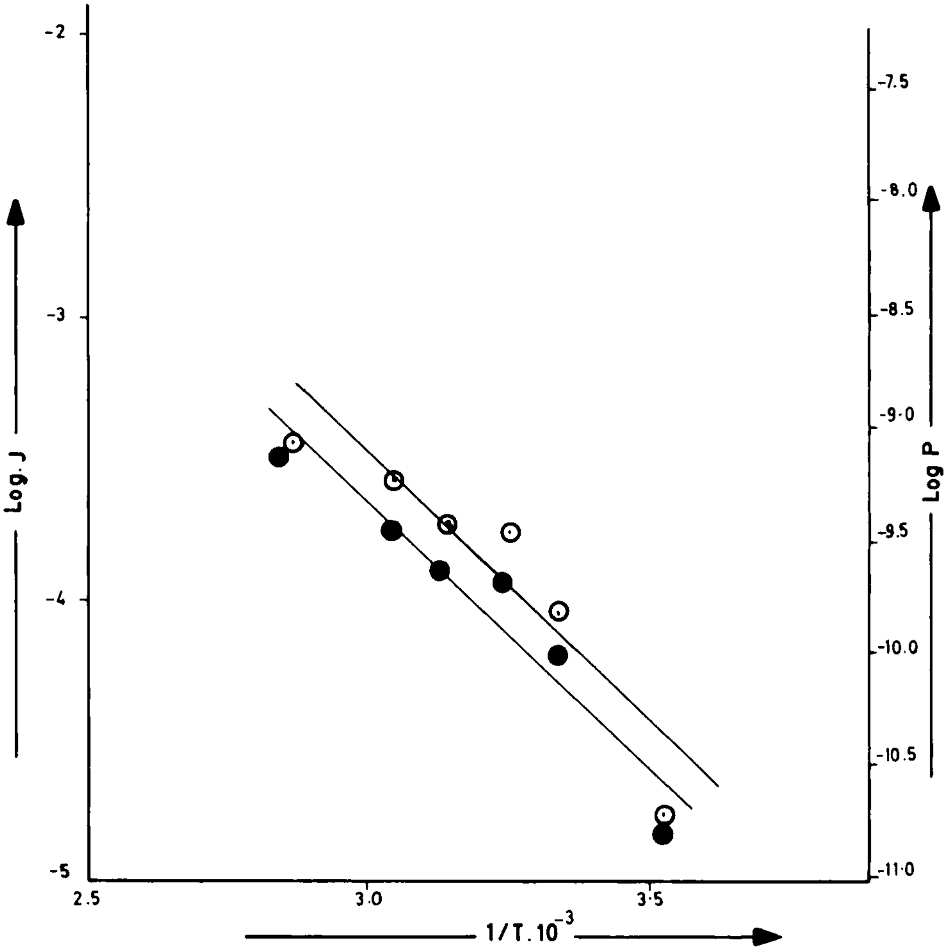


FIG. 11. Log J (○) and log P (●) versus $1/T$.

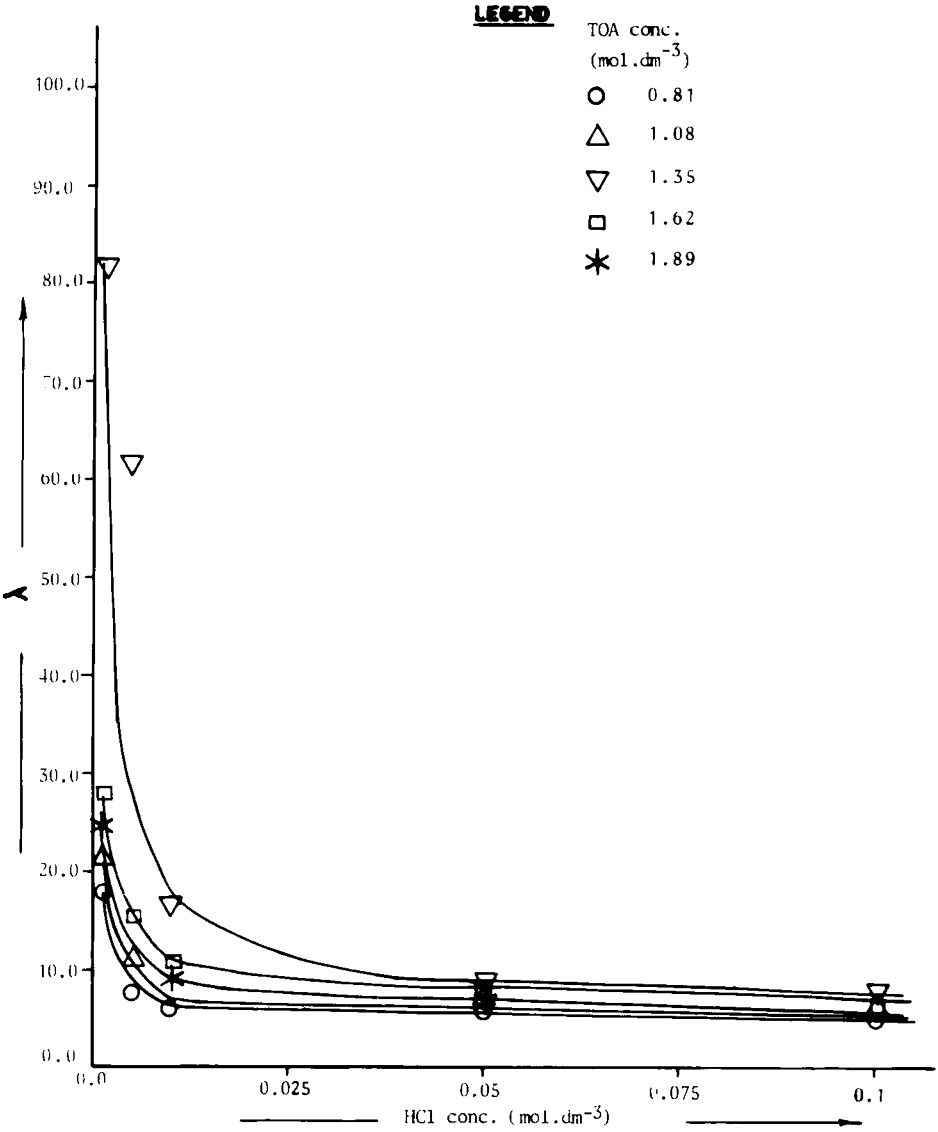


FIG. 12. λ versus HCl concentration at various TOA concentrations.

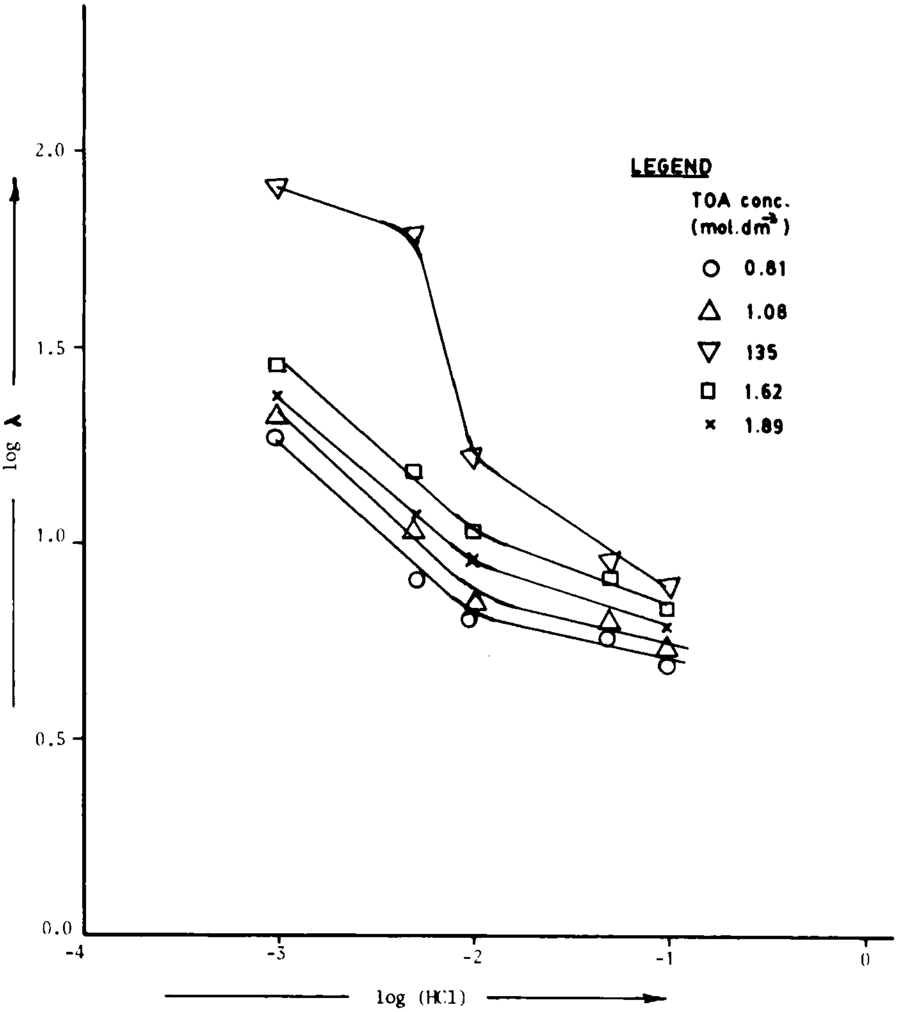


FIG. 13. Log λ versus log [HCl] for Mo(VI) at various TOA concentrations.

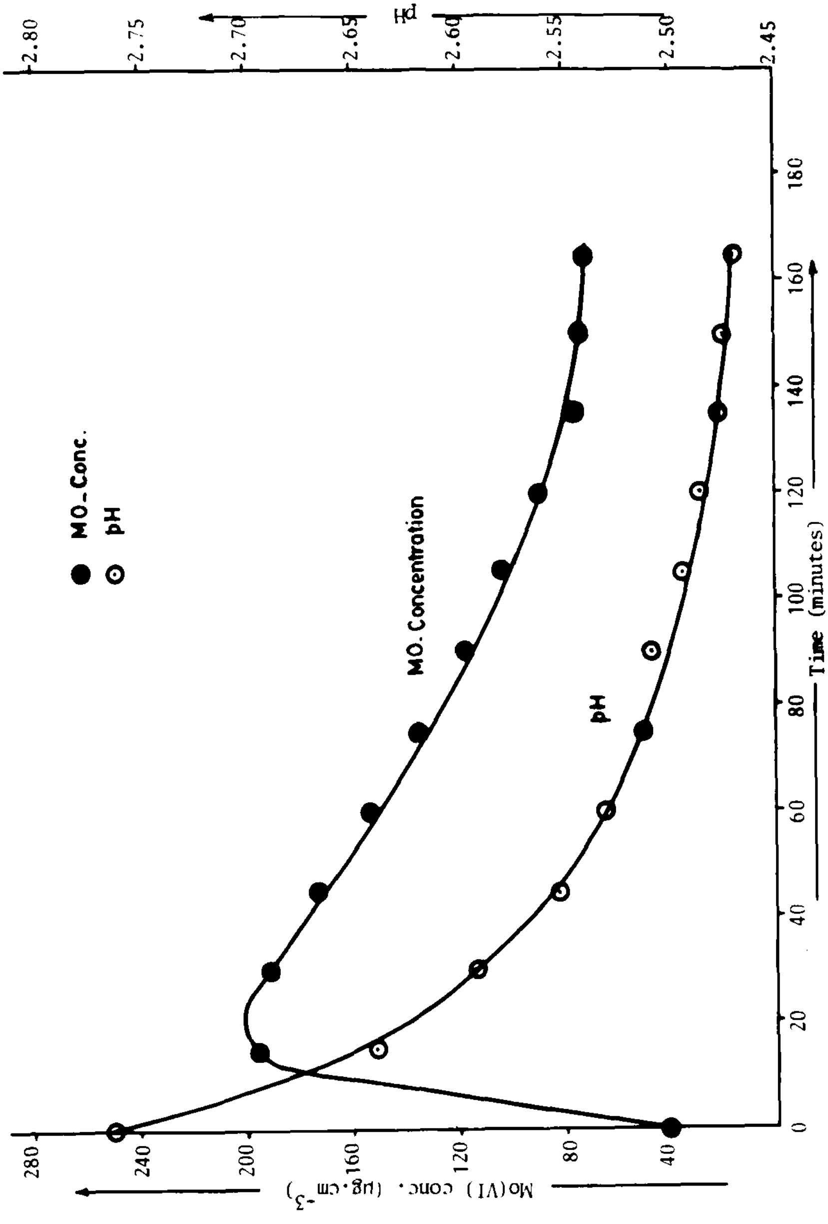


FIG. 14. Mo(VI) concentration and pH versus time.

there will be decrease in flux through the membrane. Because protons are produced by the above-mentioned reaction, there is no problem of proton scarcity in this case.

There is increase in pH from 2.5 to 2.69 within 15 min, after which pH starts decreasing. The concentration of Mo(VI) ions in the feed has also been monitored as a function of time, so the protons transported across the membrane per mole of Mo(VI) ions can be determined with the change in pH of the feed solution. Let the pH at $t = 0 = \mathrm{pH}_{t0}$ and at $t = t_1 = \mathrm{pH}_{t1}$. Therefore the change in acid concentration $\Delta[\mathrm{H}^+]_1$ is given by

$$\Delta[\mathrm{H}^+]_1 = [10^{-\mathrm{pH}_{t0}} - 10^{-\mathrm{pH}_{t1}}] \tag{18}$$

If the cell volume is V, then the total protons or acid shifted toward the strip solution is given by M_{H^+}:

$$M_{\mathrm{H}^+} = \frac{\Delta[\mathrm{H}^+]_1 V}{1000} \tag{19}$$

Also, the amount of Mo(VI) ions, $\mathrm{M}_{\mathrm{Mo}1}$ transported to the strip solution is given by

$$\mathrm{M}_{\mathrm{Mo}1} = \frac{V(C_0 - C_t) \times 10^{-6}}{95.94} \tag{20}$$

Here C_0 and C_t are the concentrations of Mo(VI) ions in ppm. The rate of protons transported per mole of Mo ions transferred is r, given by

$$r = \frac{\mathrm{M}_{\mathrm{H}^+}}{\mathrm{M}_{\mathrm{Mo}}}$$

or

$$r = \frac{\mathrm{M}_{\mathrm{H}^+}}{\mathrm{M}_{\mathrm{Mo}1}} = \frac{10^3(10^{-\mathrm{pH}_{t0}} - 10^{-\mathrm{pH}_{t1}})(\text{atomic weight of Mo})}{C_0 - C_t} \tag{21}$$

The value of r determined for increasing pH has been found to be 1.097.

From the decrease in pH with the passage of time, the change in hydrogen ion concentration $\Delta[H^+]_2$ can also be determined for a given amount of metal ions transport:

$$\Delta[H^+]_2 = \frac{V[10^{-pH_{t2}} - 10^{-pH_{t1}}]}{1000} \tag{22}$$

also

$$M_{Mo2} = \frac{V(C_{t1} - C_{t2}) \times 10^{-6}}{95.94} \tag{23}$$

All concentrations units are in µg/cm^3 and V is in cm^{-3}. As the rate of transport of H^+ ions through the liquid membrane is r, therefore the total H^+ ions transported during the time interval $(t_1 - t_2)$ is rM_{Mo2}.

Keeping in mind the decrease in pH, the total amount of protons produced during time $(t_1 - t_2)$ is

$$\Delta[H^+] = rM_{Mo2} + \Delta[H^+]_2$$

$$= \frac{1000(10^{-pH_{t0}} - 10^{-pH_{t1}})}{C_0 - C_t} \quad \frac{V(C_{t1} - C_{t2}) \times 10^{-6}}{95.94}$$

$$+ \frac{(10^{-pH_{t2}} - 10^{-pH_{t1}}V)}{1000} \tag{24}$$

According to Reaction (17), 1.142 moles of protons are produced per mole atom of Mo, so the number of mole atoms of Mo decomposed during the time interval $(t_1 - t_2)$ are $\overline{M}$, i.e.,

$$\overline{M} = \Delta[H^+]/1.142 \tag{25}$$

and the moles of $(Mo_7O_{24})^{6-}$ decomposed are

$$M = \Delta[H^+]/(1.142 \times 7) \tag{26}$$

and so the rate of decomposition of $(Mo_7O_{24})^{6-}$ is

$$r_1 = \Delta[H^+]/(1.142 \times 7)(t_1 - t_2) \tag{27}$$

The rate of $(Mo_7O_{24})^{6-}$ decomposition in the present case is therefore 6.29 × 10^{-9} mol/s.

(viii) The mechanism of Mo(VI) ion transport through the membrane under study is given in Fig. 1, i.e., association of metal ions with protonated TOA molecules on the feed side of the membrane interface, diffusion through the membrane and decomposition of the complex on the strip side under alkaline conditions, backdiffusion of TOA molecules, and decomposition of polymetal anions in the strip solution. The transport from feed to strip solution is possible against a concentration gradient of metal ions and in the membrane in the direction of the concentration gradient of the metal–TOA complex. Because decomposition of $(Mo_7O_{24})^{6-}$ ions may occur, the species complexing with TOA may vary, and mixed species or complexes may be formed. The transport of Mo(VI) ions is therefore based on the diffusion of these complexes through the membrane, ending in their decomposition at the strip solution interface. Because D values are very small compared to λ, D is the controlling factor in the transport of Mo(VI) ions through such membranes.

CONCLUSION

Mo(VI) ions can be moved against their concentration gradient through supported liquid membranes. For molybdenum(VI), the optimum conditions of flux have been found and are 0.005 mol/dm^3 HCl concentration in the feed solution, 1.35 mol/dm^3 TOA in xylene in the liquid membrane, and 0.1 eq/dm^3 sodium hydroxide in the stripping solution. (The maximum flux is 1.62×10^{-4} mol · m^{-2} · s^{-1} and the maximum permeability is 2.51×10^{-10} m^2/s). The flux of metal ions increases with an increase in temperature. It is concluded that this method can be applied on a large scale for the separation of these metal ions because of the low energy consumption, the small amount of carriers involved, and the high flux value. The work has also furnished information about Mo(VI) ions decomposition in solution during membrane extraction. The mechanism of transport of these metal ions appears to be similar to that presented in Fig. 1, but the mechanism can be confirmed only after there is knowledge about all the species involved. Further studies are required.

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REFERENCES

1. R. Shanker and K. S. Venkateswarlu, *Sep. Sci.*, *11*(6), 591–596 (1976).
2. R. E. Boyd, *Radiochim. Acta*, *30*, 123–145 (1982).
3. M. A. Chaudry, Noor-ul-Islam, and D. Mohammad, *J. Radioanal. Nucl. Chem.*, *109*, 11 (1987).
4. A. Rusheed. "Studies on the Aggregation of Molybdates," PhD Thesis, University of Surrey, England, 1967.
5. C. R. Wilke and P. Chang, *AIChE J.*, *1*, 264 (1960).
6. G. Jander, K. F. Jahr, and W. Heuksharen, *Z. Anorg. Allgem. Chem.*, *194*, 383 (1930); *215*, 310 (1933).
7. G. Jander and K. F. Jahr, *Kolloid-Beihefte*, *41*, 1–57 (1935).
8. H. Brintzinger and W. Brintzinger, *Z. Anorg. Allgem. Chem.*, *196*, 55 (1931).
9. M. Chaudry, Noor-ul-Islam, and D. Mohammad, *J. Radioanal. Nucl. Chem.*, *111*(1), 211–231 (1987).
10. M. A. Chaudry, Noor-ul-Islam, and D. Mohammad, *Nucleus*, *23*(1,2), 7–12 (1986).

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