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Transport of Chromium(VI) through a Supported Liquid Membrane Containing Tri-*n*-octylphosphine Oxide

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ABSTRACT

In this study the transport of chromium(VI) from aqueous solutions of pH 2–4 through a supported liquid membrane (SLM) with tri-*n*-octylphosphine oxide (TOPO) dissolved in kerosene as a mobile carrier was investigated. The transport flux of Cr(VI) increased with an increase in the concentrations of Cr(VI) in the feed phase and of TOPO in the membrane phase, but with a decrease in pH of the feed phase. Considering the equilibria of various Cr(VI) species in the aqueous phase and of the Cr(VI)–TOPO complexes formed in the membrane phase, a permeation model including the aqueous film diffusion of $HCrO_4^-$ and $Cr_2O_7^{2-}$ toward the membrane, the interfacial chemical reaction between them and TOPO, and the membrane diffusion of the Cr(VI)–TOPO complexes ($\overline{H_2CrO_4\cdot(TOPO)}$ and $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$) was proposed to describe the transport of Cr(VI) through the SLM. By best fitting the transport flux equations of Cr(VI) with the experimental data using the Rosenbrock method, the apparent mass-transfer coefficients of $HCrO_4^-$ and $Cr_2O_7^{2-}$ across the aqueous film, and those of $\overline{H_2CrO_4\cdot(TOPO)}$ and $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$ across the membrane phase, were obtained. This work helps to clarify the transport mechanism of Cr(VI) through an SLM.

INTRODUCTION

The liquid membrane process is a novel technique for the selective separation and concentration of the solute of interest from dilute solutions (1, 2).

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This simultaneous extraction and stripping operation is very attactive because the solute of interest can move from a low-concentration solution to a high-concentration solution with suitable carriers (3). Supported liquid membranes (SLM), which use a porous polymer membrane impregnated with complexing carriers to separate feed solution and stripping solution, represent one of the feasible types of liquid membranes. They have been widely utilized in the recovery of heavy metals such as copper (2, 4–6), cobalt (3, 7–9), nickel (3, 7, 8), zinc (2, 10–13), uranium (1, 14), vanadium (15), etc.

Chromium(VI) has been widely used in the electroplating process. It is highly toxic and must be removed from wastewater before it is discharged into surface water (16, 17). The liquid membrane process is one method for treating wastewater containing Cr(VI). Although several preliminary results of the recovery and separation of Cr(VI) from aqueous solution using liquid membrane processes have been reported in the literature (18–26), the mechanism for the transport of Cr(VI) through a liquid membrane was unspecified. Most studies described the transport flux equation of Cr(VI) through a liquid membrane based on either the total concentration of Cr(VI) or the concentration of a single form of Cr(VI).

In fact, the fractions of various forms of Cr(VI) in the aqueous phase vary with the concentrations of Cr(VI) and the solution pH. The diffusivities of various forms of Cr(VI) also are different from each other. In order for the equilibrium relations of various Cr(VI) species to hold, the instantaneous reactions for the equilibria of various Cr(VI) species must take place during the transport procedure. Therefore, the extent of the contribution of various forms of Cr(VI) to the total molar flux of Cr(VI) is difficult to determine. Accordingly, much work must be done to clarify the transport mechanism of Cr(VI).

Tri-*n*-octylphosphine oxide (TOPO) has been shown to be an effective extractant for the separation and purification of a number of metals (27–32) and organic acids (33, 34) due to its excellent chemical stability, high boiling point, and low solubility in water. It is highly selective for the extraction of Cr(VI) (35, 36).

We recently studied the extraction equilibria of Cr(VI) from aqueous solutions of pH 2–4 with kerosene solutions of TOPO (37). Considering the distribution of various Cr(VI) forms in the aqueous phase and the effect of the ionic strength of the solution on the equilibrium constants, the equilibria can be represented by the following reactions:

$$\mathrm{HCrO_4^-} + \mathrm{H^+} + \overline{\mathrm{TOPO}} \Leftrightarrow \overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}$$

$$K_{\mathrm{e1}}^{\mathrm{T}} = \frac{[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]}{[\mathrm{HCrO_4^-}][\mathrm{H^+}][\overline{\mathrm{TOPO}}]} \frac{\gamma_{\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}}}{\gamma_{\mathrm{HCrO_4^-}}\gamma_{\mathrm{H^+}}\gamma_{\overline{\mathrm{TOPO}}}} = 2.02 \times 10^3 \tag{1}$$

and

$$Cr_2O_7^{2-} + 2H^+ + 3\overline{TOPO} \Leftrightarrow \overline{H_2Cr_2O_7\cdot(TOPO)_3}$$

$$K_{e2}^T = \frac{[\overline{H_2Cr_2O_7\cdot(TOPO)_3}]}{[Cr_2O_7^{2-}][H^+]^2[\overline{TOPO}]^3} \frac{\gamma_{\overline{H_2Cr_2O_7\cdot(TOPO)_3}}}{\gamma_{Cr_2O_7^{2-}}\gamma_{H^+}^2\gamma_{\overline{TOPO}}^3} = 3.69 \times 10^8 \tag{2}$$

in which $\overline{H_2CrO_4\cdot(TOPO)}$ is in equilibrium with $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$, i.e.,

$$2\overline{H_2CrO_4\cdot(TOPO)} + \overline{TOPO} \Leftrightarrow \overline{H_2Cr_2O_7\cdot(TOPO)_3} + H_2O$$

$$K_9^T = \frac{[\overline{H_2Cr_2O_7\cdot(TOPO)_3}]}{[\overline{H_2CrO_4\cdot(TOPO)}]^2[\overline{TOPO}]} \frac{\gamma_{\overline{H_2Cr_2O_7\cdot(TOPO)_3}}}{\gamma_{\overline{H_2CrO_4\cdot(TOPO)}}^2\gamma_{\overline{TOPO}}} = 3.22 \times 10^3 \tag{3}$$

In the present work the mechanism for the transport of Cr(VI) from aqueous solutions of pH 2–4 through an SLM with tri-*n*-octylphosphine oxide (TOPO) dissolved in kerosene as a mobile carrier was studied at 25°C. The transport fluxes of Cr(VI) through the SLM were measured with varying concentrations of Cr(VI) and pH values in the feed phases, and with varying TOPO concentrations in the membrane phases. A permeation model including the aqueous film diffusion of $HCrO_4^-$ and $Cr_2O_7^{2-}$ toward the membrane, the interfacial chemical reaction between them and TOPO, and the membrane diffusion of $\overline{H_2CrO_4\cdot(TOPO)}$ and $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$ was proposed to describe the transport of Cr(VI) through the SLM. Considering the equilibria between $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the aqueous phase and between $\overline{H_2CrO_4\cdot(TOPO)}$ and $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$ in the membrane phase during the transport procedure, the transport mechanism was studied.

EXPERIMENTAL

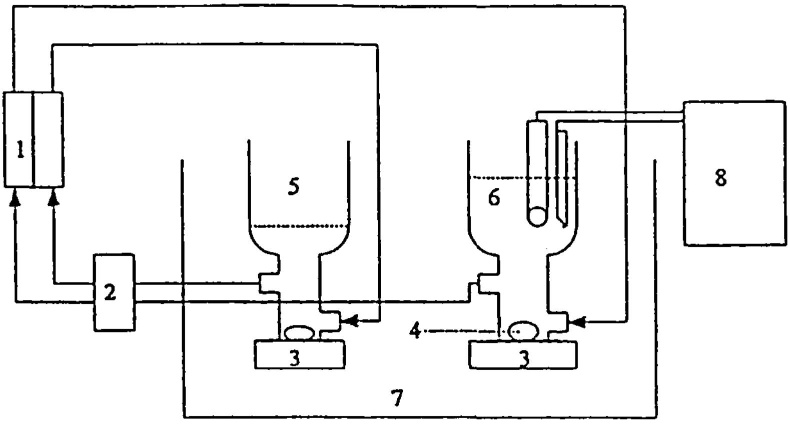
Reagents and Membranes

Tri-*n*-octylphosphine oxide (TOPO) with a purity of 99% from E. Merck Co. (Darmstadt) was used without further purification. The diluent kerosene supplied by Union Chemical Works Ltd. (Taiwan) was washed five times with 20 vol% sulfuric acid to remove aromatics, and then with water several times until the water recovered from washing showed no change from its initial pH values (38). All other chemicals (CrO_3, H_2SO_4, and NaOH) purchased from Hayashi Pure Chemical Ind. Ltd. (Osaka) were analytical grade reagents. The water used throughout this work was produced by Milli-Q SP Ultra-Pure-Water Purification System of Nihon Millipore Ltd. (Tokyo).

The porous membrane made of polyvinylidene difluoride (PVDF) was a product of Millipore Co. with a mean pore size of 0.45 μm, a typical porosity of 75%, and a nominal mean thickness of 125 μm.

Measurement of Permeation Rate

The experimental apparatus used to transport Cr(VI) through an SLM is illustrated in Fig. 1. The frame of the permeation cell was made of Teflon. The feed compartment was 3.5 cm in diameter and 0.15 cm thick. The stripping compartment was 3.5 cm in diameter and 0.35 cm thick. The feed solutions (0.1 dm^3) were prepared by dissolving appropriate amounts of CrO_3 in water to the desired concentrations, and the stripping solutions (0.025 dm^3) were NaOH solutions of 0.2–1.0 mol/dm^3. A membrane impregnated with the kerosene solution of TOPO was clamped in the permeation cell. The effective membrane area was 9.62 cm^2. The pH values of the feed solutions were controlled with a pH stat (TOA AUT-211) using a sulfuric acid solution.



1:permeation cell
2:micro tube pump
3:submersible magnetic stirrer
4:spinbar
5:stripping solution
6:feed solution
7:water bath
8:pH stat

FIG. 1 A schematic diagram of the experimental apparatus for the permeation of Cr(VI) through the SLM.

During experimental procedures the glass cells containing feed and stripping solutions were immersed in a water bath controlled at 25°C. When steady state was reached (about 30 minutes), 3 cm^3 of the stripping solution was taken at preset intervals and then the original stripping solution was added to maintain the volume unchanged. To prevent the migration of the membrane liquid, the aqueous solutions were presaturated with the kerosene solution of TOPO beforehand.

The concentrations of Cr(VI) in the sample were determined with an atomic absorption spectrophotometer (Hitachi Z-6100) at a wavelength of 359.3 nm, and corrections due to volume replacement were made. The transport flux of Cr(VI) was thus obtained from

$$J = (V_s/A_r)(d[\mathrm{Cr}]_s/dt) \tag{4}$$

where A_r is the effective membrane area, V is the solution volume, and the subscript "s" represents the stripping phase.

RESULTS AND DISCUSSION

Supported Liquid Membrane Permeation

Effect of the Flow Rate

Since the permeation experiments must be carried out with an appropriate flow rate of aqueous feed and stripping solutions to minimize the thickness of the aqueous films, the influence of the flow rate of aqueous feed and stripping solutions on the molar flux of Cr(VI), J, was studied first (Fig. 2). It was found that J increased as the flow rate increased, and finally plateaued when the flow rate was larger than 5×10^{-3} dm^3/min. To make sure that the thickness of the aqueous films reached its minimum value, a flow rate ranging from 8.8 to 10.3×10^{-3} dm^3/min was subsequently adopted in all runs.

Effect of NaOH Concentration in the Stripping Phase

The effect of NaOH concentration in the stripping solutions on the molar flux of Cr(VI) is shown in Fig. 3 which indicates that the molar flux of Cr(VI) was independent of the NaOH concentration ranging from 0.2 to 1.0 $mol \cdot dm^{-3}$. For the described condition, the permeation process was not controlled by the aqueous film diffusion of the stripping phase.

Effect of Cr(VI) Concentration in the Feed Phase

When the permeation process is controlled by the diffusion of Cr(VI) ions in the aqueous film, a large molar flux of Cr(VI) is obtained from the concen-

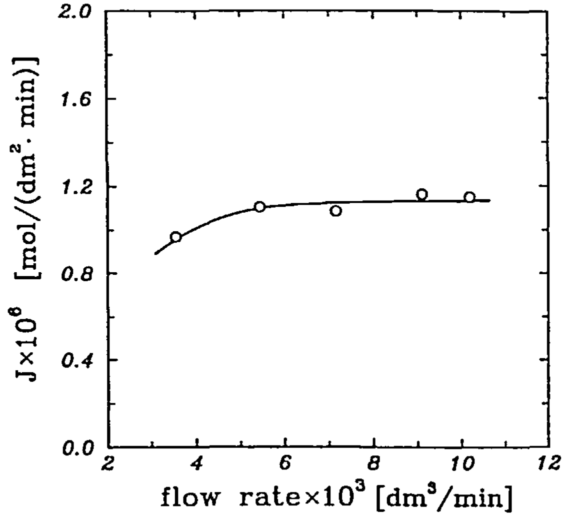


FIG. 2 Effect of flow rate in the feed and stripping solutions on the molar flux of Cr(VI). Feed: $[Cr]_f$ = 0.00405 mol/dm^3, pH_f 2.2. SLM: $\overline{[TOPO]}_0$ = 0.1 mol/dm^3. Strip: $[NaOH]_s$ = 1.0 mol/dm^3.

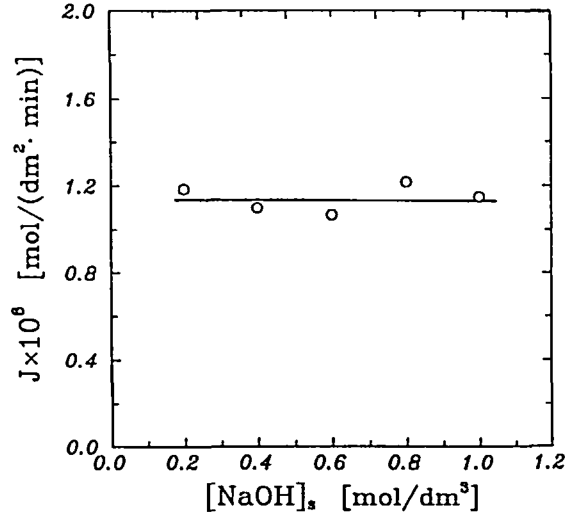


FIG. 3 Effect of NaOH concentration in the stripping solution on the molar flux of Cr(VI). Feed: $[Cr]_f$ = 0.00406 mol/dm^3, pH_f 2.2. SLM: $\overline{[TOPO]}_0$ = 0.1 mol/dm^3.

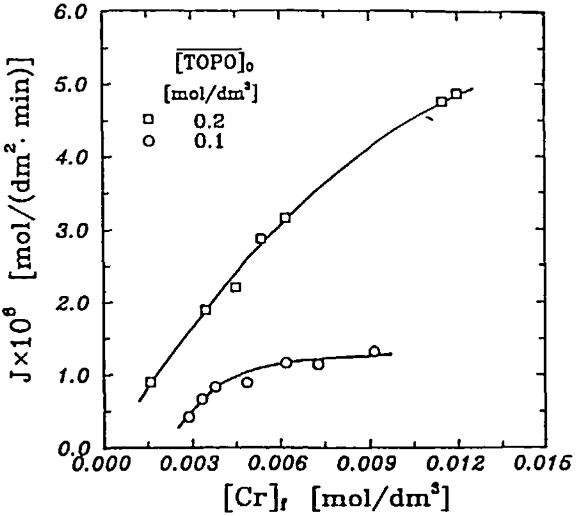


FIG. 4 Effect of Cr(VI) concentration in the aqueous feed solutions on the molar flux of Cr(VI). Feed: pH_f 2.2. Strip: $[\text{NaOH}]_s$ = 1.0 mol/dm^3.

tration gradient established by the high concentration of Cr(VI) in the aqueous feed phase. Figure 4 shows the effect of the concentration of Cr(VI) in the aqueous feed solution on the molar flux of Cr(VI), J. In the region of low $[\text{Cr}]_f$, which corresponded to the case of aqueous film diffusion control, J increased with the increase of $[\text{Cr}]_f$. However, in the case of high $[\text{Cr}]_f$, J gradually plateaued as $[\text{Cr}]_f$ increased. Under this condition the resistance of the diffusion of Cr(VI) ions in the feed solution became less dominant. The permeation process may be governed by membrane diffusion and, to some extent, by equilibrium distribution at the feed–membrane interface.

To determine the rate-controlling step for the transport of Cr(VI) through the SLM at high $[\text{Cr}]_f$, the interfacial kinetics were investigated using a constant interfacial area cell. When an experiment was performed at $[\text{Cr}]_f$ = 0.00486 mol/dm^3, pH 2.6, $\overline{[\text{TOPO}]}_0$ = 0.1 mol/dm^3, and a stirring rate of 100 rpm (as in the case of interfacial chemical reaction control), the molar flux of Cr(VI) was 3.13 × 10^{-6} mol/(dm^2·min). Under similar conditions ($[\text{Cr}]_f$ = 0.00533 mol/dm^3, pH 2.6, and $\overline{[\text{TOPO}]}_0$ = 0.1 mol/dm^3) for the permeation of Cr(VI) through the SLM, the molar flux of Cr(VI) was 1.83 × 10^{-7} mol/(dm^2·min). The results indicated that the transport resistance of Cr(VI) increased due to the use of a porous membrane impregnated with complexing carriers. It was suggested that the resistance of the interfacial chemical reaction compared to that of the membrane diffusion could be neglected. Therefore, the permeation process is governed by membrane diffusion in the case of high $[Cr]_f$.

Effect of pH Value of the Feed Phase

The transport of Cr(VI) from aqueous solutions through an SLM containing TOPO as the mobile carrier is a "cotransport" process in which the concentration gradient of hydrogen ion is the main driving force. The dependence of the molar flux of Cr(VI), *J*, on the pH value of the aqueous feed solution is shown in Fig. 5. It is evident that *J* decreased with increasing pH value of the aqueous feed solution.

Effect of TOPO Concentration in the Membrane Phase

As shown in Fig. 4, the molar flux of Cr(VI), *J*, increased with increasing carrier concentration, and the difference between *J* obtained at a TOPO concentration of 0.1 mol·dm^{-3} and that obtained at a TOPO concentration of 0.2 mol·dm^{-3} increased with the increase of $[Cr]_f$. This is due to the fact that the permeation process is controlled by the aqueous film diffusion of the feed phase at low $[Cr]_f$ and by the membrane diffusion at high $[Cr]_f$, with the result

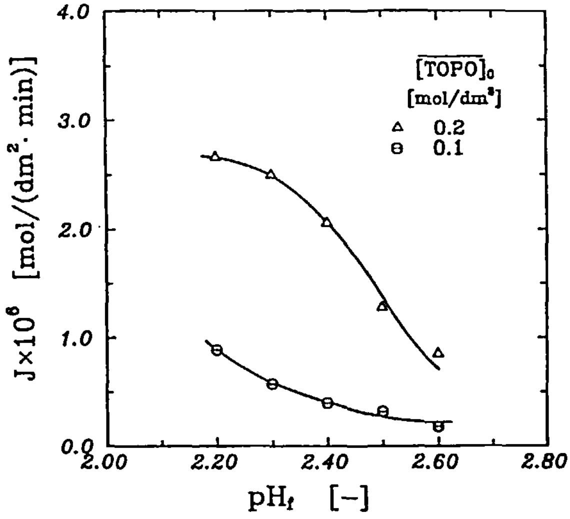


FIG. 5 Effect of aqueous pH in the feed solutions on the molar flux of Cr(VI). (△) Feed: $[Cr]_f$ = 0.00533 mol/dm^3; strip: $[NaOH]_s$ = 1.0 mol/dm^3. (⊖) Feed: $[Cr]_f$ = 0.00523 mol/dm^3; strip: $[NaOH]_s$ = 1.0 mol/dm^3.

that the influence of carrier concentration in a supported liquid membrane on J at high $[Cr]_f$ is more significant than that at low $[Cr]_f$.

On the other hand, Fig. 5 also illustrates the effect of carrier concentration on the molar flux of Cr(VI), J, at different pH values of the aqueous feed phase. It indicates that J increased with increasing carrier concentration. According to the equilibrium data for the extraction of Cr(VI) from aqueous solutions of pH 2–4 with TOPO in our previous studies (37), the distribution ratios of Cr(VI), $[\overline{Cr}]/[Cr]$, increased as $[\overline{TOPO}]_0$ increased. Based on the total concentration of Cr(VI) in the organic phase, the fractions of $[\overline{H_2Cr_2O_7 \cdot (TOPO)_3}]$ increased as $[\overline{Cr}]$ increased. Furthermore, the effect of hydrogen ion concentration on the extraction of $Cr_2O_7^{2-}$ was more sensitive than that of $HCrO_4^-$ as indicated in Eqs. (1) and (2). Therefore, as pH values of the aqueous feed phase increase in permeation experiments with an SLM, $[\overline{H_2Cr_2O_7 \cdot (TOPO)_3}]$ at the feed–membrane interface at a TOPO concentration of 0.2 mol/dm^3 decrease more than at a TOPO concentration of 0.1 mol/dm^3. As a result, the molar flux of Cr(VI) decreased slightly at a TOPO concentration of 0.1 mol/dm^3 but decreased significantly at a TOPO concentration of 0.2 mol/dm^3.

Transport Mechanism

Permeation Model in SLM

In the pH range of 2 to 4 in the aqueous phase, the predominant species of Cr(VI) are $HCrO_4^-$ and $Cr_2O_7^{2-}$. The concentration profiles of $HCrO_4^-$ and $Cr_2O_7^{2-}$ permeating through the SLM are schematically shown in Fig. 6. The transport steps are as follows: 1) $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the bulk feed solution diffuse through the aqueous film to the feed–membrane interface; 2) $HCrO_4^-$ and $Cr_2O_7^{2-}$ are extracted by TOPO at the feed–membrane interface; 3) $\overline{H_2CrO_4 \cdot (TOPO)}$ and $\overline{H_2Cr_2O_7 \cdot (TOPO)_3}$ complexes formed at the feed–membrane interface permeate through the membrane phase to the stripping side of the membrane phase; and 4) Cr(VI) ions are stripped by NaOH solution at the stripping-side interface. The aqueous film diffusion fluxes of $HCrO_4^-$ (J_{w1}) and $Cr_2O_7^{2-}$ (J_{w2}) in Step 1 are

$$J_{w1} = k_{w1}([HCrO_4^-]_f - [HCrO_4^-]_{iw}) \tag{5}$$

and

$$J_{w2} = 2k_{w2}([Cr_2O_7^{2-}]_f - [Cr_2O_7^{2-}]_{iw}) \tag{6}$$

The reversible reaction for conversion of $HCrO_4^-$ to $Cr_2O_7^{2-}$ or conversion of $Cr_2O_7^{2-}$ to $HCrO_4^-$ will maintain the equilibrium between $HCrO_4^-$ and $Cr_2O_7^{2-}$ during the permeation process. The terms k_{w1} and k_{w2} represent the apparent mass-transfer coefficients of $HCrO_4^-$ and $Cr_2O_7^{2-}$ across aqueous

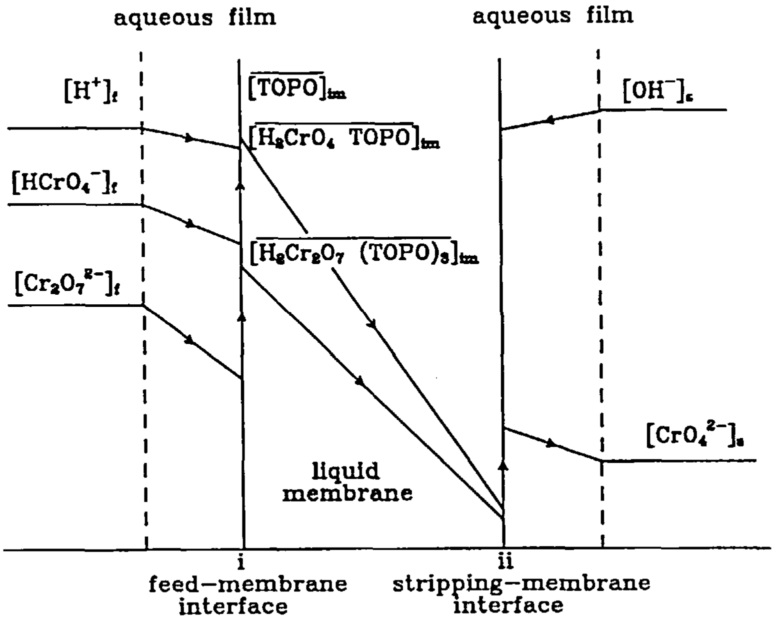


FIG. 6 Concentration profile of each species through an SLM containing TOPO as a mobile carrier.

film diffusion, respectively, and the subscript "w" indicates the location on the water side.

Addition of Eqs. (5) and (6), the total molar flux of Cr(VI), was obtained as follows:

$$\begin{aligned} J_w &= J_{w1} + J_{w2} \qquad (7) \\ &= k_{w1}([HCrO_4^-]_f - [HCrO_4^-]_{iw}) + 2k_{w2}([Cr_2O_7^{2-}]_f - [Cr_2O_7^{2-}]_{iw}) \end{aligned}$$

In Step 2 the resistance of the interfacial chemical reaction can be neglected as mentioned in the previous section. The equilibrium relations holds at the feed–membrane interface, i.e.,

$$\overline{[H_2CrO_4\cdot(TOPO)]}_{im} = K^T_{e1}\gamma_{HCrO_4^-,iw}\gamma_{H^+,iw}[HCrO_4^-]_{iw}[H^+]_{iw}\overline{[TOPO]}_{im} \qquad (8)$$

and

$$[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{im}} = K^{\mathrm{T}}_{\mathrm{e2}}\gamma_{\mathrm{Cr_2O_7^{2-}},\mathrm{iw}}\gamma^2_{\mathrm{H^+},\mathrm{iw}}[\mathrm{Cr_2O_7^{2-}}]_{\mathrm{iw}}[\mathrm{H^+}]^2_{\mathrm{iw}}[\overline{\mathrm{TOPO}}]^3_{\mathrm{im}} \tag{9}$$

where the subscript "m" indicates the location on the membrane phase side. The γ's represent the activity coefficients of ions in aqueous solutions and were estimated from the Güntelberg equation with constant b taken to have a value of 1 $(\mathrm{mol/dm^3})^{-1/2}$:

$$\log \gamma_{\mathrm{i}} = \frac{-AZ_{\mathrm{i}}^2 I^{0.5}}{1 + bI^{0.5}} \tag{10}$$

in which $A = 0.51128$ at 25°C, I is the ionic strength, and Z is the charge number. In addition, the activity coefficients of the complexes $\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}$ and $\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}$ in the membrane phase were taken as 1. The concept concerning the activity coefficients used for the ions of aqueous solutions was employed to adapt the model to different aqueous compositions.

For simplicity in the actual calculations, we neglected the difference between the molality and molarity scales since the densities of aqueous solutions were about 1 g/mL in this work.

In Step 3, the total molar flux of Cr(VI) was

$$\begin{aligned} J_{\mathrm{m}} &= J_{\mathrm{m1}} + J_{\mathrm{m2}} \\ &= k_{\mathrm{m1}}([\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{\mathrm{im}} - [\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{\mathrm{iim}}) \\ &\quad + 2k_{\mathrm{m2}}([\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{im}} - [\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{iim}}) \end{aligned} \tag{11}$$

Similar to Step 1, the reversible reaction for conversion of $\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}$ to $\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}$ or conversion of $\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}$ to $\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}$ will maintain the equilibrium indicated in Eq. 3) during the permeation process. The terms k_{m1} and k_{m2} represent the apparent mass-transfer coefficients of $\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}$ and $\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}$ across the membrane phase, respectively.

When an effective stripping solution such as NaOH solution was used, as shown in Fig. 2, the values of $[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{\mathrm{iim}}$ and $[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{iim}}$ compared with those of $[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{\mathrm{im}}$ and $[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{im}}$, respectively, could be considered to be negligible. Also, the mass-transfer resistances of the stripping side of the membrane phase were negligible. Thus, Eq. (11) can be simplified to

$$\begin{aligned} J_{\mathrm{m}} &= J_{\mathrm{m1}} + J_{\mathrm{m2}} \\ &= k_{\mathrm{m1}}[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{\mathrm{im}} + 2k_{\mathrm{m2}}[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{im}} \end{aligned}$$

In addition, the total concentration of TOPO at the feed–membrane interface, $[\overline{\mathrm{TOPO}}]_0$, can be expressed as

$$[\overline{\mathrm{TOPO}}]_0 = [\overline{\mathrm{TOPO}}]_{\mathrm{im}} + [\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{\mathrm{im}} + 3[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{im}} \tag{13}$$

Evaluation of the Apparent Mass-Transfer Coefficients

Under steady state, $J = J_w = J_m$, and there are 15 parameters including k_{w1}, k_{w2}, k_{m1}, k_{m2}, $[\mathrm{HCrO_4^-}]_f$, $[\mathrm{Cr_2O_7^{2-}}]_f$, $[\mathrm{HCrO_4^-}]_{iw}$, $[\mathrm{Cr_2O_7^{2-}}]_{iw}$, $[\mathrm{H^+}]_{iw}$, $[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{im}$, $[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{im}$, $[\overline{\mathrm{TOPO}}]_{im}$, $\gamma_{\mathrm{HCrO_4^-},iw}$, $\gamma_{\mathrm{H^+},iw}$, and J_{Cr} in Eqs. (7), (8) (10), (12), and (13), as mentioned above. In general, the diffusivity of $\mathrm{H^+}$ is larger than that of any metal; it can thus be assumed that $[\mathrm{H^+}]_{iw}$ is equal to $[\mathrm{H^+}]_f$. The concentration of $\mathrm{HCrO_4^-}$ and $\mathrm{Cr_2O_7^{2-}}$ in the feed phase could be obtained from a calculation of the aqueous composition of Cr (VI) as reported in our previous study (37). Furthermore, the following concentration relationships between $\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}$ and $\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}$ (as rewritten from Eq. 3) and between $\mathrm{Cr_2O_7^{2-}}$ and $\mathrm{HCrO_4^-}$ (37) at the feed–membrane interface must be obeyed:

$$[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{\mathrm{im}} = 3.22 \times 10^3[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]^2_{\mathrm{im}}[\overline{\mathrm{TOPO}}]_{\mathrm{im}} \tag{14}$$

and

$$[\mathrm{Cr_2O_7^{2-}}]_{iw} = 35.5[\mathrm{HCrO_4^-}]^2_{iw}\gamma^2_{\mathrm{HCrO_4^-}}/\gamma_{\mathrm{Cr_2O_7^{2-}}} \tag{15}$$

From Eq. (10), the relationships of the activity coefficients of $\mathrm{HCrO_4^-}$, $\mathrm{Cr_2O_7^{2-}}$, and $\mathrm{H^+}$ at the feed–membrane interface were obtained as follows:

$$\gamma_{\mathrm{HCrO_4^-},iw} = \gamma_{\mathrm{H^+},iw} = \gamma^{1/4}_{\mathrm{Cr_2O_7^{2-}},iw} \tag{16}$$

Substitution of Eq. (16) into Eq. (15) yields

$$[\mathrm{Cr_2O_7^{2-}}]_{iw} = 35.5[\mathrm{HCrO_4^-}]^2_{iw}/\gamma^2_{\mathrm{HCrO_4^-}} \tag{17}$$

Therefore, for a set of the apparent mass-transfer coefficients (i.e., k_{w1}, k_{w2}, k_{m1}, and k_{m2}), $[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{im}$, $[\overline{\mathrm{TOPO}}]_{im}$, $[\mathrm{HCrO_4^-}]_{iw}$, $\gamma_{\mathrm{HCrO_4^-},iw}$, and J could be evaluated by solving a system of five nonlinear equations (Eqs. 7, 8, 10, 12, and 13) in which $[\overline{\mathrm{H_2Cr_2O_7{\cdot}(TOPO)_3}}]_{im}$, $\gamma_{\mathrm{H^+},iw}$, and $[\mathrm{Cr_2O_7^{2-}}]_{iw}$ were replaced, respectively, by $[\overline{\mathrm{H_2CrO_4{\cdot}(TOPO)}}]_{im}$, $\gamma_{\mathrm{HCrO^{-}4},iw}$, and $[\mathrm{HCrO_4^-}]_{iw}$ using Eqs. (14), (16), and (17). In this calculation the optimal method used to search for the best set of k_{w1}, k_{w2}, k_{m1}, and k_{m2} that would minimize the deviations of J_{cal} and J_{expt} was the Rosenbrock method (39). The optimal values of k_{w1}, k_{w2}, k_{m1}, and k_{m2} were 3.68×10^{-4}, 2.71×10^{-4}, 2.25×10^{-5}, and 1.36×10^{-5} cm/s, respectively.

Teramoto et al. (19) studied the transport of Cr(VI) through a spiral-type flowing liquid membrane with tri-*n*-octylamine (TOA) as a mobile carrier. According to their data, the overall mass transfer coefficient of Cr(VI) in the

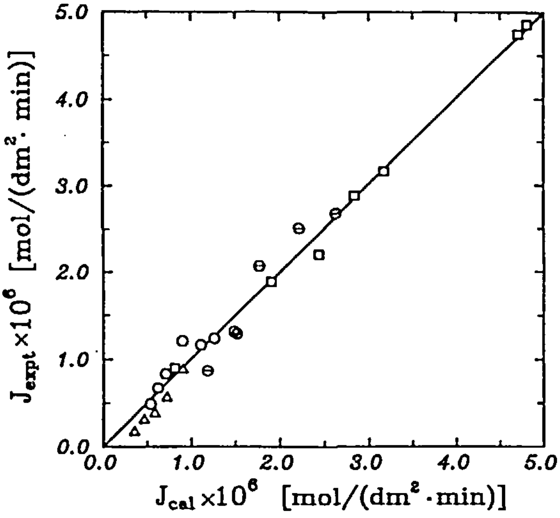


FIG. 7 Comparison of the calculated and the experimental molar fluxes of Cr(VI). The meanings of the symbols □, ○, △, and ⊖ are the same as those in Figs. 4 and 5.

aqueous diffusion film could be estimated to be 8.55 × 10^{-4} cm/s in the limiting of the aqueous film diffusion control. In addition, from the studies of Huang (41) for the transport of Cr(VI) through an SLM from HCl media with triisooctylamine (TIOA) dissolved in *o*-xylene as a mobile carrier, the overall mass transfer coefficient of Cr(VI)–TIOA in membrane diffusion was 7.58 × 10^{-5} cm/s using a 0.1 mol/dm^3 TIOA solution. On the other hand, the kinetics of Cr(VI) extraction with 3-(4-pyridyl)-1,5-diphenyl pentane using a constant interfacial area cell were investigated by Takahashi et al. (42). The overall mass transfer coefficient of Cr(VI)–extractant estimated from modifying the results of iodine transfer was 7.4 × 10^{-5} cm/s with a stirring rate of 2.5 rps. Comparing of the result obtained in the present work with the literature, our optimal values of k_{w1}, k_{w2}, k_{m1}, and k_{m2} are reasonable.

As shown in Fig. 7 the calculated molar fluxes of Cr(VI) are in good agreement with the measured results with a standard deviation of 1.693 × 10^{-7} mol/(dm^2·min).

Description of the Transport Mechanism

It is well known that the fraction of $HCrO_4^-$ increases with a decreasing concentration of Cr(VI) when the predominant forms of Cr(VI) in the aqueous phase are $Cr_2O_7^{2-}$ and $HCrO_4^-$ (37, 40). From the mass point of view, the diffusivity of $HCrO_4^-$ in the aqueous film of the feed phase is larger than that of $Cr_2O_7^{2-}$ because the mass of $Cr_2O_7^{2-}$ is greater than that of $HCrO_4^-$. Thus, under steady state, conversion of $Cr_2O_7^{2-}$ to $HCrO_4^-$ will take place during aqueous film diffusion to obey the equilibrium relationship between $HCrO_4^-$ and $Cr_2O_7^{2-}$ indicated by Eq. (15). The concentration of $HCrO_4^-$ at the feed–membrane interface is not only contributed to by the diffusion of $HCrO_4^-$ itself from the bulk feed phase but also by the conversion of $Cr_2O_7^{2-}$.

For the interfacial chemical reaction in Step 2, the instantaneous equilibria among $HCrO_4^-$, $Cr_2O_7^{2-}$, $\overline{H_2CrO_4\cdot(TOPO)}$, and $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$ indicated in Eqs. (1), (2), (14), and (15) takes place at the feed–membrane interface. Furthermore, during the membrane diffusion in Step 3, the reaction indicated by Eq. (3) for the conversion of $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$ to $\overline{H_2CrO_4\cdot(TOPO)}$ occurs based on the fact that the fraction of $\overline{H_2CrO_4\cdot(TOPO)}$ increases with decreasing Cr(VI) concentration in the organic phase, and the mass point of view as similar to that in Step 1. Therefore, the molar fluxes of $HCrO_4^-$ and $Cr_2O_7^{2-}$ are not equal to those of their corresponding complexes in the membrane phase under steady state, i.e., $J_{w1} \neq J_{m1}$ and $J_{w2} \neq J_{m2}$.

CONCLUSIONS

In this work we investigated the transport of Cr(VI) from aqueous solutions of pH 2–4 through an SLM containing TOPO dissolved in kerosene as a mobile carrier. The transport molar flux of Cr(VI) was dependent on the concentration of chromium (VI) in the feed phase, the pH of the feed phase, and the concentration of TOPO in the membrane phase. A permeation model was proposed to describe the transport of Cr (VI) through the SLM by considering the aqueous film diffusion, the interfacial chemical reaction, and the membrane diffusion as a series of steps in which the equilibria between $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the aqueous phase and between $\overline{H_2CrO_4\cdot(TOPO)}$ and $\overline{H_2Cr_2O_7\cdot(TOPO)_3}$ in the membrane phase took place during the transport procedure. The transport mechanism of Cr(VI) through an SLM under steady state was clarified. This work enables us to predict the transport flux of Cr(VI) through an SLM containing TOPO as a mobile carrier with satisfactory precision.

NOTATION

A	constant, $A = 0.51128$ at 25°C
A_r	effective membrane area (dm^2)
I	ionic strength (mol/kg)
J	molar flux [mol/(dm^2·min)]
K	stoichiometric equilibrium constant
K^T	thermodynamic equilibrium constant
k	apparent mass-transfer coefficient (cm/s)

V	solution volume (dm^3)
Z	charge number
[]	molar concentration of species in the bracket (mol/dm^3)
γ	activity coefficient

Subscripts

cal	calculation data
e	extraction
expt	experimental data
f	feed phase
m	membrane phase side
s	stripping phase
t	time
w	aqueous phase side
i	location at the feed–membrane interface
ii	location at the stripping-side of the membrane phase
0	initial data

Superscript

—	organic-phase species

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