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Supported Liquid Membrane Extraction Study of $(MoO_4)^{2-}$ Ions Using Tri-*n*-octylamine as Carrier

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Abstract

The transport of $(MoO_4)^{2-}$ ions across a tri-*n*-octylamine (TOA) xylene-based supported liquid membrane has been studied at various HCl concentrations in the feed, TOA concentrations in the membrane, and NaOH concentrations in the strip solution. The distribution coefficient and flux of the Mo(VI) ion species vary with the HCl concentration, indicating that different polymeric species of this metal ion are present in the aqueous solution. A TOA concentration increase of up to 1.308 mol/dm^3 enhances flux and permeability of this metal ion, which beyond this concentration is reduced due to an increase in carrier liquid viscosity. An increase in NaOH solution concentration has been found to increase flux and permeability values. The continuous increase in pH of the feed with the transport of metal ions indicates that the $(MoO_4)^{2-}$ transport does not involve a decrease or increase in concentration as a result of association of lower to higher or decomposition of higher to lower metal ions polymeric species. The optimum conditions of transport of Mo(VI) metal ions across these membranes have been found to be HCl = 0.01, [NaOH] = 1, and [TOA] = 1.308, furnishing flux and permeability values of the order of 2.49×10^{-4} mol·m^{-2}·s^{-1} and 2.32×10^{-10} m^2·s^{-1}, respectively.

INTRODUCTION

Molybdenum extraction, as its Mo(VI) anionic species from aqueous solutions in the form of ion pairs, has been performed by a number of authors (*1–4*). Studies on a liquid membrane based on tri-*n*-octylamine (TOA) in xylene supported on a microporous polypropylene film have been performed in our laboratory. $(Mo_7O_{24})^{6-}$ ions were used for this transport study (*5*). The ions were found to move against their concentration gradient. The present study is an extension of the same work, with $(MoO_4)^{2-}$ ions. In the previous work it as discovered that the $(Mo_7O_{24})^{6-}$ ions decompose to furnish protons to support the coupled transport process. In

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the present work the $(MoO_4)^{2-}$ ions are used in the feed solution to study such parameters as the effect of HCl concentration in the feed, TOA concentration within the membrane, and NaOH concentration in the stripping solution. The flux and permeability of the given metal ions were determined under the various conditions. The objective behind this work was to study the transport of $(MoO_4)^{2-}$ ionic species across a liquid membrane and to compare it with $(Mo_7O_{24})^{6-}$. This will help to optimize the conditions of transport of this metal ion from aqueous solutions.

2. EXPERIMENTAL

2.1. Apparatus

2.1.1. Liquid Membrane Cell

The cell is described in Ref. 5. It consists of two half cells, each of 106 cm^3 volume. Membranes of 12.56 cm^2 effective area could be supported between the two cell halves, with electric stirrers to agitate the solution at a speed > 1500 rpm.

2.1.2. Liquid Membranes

Celgard 2400, a polypropylene microporous film, hydrophobic in nature, 25 μm thick and 0.2 μm pore size, was used to prepare the membrane by soaking it in the TOA given concentration solution in xylene for more than 24 hours.

2.1.3. Analytical Instruments

Spectrophotometer M/s Shimadzu, Japan, and pH meter from Orion Research were used for analysis of these sample solutions.

2.2. Chemicals and Reagents

2.2.1. Chemicals

Sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ (G.P.R.), methanol, HCl, sodium acetate, acetic acid, and NaOH AnalR grade were all obtained from BDH; AnalR grade Tri-*n*-octylamine; Practical grade and Eriochrome Black-T, Standard grade from Fluka were used without further purification. Milli-Q water, purified through reverse osmosis and ion-exchange columns, was used throughout this study.

2.2.2. Reagents

The reagents used were the same as given in Ref. 5 and were prepared in the same fashion except that $(MoO_4)^{2-}$ solution was prepared from a known quantity of its salt by dissolving it in the given acid concentration solution.

2.3. Flux Measurement and Analytical Procedure

The flux measurement was performed in the same way as described in Ref. *5* except that all these experiments were performed at 25 ± 2°C. The samples were also analyzed in the same way.

3. THEORETICAL

The $(MoO_4)^{2-}$ ions present in solution may become associated in the feed side membrane face:

$$R_3N + 2H^+ \rightleftharpoons R_3NH^+ \qquad (1)$$

$$2R_3N^+H + (MoO_4)^2 \rightleftharpoons (R_3NH)_2 \cdot MoO_4 \qquad (2)$$

or

$$2R_3N + 2H^+ + (MoO_4)^{2-} \rightleftharpoons (R_3NH)_2 \cdot MoO_4 \qquad (3)$$

The associated $(MoO_4)^{2-}$ ions as $(R_3NH)_2 \cdot MoO_4$ will then diffuse through the membrane under this complex concentration gradient and will be dissociated on the alkaline side of the membrane:

$$(R_3NH_4) \cdot MoO_4 + 2NaOH \rightarrow Na_2MoO_4 + 2H_2O + 2R_3N \qquad (4)$$

This means that two protons are coupled when $(MoO_4)^{2-}$ ions transport across the membrane. Therefore, the concentration of protons on the feed solution side of the membrane will reduce with the passage of time as the Mo(VI) ions pass through the membrane.

In neutral and alkaline aqueous medium, the molybdate anion $(MoO_4 \cdot XH_2O)^{2-}$ is the only Mo(VI) species. In the acid solution its protonation takes place stepwise and a four protons addition $(MoO_2 \cdot YH_2O)^{2+}$ is formed (in the strongly acidic medium) as the final mono-nuclear product. In diluted ($<10^{-5}$ mol/dm^3) Mo(VI) ions the condensation products are not formed, and that is why the $(MoO_4)^{2-}$ ion has been considered to be the associating anion in the complex formation with amine molecules.

It was observed in a previous paper (*5*) that $(Mo_7O_{24})^{6-}$ anions are decomposed during transfer of Mo(VI) metal ions across TOA xylene-based supported liquid membranes, and equations representing the flux and permeability of the given membranes were developed. In the same way, keeping Reaction (3) in mind, the equilibrium constant K_{Mo} for Mo can be represented as

$$K_{Mo} = \frac{[(R_3NH)_2 \cdot MoO_4] \cdot G}{\underset{org}{[R_3N]^2}\underset{aq}{[H^+]^2}\underset{aq}{[MoO_4^{2-}]}} \tag{5}$$

where G represents an activity coefficient-based factor of the various species involved and will be nearly equal to 1 at low metal ion concentrations.

It can be shown that

$$\lambda = K_{Mo}[H^+]^2 \cdot [NR_3]^2 \tag{6}$$

where λ is the ratio of the Mo(VI) ion concentration in the organic to that in the aqueous phase.

Proceeding in the same way as in Ref. 5, the relation between flux J and diffusion coefficient D is given by

$$J = \frac{D\epsilon C_1}{\delta\eta} \underset{aq}{[H^+]}\underset{org}{[NR_3]} \tag{7}$$

Using the same idea as in Ref. 5, it can further be shown that

$$J = \frac{\bar{A}T}{\delta\eta} \underset{aq}{[H^+]^2}\underset{org}{[NR_3]^2} C_1^\circ \tag{8}$$

In Eqs. (7) and (8), C_1° represents the Mo(VI) ion concentration in the feed solution, δ is the membrane thickness, ϵ is the porosity of the membrane, and D is the diffusion coefficient of the complexed Mo(VI) ions species through the membrane phase. η is the viscosity of the membrane organic phase. $\bar{A}$ is a constant at constant T, the absolute temperature. The logarithmic from Eq. (8) becomes

$$\log J = \log \bar{A}T - \log \eta + 2 \log \underset{aq}{[H^+]} + 2 \log \underset{org}{[NR_3]} + \log C_1^\circ \tag{9}$$

For P, the permeability of the membrane, the equation used is

$$-\ln \frac{C_{1t}^\circ}{C_1^\circ} = \frac{APt}{V\delta} \tag{10}$$

where A is the effective membrane area and V is the feed solution volume used. C_0 and C_{1t} represent the feed solution concentrations of Mo(VI) ions at time $t = 0$ and at $t = t$. The slope of the line from a plot of $-\ln C^{\circ}_{1t}/C^{\circ}_{1}$ versus t will furnish the value of P.

4. RESULTS AND DISCUSSION

The results are shown in Figs. 1–3. Figure 1 represents the plot of feed solution Mo(VI) ions concentration versus time at different HCl concentrations in the feed. Plots of Mo(VI) ions concentration in the feed as a function of time are given in Fig. 2 at various TOA concentrations in the

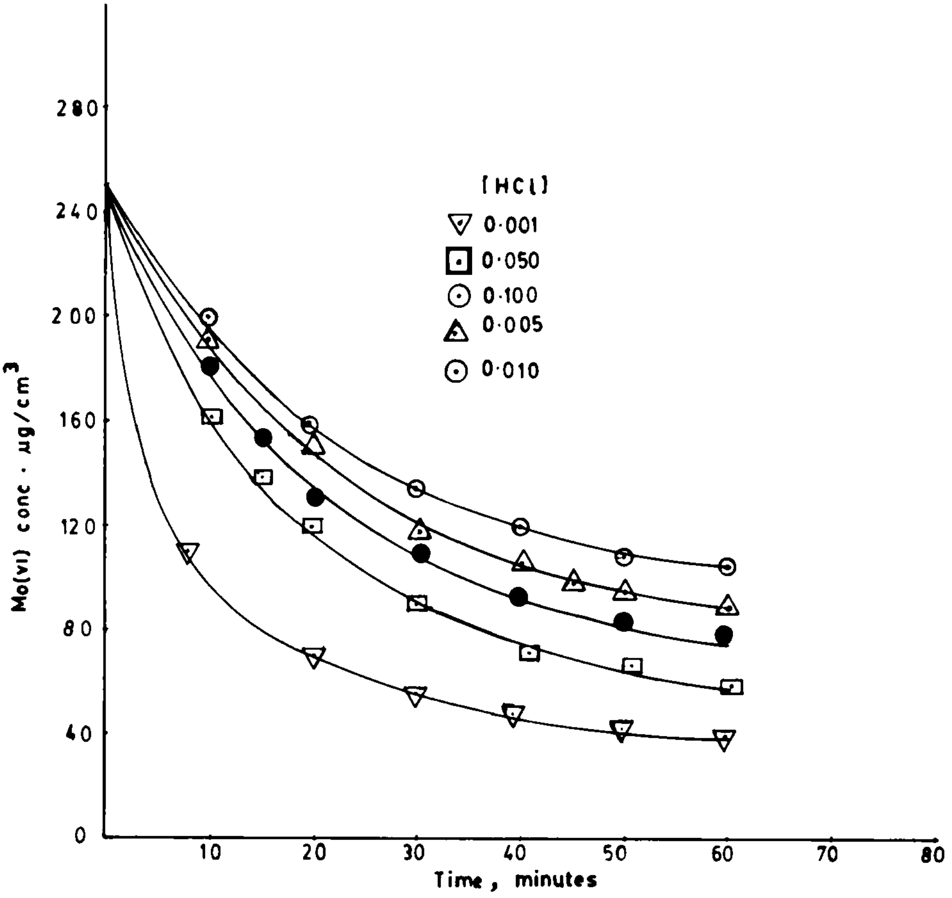

FIG. 1. Plot of feed solution Mo(VI) concentration versus time at various HCl concentrations.

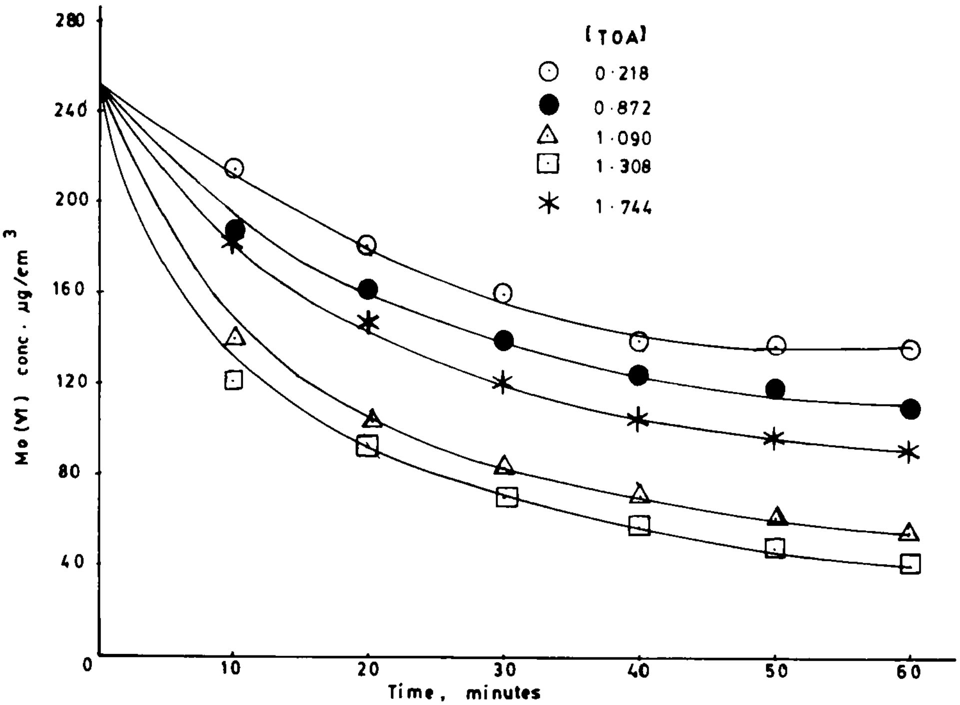

FIG. 2. Plot of Mo(VI) ions concentrations in the feed versus time at different TOA concentrations in the membrane.

membrane. Figure 3 is a plot of Mo(VI) concentration as a function of time at various NaOH concentrations in the stripping solution.

4.1. Effect of HCl Concentration in Feed

It can be seen from Figs. 1 and 4 that both the flux and distribution coefficient (DC) of $(MoO_4)^{2-}$ ions decrease from 0.001 to 0.01 mol/dm^3 HCl concentration and then start increasing. This trend is maintained up to 0.05 mol/dm^3. After that, both the flux and DC values decrease. This means that distribution into the organic membrane phase plays an important role. In our previous work (*5*), when $(Mo_7O_{24})^{6-}$ ions were used, the flux of Mo(VI) ions through a similar liquid membrane increased up to 0.005 mol/dm^3 HCl concentration and continuously decreased beyond that concentration. The range of HCl concentration selected was from 0.001 to 0.1 mol/dm^3. The fast transport at lower acid concentration was attributed to the possibility of higher charge containing species like $(Mo_{12}O_{14})^{10-}$ which may be present in the solution at pH 1–2.5. The HCl concentration used in the feed solution with $(MoO_4)^{2-}$ ions has also been kept from 0.001 to

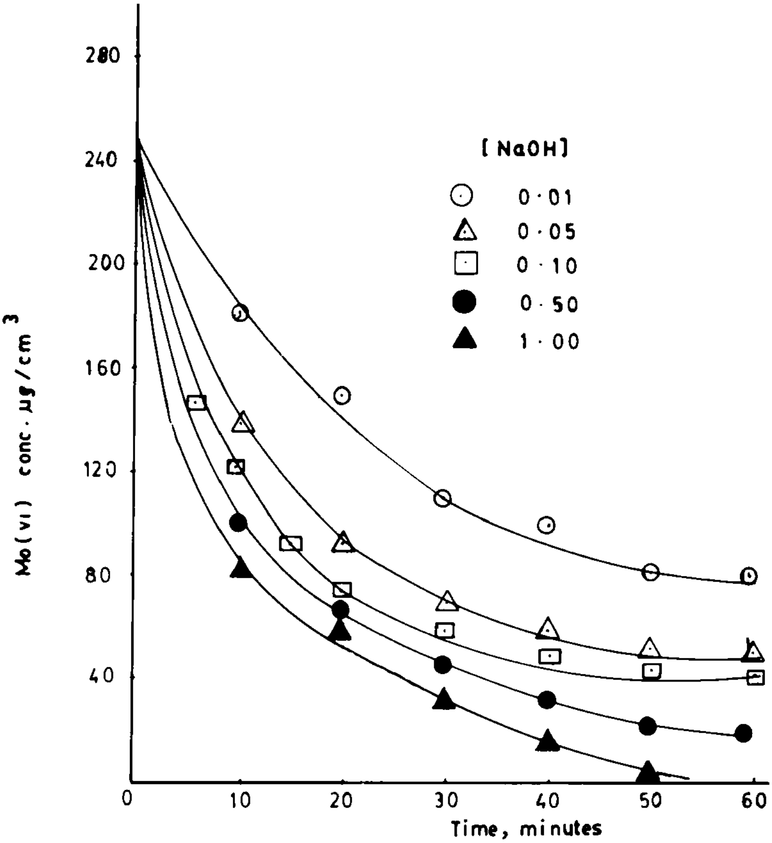

FIG. 3. Plot of Mo(VI) concentration versus time at different NaOH concentrations.

0.1 mol/dm^3, i.e., within the pH range of 3 to 1. $(Mo_6O_{21})^{6-}$ species may be present between pH 4.5 to 2, and $(M_{12}O_{41})^{10-}$ at pH 1.5 to 1. This means that $(MoO_4)^{2-}$ ions are converted at the related concentration. $(MoO_4)^{2-}$ ions are present in the aqueous solution at pH 6.5. Trimolybdate $(Mo_3O_{11})^{4-}$ species are present at pH 6.5 to 5. The $(MoO_4)^{2-}$ ions are converted to other species as by Eq. (4):

$$\begin{tikzcd}
(MoO_4)^{2-} \arrow[r] & \text{dimer} \arrow[r] & \text{timer} \arrow[r] & \text{hexamolybdate} \\
 & & (H_3Mo_6O_{21})^{3-} \arrow[d, leftrightarrow] & \\
\left.\begin{matrix}(Mo_{10}O_{32})^{4-} \\ (Mo_6O_{26})^{6-}\end{matrix}\right] & (Mo_7O_{24})^{6-} \arrow[l] & (H_3Mo_6O_{22})^{3-} \arrow[l] &
\end{tikzcd}$$

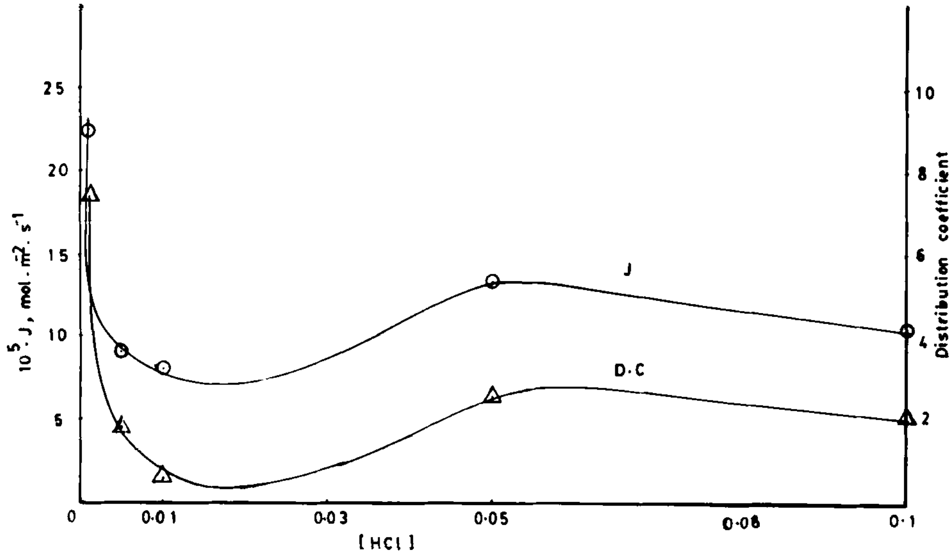

FIG. 4. Plot of flux (O) and distribution coefficient (△) versus HCl concentration.

As observed in Fig. 4, the flux is maximum at pH 3, i.e., at a HCl concentration of 0.001 mol/dm^3. This means that the $(MoO_4)^{2-}$ species has been converted to $(Mo_6O_{21})^{6-}$ ions and that the (MoVI) ion concentration is low. It may be present not as $(H_3MoO_{21})^{3-}$ ions but in ionized form at pH 3 and as $(H_3Mo_6O_{21})^{3-}$ at pH 2, and as a consequence at 0.001 mol/dm^3 HCl concentration the flux is higher, which is due to the higher charge-containing species. The continuous reduction in flux and distribution coefficient of Mo(VI) ions reflects that at 0.001 or lower acid concentration, Mo(VI) ions species like $(Mo_6O_{21})^{6-}$ may be free from protons, and the portion addition takes place continuously as the pH is decreased to 2, when the Mo will be present as $(H_3Mo_6O_{21})^{3-}$ or $(H_3Mo_6O_{22})^{3-}$ which is less extractable after association with (R_3NH^+) ions compared to $(Mo_6O_{21})^{6-}$ species. At further higher acid concentrations, conversion of these polymeric species may take place to $(Mo_6O_{26})^{4-}$, $(Mo_{10}O_{26})^{4-}$, and $(Mo_{12}O_{41})^{10-}$ up to 0.05 mol/dm^3 HCl concentration. All these mixed species have higher charges and are more extractable given higher DC and *J* values at acid concentrations from 0.01 to 0.05 mol/dm^3. Perhaps at still higher acid concentrations these species become protonated or more polynuclear with respect to Mo and present lower fluxes. The same effect is shown in Fig. 5 from plots of *P* and *J* versus HCl concentration in the feed.

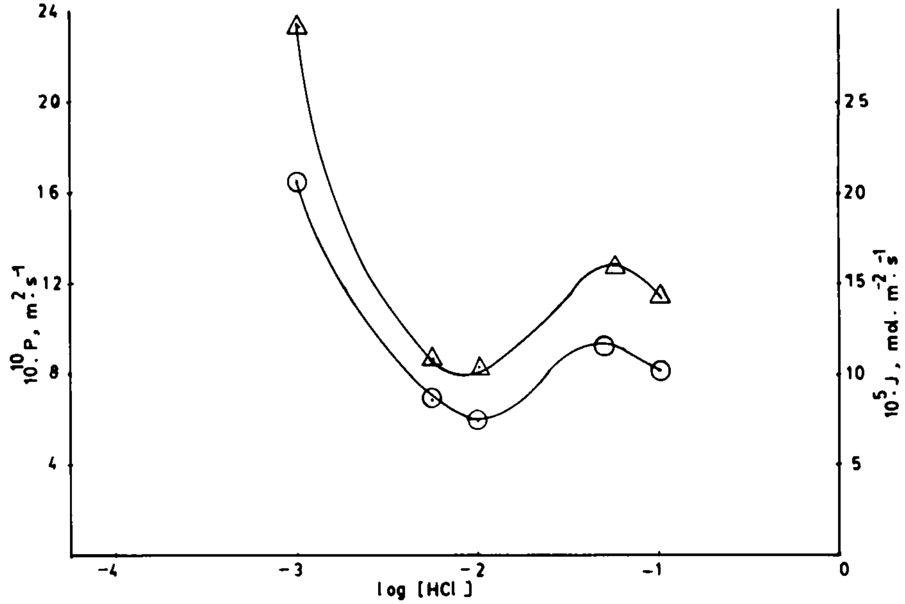

FIG. 5. Plot of permeability (△) and flux (○) of Mo(VI) ions versus log [HCl].

4.2. Effect of TOA Concentration in the Membrane

The plots of Mo(VI) ions concentration versus time in Fig. 2 show that maximum transfer of the metal ions across the membrane takes place at a TOA concentration of 1.308 mol/dm^3. Below and above this concentration the flux is lower and it increases with an increase in concentration of TOA from 5.8 × 10^{-5} to 19.7 × 10^{-5} mol/m^2·s and then decreases to 10.3 × 10^{-5} mol/m^2·s at 1.744 mol/dm^3 TOA concentration. This effect can be explained by keeping in view Eq. (8) where $J \propto [NR_3]^2$, i.e., J increases with an increase in amine concentration. Above 1.308 mol/dm^3 TOA concentration, the observed decrease in flux is attributed to the increase in viscosity of the membrane liquid, which affects inversely to reduce the J value (Eq. 8). The same effect has been presented in Fig. 6 by the plots of J and P versus TOA concentration, where both the parameters have the same trend.

4.3. pH Variation of Feed Aqueous Solution

The variation in pH of the feed solution as a function of time at different TOA concentrations in the membrane with 0.005 mol/dm^3 HCl initial concentration is shown in Fig. 7. It is clear that with the transport of Mo(VI)

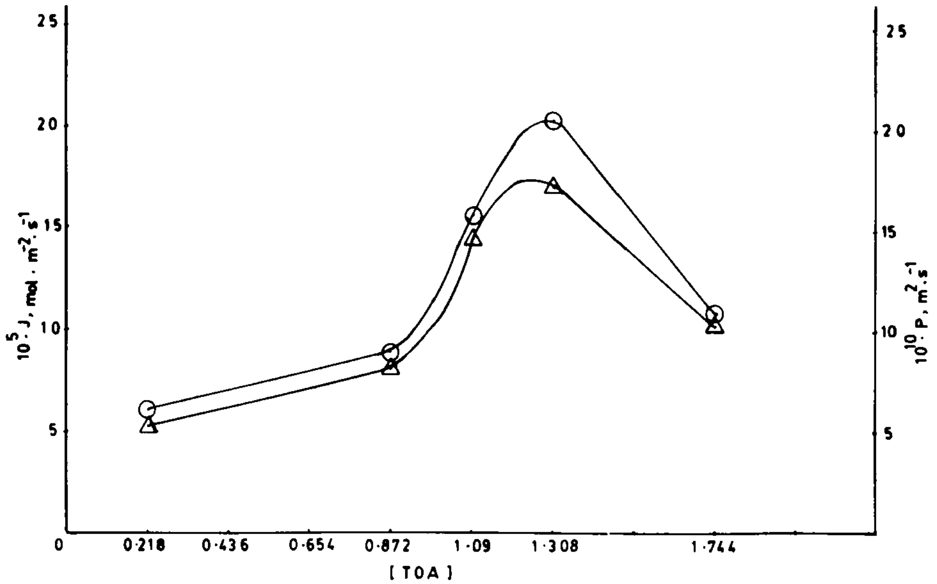

FIG. 6. Plot of flux (○) and permeability (△) of Mo(VI) ions versus TOA concentrations.

ions across the membrane into the stripping phase, the pH of the feed solution increases, indicating the flux of protons along with Mo(VI) ions. This also indicates that the same number of protons are involved during polymeric species formation or decomposition to lower Mo species during their transport across the membrane. If there had been a release or consumption of protons during the interconversion of various Mo(VI) species, this would have been reflected in the pH versus time curves given in Fig. 7. In our previous work it was observed that the $(Mo_7O_{24})^{6-}$ species is decomposed with the transport of Mo(VI) ions along with protons from the membrane to furnish more protons and after some time to work as a source of self-energy for Mo(VI) ions transport across the TOA xylene-based supported liquid membrane. There it was observed that pH first increases and then decreases with time, as the Mo(VI) ions concentration decreases in the feed solution (*5*).

4.4. Effect of NaOH Concentration in the Stripping Solution

This effect has been indicated in Fig. 3, where the plot of Mo(VI) ions concentration versus time has been recorded in the form of different curves at various NaOH concentrations in the strip solution. The plots of *J* and *P* for Mo(VI) ions are recorded in Fig. 8. From both figures it can be

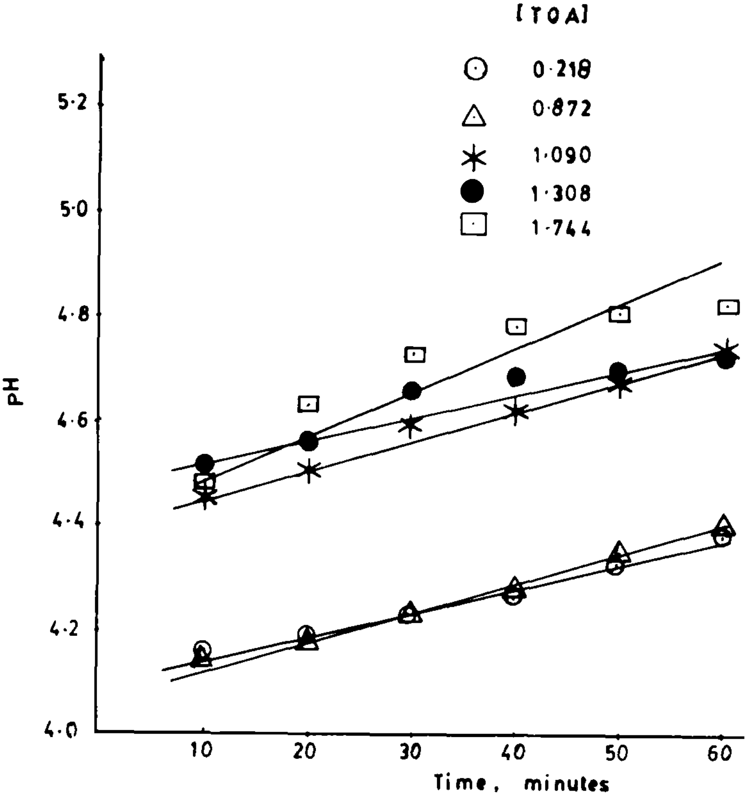

FIG. 7. Plot of pH variation with time at various TOA concentrations in feed solution with the transport of Mo(VI) ions across the membrane.

observed that *J* and *P* values increase with NaOH concentration in the feed solution, which is attributable to the increased rate of reaction between the transported species and the alkali with an increase in concentration and hence high distribution coefficient of Mo(VI) ions from the organic membrane phase to the alkaline aqueous phase. This means that up to 1 mol/dm^3 NaOH concentration in the membrane, the flux is enhanced.

5. CONCLUSIONS

The flux and permeability parameters as a function of HCl, TOA, and NaOH concentration in the feed, membrane, and strip solution have been determined. These values vary according to the pH or protons present in the feed solution. 1.308 mol/dm^3 is found to be the optimum condition of TOA concentration in the membrane. Up to 1.0 mol/dm^3 NaOH concen-

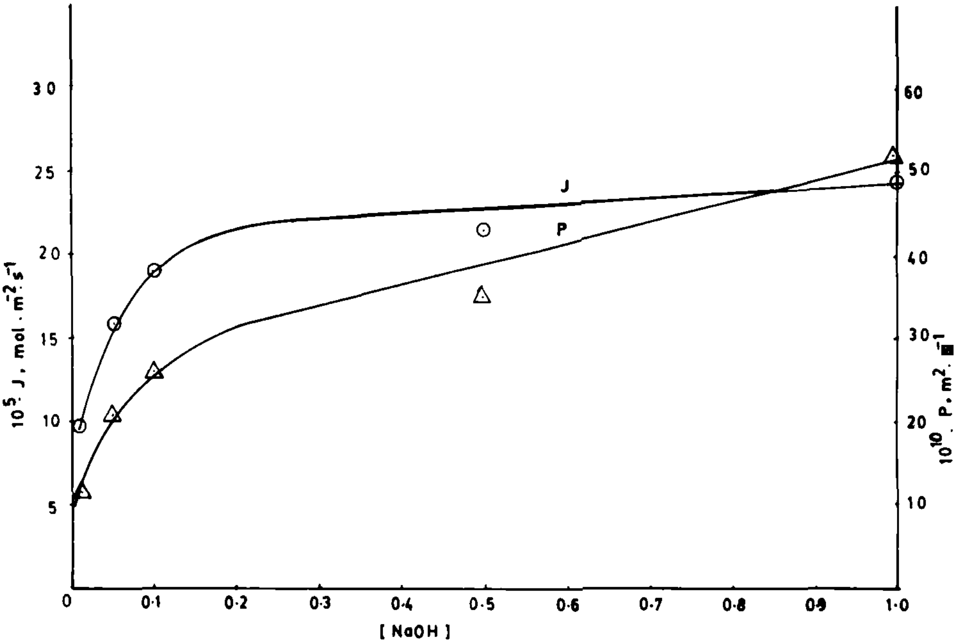

FIG. 8. Plot of flux (O) and permeability (△) versus NaOH molarity.

tration in the strip solution can be tolerated by the polypropylene film, and the increase in alkaline concentration in the strip solutions affects the flux of Mo(VI) ions positively. The increase in the pH of the feed solution indicates coupling of a proton with the Mo(VI) ionic species, and hence is responsible for the transport of these metal ions across the membrane. The depletion of protons in the feed is made up during extraction of these metal ions by continuous dosing. Different species appear to be present in the feed solution as a function of H^+ concentration, which affects the flux. A lower acid concentration, i.e., 0.001 mol/dm^3 in the feed, must be kept to have the maximum flux of Mo(VI) ions across the membrane.

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