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FACILITATED TRANSPORT OF CR(VI) THROUGH A SUPPORTED LIQUID MEMBRANE WITH TRIOCTYLMETHYLAMMONIUM CHLORIDE AS A CARRIER

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ABSTRACT

This paper has applied a simple model (H_2CrO_4 + Aliquat 336 $\leftrightarrow$ complex) to the mass transfer mechanism of Cr(VI) with Aliquat 336 in a batch-type, supported liquid membrane module. Concentrations at pH 3 are as follows: 0.019 kmol/m^3 $\leq$ Aliquat 336 $\leq$ 0.035 kmol/m^3 and 20 g/m^3 $\leq$ Cr (VI) $\leq$ 500 g/m^3. The measured values of forward- and backward-reaction rate constants between Cr(VI) and Aliquat 336 were used to simulate the model with the mass conservation equation and associated boundary conditions. Comparison between the experimental and simulated facilitated factors of Cr(VI) transport led to classification of reaction regions.

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Key Words: Facilitated transport; Immobilized liquid membrane; Cr(VI); Trioctylmethylammonium chloride; Mass transfer coefficient

INTRODUCTION

Hexavalent chromium, Cr(VI), has received considerable attention because it is used extensively in such industrial applications as electroplating, electrofinishing, steelmaking, leather tanning, and corrosion inhibition, and it has long been recognized as a toxic substance due to its strong oxidizing potential and the ease with which it can cross biological membranes (1). The removal of Cr(VI) from industrial wastewater is of great interest mostly due to the high toxicity of chromium (VI) compounds. During recent years, the application of different solvent extraction technologies to chromium removal and concentration has been widely studied; conventional liquid-liquid extraction (2), emulsion liquid membranes (3), supported liquid membranes (SLMs) (4), and nondispersive extraction (5) are some of the new alternatives that have been reported in the literature.

In the case of a SLM, an organic extractive phase is immobilized by capillary forces in the micropores of a polymer membrane that separates a feed solution from a stripping solution. The mass transfer rate of solute across a SLM increases with the increase of the distribution coefficient between the membrane/feed phase and with the presence of chemical reactions at the membrane/feed and/or the membrane/stripping solution interfaces. Further rate enhancement can be expected by the addition of an active carrier, which facilitates transport, to the liquid membrane. Quaternary ammonium salts have been shown to be very effective carriers for the removal of chromate ions, such as trioctylamine (4), tridodecylamine (6), tri-*iso*-octylamine (7), and trioctylmethylammonium chloride (Aliquat 336), from acid solutions in the liquid membrane (5,8–10).

Because various chemical species of Cr(VI) in the aqueous solution are formed according to the total concentration of Cr(VI) and pH (11), several models have been used to analyze the transport of Cr(VI) with a carrier. Teramoto et al. (4) presented the extraction model $HCrO_4^- + H^+ +$ Aliquat 336 $\leftrightarrow$ complex and studied the stability and performance of a spiral-type flowing liquid membrane module by using the measured flux of Cr(VI) and the feed-side mass transfer coefficient. However, they did not consider the transport mechanism of Cr(VI) with chemical reactions in the liquid membrane. Alonso, Irabien, and Ortiz (9) studied the kinetics of the extraction of Cr(VI) with Aliquat 336. Their experiments were performed in hollow fiber modules with the model $CrO_4^{2-} + 2$ Aliquat 336 $\leftrightarrow$ complex $+ 2\ Cl^-$.

In the present work, the extraction of Cr(VI) from aqueous solutions of pH 3 through a SLM with Aliquat 336 dissolved in toluene as a mobile carrier was studied at 25°C. The overall mass transfer coefficients with and without the carrier were measured by the time dependence of Cr(VI) concentration in the feed side and were used to get the facilitated factor of Cr(VI) transport.

The measured forward- and backward-reaction rate constants of the reversible reaction between Cr(VI) and Aliquat 336 were used to simulate the extraction model, which was based on the model of Teramoto et al. (4). The reaction regions of the reaction between Cr(VI) and Aliquat 336 were classified by comparing the measured facilitated factors with the simulated ones.

THEORY

Chromate Chemistry

Cr(VI) may exist in the aqueous solution in different ionic forms as illustrated by the following equilibrium reactions (11):

$$H_2CrO_4 \Leftrightarrow H^+ + HCrO_4 \qquad (1)$$

$$HCrO_4^- \Leftrightarrow H^+ + CrO_4^{2-} \qquad (2)$$

$$2HCrO_4^- \Leftrightarrow Cr_2O_7^{2-} + H_2O \qquad (3)$$

Note that the amount of each ion is influenced by pH value and total Cr(VI) concentration.

The equilibrium constants in Eqs. (1–3) are defined as follows:

$$K_1 = \frac{[H^+][HCrO_4^-]}{[H_2CrO_4]} \qquad (4)$$

$$K_2 = \frac{[H^+][CrO_4^{2-}]}{[HCrO_4^-]} \qquad \text{(50}$$

$$K_3 = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} \qquad (6)$$

where the brackets refer to concentration.

Using the mass balance of Cr(VI) and equilibrium constants, various chromate species existing in the aqueous solution can be obtained for specific pH values and total concentrations of Cr(VI). Figure 1 shows a typical phase diagram of Cr(VI) species as a function of pH and total Cr(VI) concentration using K_1, K_2, and K_3 as 0.1585 kmol/m^3, 0.2239 kmol/m^3, and 33.1131 m^3/kmol at 25°C, respectively, as in the literature (11). The $HCrO_4^-$ ion is predominate at 50 and 500 ppm Cr(VI) and pH values 2–5; however, chromium is largely present as CrO_4^{2-} in the basic aqueous solution.

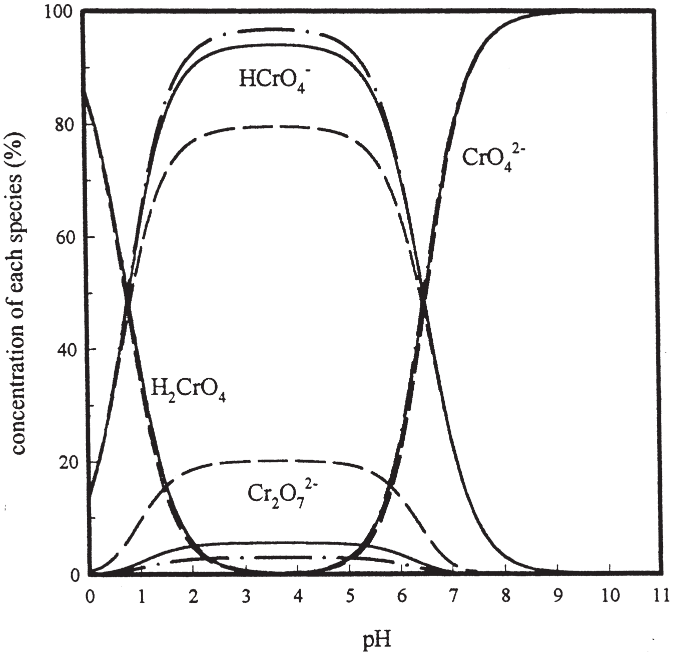

Figure 1. Phase diagram of Cr(VI) species as function of pH and total Cr(VI) concentration at 25°C. —·— Cr(VI) = 50 ppm; —— Cr(VI) = 100 ppm; ---- Cr(VI) = 500 ppm.

Modeling of Cr(VI) Transport Through a SLM

In the feed side of acid solution, the chromium can be present in significant amounts as $HCrO_4^-$, H_2CrO_4, Cr_2O_7, and CrO_4^{2-} according to pH value and total Cr(VI) concentration. The transport mechanism of Cr(VI) through an Aliquat 336 membrane when NaOH aqueous solution is used as a strip solution is shown in Fig. 2. The extraction and stripping reactions are expressed as follows:

$$HCrO_4^- + H^+ + \overline{QCl} \Leftrightarrow \overline{\text{complex}} \tag{7}$$

$$\overline{\text{complex}} + 2OH^- \Leftrightarrow \overline{QCl} + CrO_4^{2-} + 2H_2O \tag{8}$$

where QCl represents Aliquat 336, and the overbar refers to the membrane phase. The overall reaction is expressed by

$$HCrO_4^- + H^+ + 2OH^- \Leftrightarrow CrO_4^{2-} + 2H_2O \tag{9}$$

According to this mechanism, $HCrO_4^-$ and H^+ are transported simultaneously from the feed to the strip solution. Although sulfuric acid is extracted by the carrier (6) and transported across the liquid membrane, the transport of sulfuric acid is ignored. When $HCrO_4^-$ and H^+ dissolve in the membrane, they react to form an ion pair, H_2CrO_4. Then, within membrane, the ion pair and Aliquat 336 react:

$$H_2CrO_4 + \overline{QCl} \Leftrightarrow \overline{\text{complex}} \tag{10}$$

At either side of the membrane, $HCrO_4^-$ in water is in equilibrium with ion pairs, H_2CrO_4, in the membrane:

$$H^+ + HCrO_4^- \Leftrightarrow H_2CrO_4 \tag{11}$$

At the acid side of the membrane, the equilibrium between ions and pairs can be represented as a shift to the right-hand term of Eq. (11); at the basic side, it can be represented as a shift to the left-hand term. In the stripping alkaline solution, H_2CrO_4 and OH^- react:

$$H_2CrO_4 + 2OH^- \Leftrightarrow CrO_4^{2-} + 2H_2O \tag{12}$$

Equation (10) of the reversible reaction between H_2CrO_4 and Aliquat 336 within the membrane is simply represented as follows:

$$A + B \underset{k_2}{\overset{k_1}{\Leftrightarrow}} AB \tag{13}$$

where A, B, and AB represent H_2CrO_4, $\overline{QCl}$, and the $\overline{\text{complex}}$, respectively.

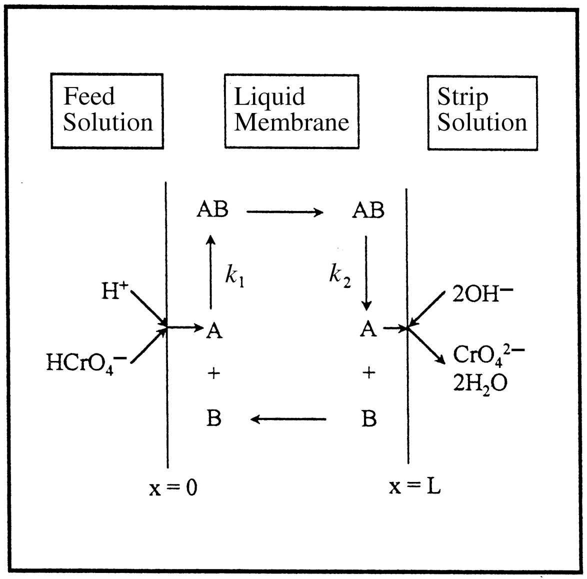

Figure 2. Mechanism of chromium transport across liquid membrane containing Aliquat 336 as a carrier.

At steady state, the one-dimensional conservation equations describing the diffusion of A, B, and AB across a liquid membrane of thickness are

$$D_A \frac{d^2 C_A}{dx^2} - k_1 C_A C_B + k_2 C_{AB} = 0 \tag{14}$$

$$D_B \frac{d^2 C_B}{dx^2} - k_1 C_A C_B + k_2 C_{AB} = 0 \tag{15}$$

$$D_{AB} \frac{d^2 C_{AB}}{dx^2} + k_1 C_A C_B - k_2 C_{AB} = 0 \tag{16}$$

The boundary conditions of Eqs. (14)–(16) are

$$x = 0, \qquad C_A = C_{Ao}, \qquad \frac{dC_B}{dx} = \frac{dC_{AB}}{dx} = 0 \tag{17}$$

$$x = L, \qquad C_A = C_{AL}, \qquad \frac{dC_B}{dx} = \frac{dC_{AB}}{dx} = 0 \tag{18}$$

where x is a measure of distance (m) and C_{Ao} and C_{AL} are the concentrations of component A in the membrane at the interface between the feed and membrane side and between the membrane and stripping side, respectively.

The continuity requirement on the carrier in the membrane phase is

$$\int_0^L (C_B + C_{AB})\, dx = C_{BT} L \tag{19}$$

where C_{BT} is the total concentration of carrier and L is the membrane thickness.

The above equations can be written in their dimensionless forms:

$$\frac{d^2 a}{dy^2} = \delta^2 ab - \frac{\delta^2}{K_{eA}} c \tag{20}$$

$$\frac{d^2 b}{dy^2} = \frac{\delta^2}{q} ab - \frac{\delta^2}{qK_{eA}} c \tag{21}$$

$$\frac{d^2 c}{dy^2} = -\frac{\delta^2}{rq} ab + \frac{\delta^2}{rqK_{eA}} c \tag{22}$$

$$\mathrm{y} = 0\,;\ a = 1,\ db/dy = dc/dy = 0 \tag{23}$$

$$\mathrm{y} = 1\,;\ a = a_L;\ db/dy = dc/dy = 0 \tag{24}$$

$$\int_0^1 (b + c)\, dy = 1 \tag{25}$$

where a is defined as C_A/C_{Ao}, b as C_B/C_{BT}, c as C_{AB}/C_{BT}, a_L as C_{AL}/C_{Ao}, y as x/L, δ as $L(k_1 C_{BT}/D_A)^{1/2}$, r as D_{AB}/D_B, q as $D_B C_{BT}/D_A C_{Ao}$, and K_{eA} as $(k_1/k_2)C_{Ao}$.

The facilitation factor, β, is defined as follows:

$$\beta = -\frac{D_A(dC_A/dx)|_{x=0}}{(D_A/L)C_{Ao}} = -\left(\frac{da}{dy}\right)\Bigg|_{y=0} \tag{26}$$

The solution of the differential equations (Eqs. 20–22) can be obtained by the approximate solution (12).

EXPERIMENTAL

Chemicals used in this study were of reagent grade and used without further purification. The supporting membrane was a hydrophobic microporous polytetrafluoroethylene membrane with nominal thickness of 1.45×10^{-4} m, porosity of 0.85, and tortuosity of 1.353.

The concentrations of Cr(VI) in the feed side, the carrier in the membrane side, and NaOH in the stripping side were varied within the range of 20–500 mg/dm^3, 0–0.035 kmol/m^3, and 0.1–2.0 kmol/m^3, respectively. The pH value of the feed solution was fixed at 3.

Aqueous Cr(VI) feed solutions were prepared by dissolving K_2CrO_7 (Junsei Chemical Co, Ltd, Japan) in deionized water, and the pH was adjusted with sulfuric acid. Aliquat 336 (Aldrich Chemical Co, Inc) dissolved in toluene was used as an organic carrier of Cr(VI). Teramoto et al. (4) suggested that aggregates of the Cr(VI)-carrier complex were deposited on the membrane surface of the feed side, which seemed to decrease the chromium flux. Three percent (v) of 3,7-dimethyl-3-octanol was added to the liquid membrane to avoid the aggregation. The impregnation of the carrier into pores of the supporting membrane was carried out by immersing the membrane in the organic extractant solution for 24 hours by the same procedure as reported by (13). Aqueous NaOH solution was used as the stripping solution. Cr(VI) concentrations in the aqueous solution were measured with a Hewlett Packard UV-Visible Spectrophotometer (Model 8452A) using a colorimetric diphenylcarbazide method (14).

The experimental procedures were the same as those reported earlier (14). The flat-plate membrane separator module was made of Pyrex glass with i.d. of 0.1 m and height of 0.03 m. After the impregnated support was set at the center of the module, 0.175 dm^3 of aqueous Cr(VI) solution was put into the lower part of the module, and the same amount of aqueous NaOH solution was added into the upper part. The lower part was agitated by a magnetic bar, and the upper part was mixed by an impeller connected to a motor. The concentration of Cr(VI) in the feed side was measured according to the change of stream time through small samples (1×10^{-3} dm^3) taken from the lower part of the module. The same volume of water was replaced after sampling. A new supporting membrane was used in each experiment. Experiments were repeated 3 times, and the overall mass transfer coefficient obtained from the time dependence of Cr(VI) concentration was averaged. All experiments were carried out at 25°C.

RESULTS AND DISCUSSION

The physical properties, such as the diffusivity, distribution coefficient, and reaction rate constants, were needed to observe quantitatively the facilitation behavior of the carrier.

The chemical forms of Cr(VI) in our study and referenced in (5) were H_2CrO_4 and CrO_4^{2-}, respectively. The diffusivity of Cr(VI) was corrected with the values in reference (5) by the viscosity and molecular weight.

The viscosity of toluene solution with an approximate Aliquat 336 concentration of 0.019–0.035 mol/L was measured by the Ubbelohde viscometer as 0.608 centipoise.

The diffusivity of Cr(VI) in a liquid membrane, D_A, was corrected with that of 2.30×10^{-9} m^2/s in water (5), and its value was 3.75×10^{-9} m^2/s. The diffusivity of Aliquat 336 in the toluene was calculated from the Wilke-Chang equation (15) as 1.55×10^{-9} m^2/s. The diffusivities of Cr(VI) and Aliquat 336 in the membrane liquid were corrected as $D\varepsilon/\tau$ (16), where D was the diffusivity of solute and ε and τ were the porosity and tortuosity of the supported membrane. Thus, the corrected diffusivities of Cr(VI) and Aliquat 336 were 2.36×10^{-9} and 0.97×10^{-9} m^2/s, respectively. The diffusivity of the complex in the membrane liquid was assumed to be equal to that of Aliquat 336.

The distribution coefficient of Cr(VI), H_A, between the acid aqueous and toluene phases was measured by the same procedure as that reported by (17). The value of H_A ratio of 0.0165 was determined as the amount of Cr(VI) concentration in toluene to its concentration in the aqueous solution.

Through the use of a batch reactor, the forward- and backward-reaction rate constants in the second-order reversible reaction of Cr(VI) with Aliquat 336 were obtained by the integral method as reported by (14): 797 m^3/kmol·s and 0.52/s, respectively. The membrane thickness was used as the corrected value multiplied by the tortuosity, and its value was 1.96×10^{-4} m.

If the total volume of the organic extractant within the micropores of the membrane is negligible when it is compared with the volume of the solution in each part, the change of Cr(VI) concentration with time in the feed solution may be equal to that in the stripping side as follows:

$$-\frac{dC_{Af}}{dt} = \frac{dC_{AS}}{dt} = \frac{S}{V}K(C_{Af} - C_{AS}) \tag{27}$$

Here, *S* and *V* are the membrane area and the volume of the solution in each part.

If the $HCrO_4^-$ ion produced at the basic side of the membrane, as shown in Eq. (11), is completely consumed by an instantaneous reaction in the alkaline stripping solution, C_{As} is equal to zero. Then, integration of Eq. (27) leads to

$$\frac{C_{Af}}{C_{Afo}} = \exp(-\frac{S}{V}Kt) \tag{28}$$

where C_{Afo} is the initial concentration of Cr(VI) in the feed side.

The overall mass transfer coefficient, *K*, was obtained from measurements of Cr(VI) concentration in the feed side in relation to time. Experimental conditions were as follows: $C_{Afo} = 50$ mg/dm³; $[NaOH]_{\phi} = 1$ kmol/m³; and agitation was at 500 rpm in the feed- and stripping-sides. The experimental feeds also contained 0.022 kmol/m³ $[QCl]_{\phi}$. The results are presented in Fig. 3, which shows a semilog plot of C_{Af}/C_{Afo} of Cr(VI) in the feed side against time. A linear relationship between C_{Af}/C_{Afo} and *t* was found from the experimental data. Therefore, the overall mass transfer coefficients, with and without the carrier, could be

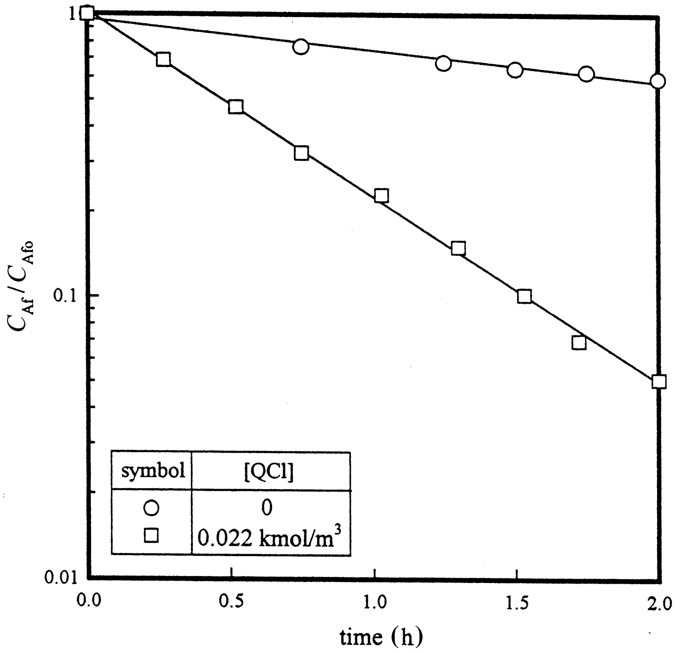

Figure 3. Dependence of Cr(VI) concentration in feed side on time. [Cr(VI)] = 50 ppm; [NaOH] = 1 kmol/m³; agitation in feed- and stripping-sides = 500 rpm.

obtained from the slopes of the solid line in the Fig. 3, 2.019×10^{-6}, and from Eq. (28), 1.101×10^{-5} m/s. The facilitation factor, 5.45, was obtained as the ratio of the overall mass transfer coefficient with the carrier to that without the carrier.

The effect of NaOH concentration in the stripping side on the overall mass transfer coefficient could be seen through measurements of the concentration of Cr(VI) in the feed side while the NaOH concentration was varied within the range of 0.1–2.0 kmol/m^3. Experimental conditions were $C_{\mathrm{Afo}} = 50$ mg/dm^3; $[\mathrm{QCl}]_{\Phi} =$ 0.022 kmol/m^3; and the agitation of the feed- and stripping-sides was 500 rpm. The overall mass transfer coefficients, which were obtained from slope line of the semilog plot of $C_{\mathrm{Af}}/C_{\mathrm{Afo}}$ vs. time, are plotted in Fig. 4. K increased sharply with increased concentrations of NaOH up to 0.5 kmol/m^3, but it remained almost constant in the higher NaOH-concentration range. This means that $\mathrm{HCrO_4^-}$ in the strip solution is completely consumed by the reaction and $\mathrm{OH^-}$ predominates when NaOH concentrations are higher than 1.0 kmol/m^3. Therefore, Eq. (28) can be used to get the overall mass transfer coefficient. The concentration of NaOH in the strip solution was fixed at 1 kmol/m^3 in all the experiments.

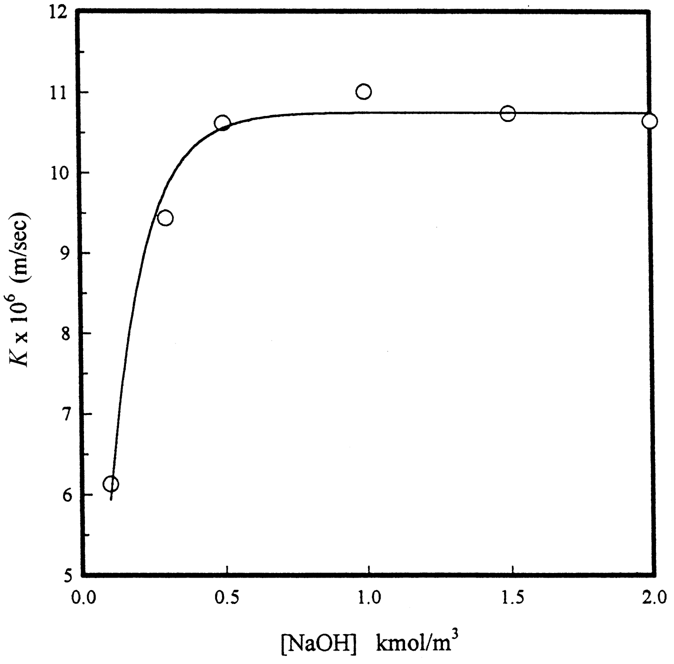

Figure 4. Effect of NaOH concentration in stripping side on overall mass transfer coefficient. [Cr(VI)] = 50 ppm; [QCl] = 0.022 kmol/m^3; agitation in feed- and stripping-sides = 500 rpm.

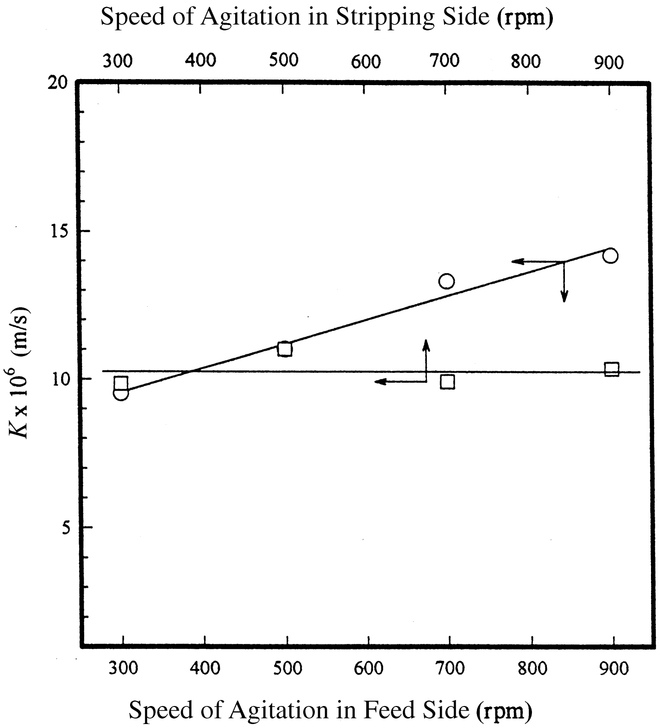

Figure 5. Effect of agitation speed in feed- and stripping-side on overall mass transfer coefficient. [Cr(VI)] = 50 ppm; [QCl] = 0.022 kmol/m³.

Figure 5 shows plots of *K* against the agitation speed in the feed side when the agitation speed in the stripping side was 500 rpm and *K* in the stripping side when the feed side is agitated at 500 rpm. Conditions in both experiments were $C_{\mathrm{Afo}} = 50$ mg/dm³ and $[\mathrm{QCl}]_{\phi} = 0.022$ kmol/m³. *K* increased as the agitation speed in the feed side was increased, but it remained constant as stripping-side agitation speed was increased. Independence of *K* with regard to agitation speed in the stripping side may be due to the consumption of $\mathrm{HCrO_4^-}$ in the strip solution. The agitation speed in the feed- and stripping-sides was fixed at 500 rpm in all experiments.

Because the amount of several ions is influenced by pH value and by total Cr(VI) concentration, the effect of the total Cr(VI) concentration on the extraction of Cr(VI) by the carrier must be considered. The concentration of Cr(VI) in the feed solution were measured at various initial concentrations of Cr(VI) at $[\mathrm{QCl}]_{\phi}$ of 0.022 kmol/m³, and Fig. 6 shows the time-dependent concentrations of Cr(VI) in the feed side. The observed data for the initial concentration of Cr(VI), in the

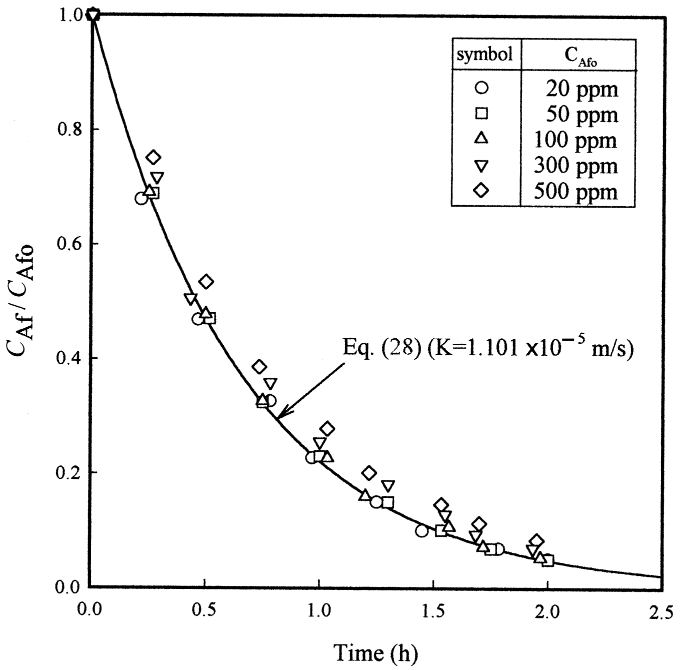

Figure 6. Time-dependent concentration of Cr(VI) in the feed side at various initial Cr(VI) concentrations and [QCl] = 0.022 kmol/m³.

range of 20–100 ppm , were in agreement with the *K* of 1.101 x10^{-5} m/s derived from Eq. (28), which is represented by the solid line in Fig. 6. However, the observed values for Cr(VI) concentrations of 300 and 500 ppm deviated from the solid line. The concentration of $HCrO_4^-$, H_2CrO_4, CrO_4^{2-}, and $Cr_2O_7^{2-}$ in the acid solution of pH 3 in Table 1 were obtained from the mass balance of the various species using Eq. (1)–(6), and the values of K_1, K_2 and K_3 mentioned in the section on chromate chemistry. As shown in the table, the fraction of $HCrO_4^-$ ionic concentration decreased from 98.1 to 79.4% and the $Cr_2O_7^{2-}$ concentration rose

Table 1. Concentration of Various Ions of Cr(VI) in Acid Solution (pH 3)

Cr(VI) (ppm)	$HCrO_4^-$ (%)	H_2CrO_4 (%)	CrO_4^{2-} (%)	$Cr_2O_7^{2-}$ (%)
20	98.12	0.62	0.03	1.23
50	96.40	0.61	0.03	2.96
100	93.78	0.59	0.03	5.60
300	85.48	0.54	0.02	13.96
500	79.40	0.50	0.03	20.07

from 1.2 to 20.1% when initial Cr(VI) concentrations were increased from 20 to 500 ppm. In addition, the percentages of H_2CrO_4 and CrO_4^{2-} were very low in the acid solution. The transfer rate of the complex between H_2CrO_4 and Aliquat 336 in the membrane liquid may be faster than that between H_2CrO_7 and Aliquat 336 due to differences in diffusion coefficients and reaction rate constants between each complex (Eq. 13).

The facilitation behavior of Cr(VI) in the liquid film was observed from the concentration profiles of Cr(VI), Aliquat 336, and the complex in the membrane liquid that were computed from the approximate solutions of Eqs. (20–22) and subjected to Eqs. (23–25). Input data were as follows: $D_A = 2.36 \times 10^{-9}$ m^2/s; $D_B = 0.97 \times 10^{-9}$ m^2/s; $k_1 = 797$m^3/kmol·s; $k_2 = 0.52$/s; Cr(VI) = 50 ppm; $C_{Ao} = 1.529 \times 10^{-5}$; $C_{AL} = 0$; $C_{BT} = 0.019$ kmol/m^3; and $L = 1.96 \times 10^{-4}$ m. The results are presented in Fig. 7 as the dimensionless concentrations. As shown in the figure, Cr(VI) as H_2CrO_4 and the complex are more concentrated at the boundary of the feed side (side 1), while the concentration of the carrier at the boundary of the stripping side (side 2) is higher than that at the feed side, and the

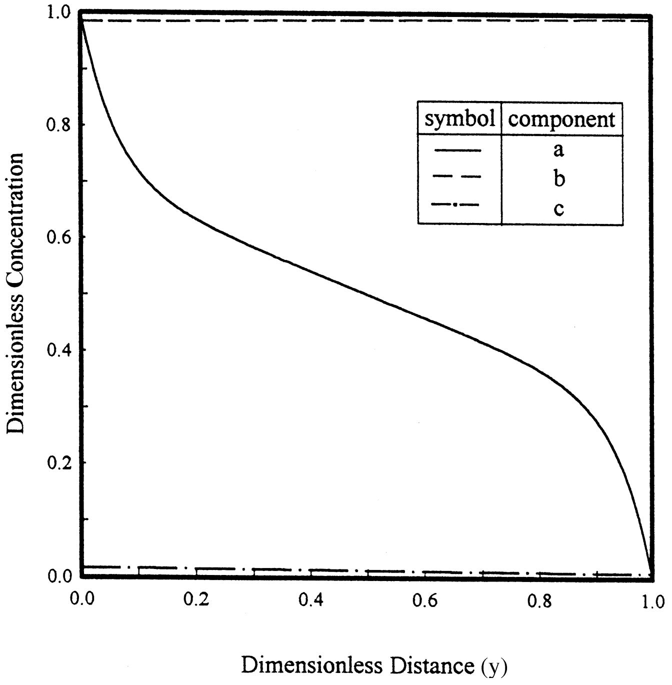

Figure 7. Dimensionless concentration profile inside liquid membrane at [Cr(VI)] of 50 ppm and [QCl] of 0.019 kmol/m^3; a, H_2CrO_4; b, Aliquat 336; c, complex.

concentration of Cr(VI) has a symmetrical form. Near side 1, the complex produced by the forward reaction of Eq. (13) diffuses across the liquid film, and near side 2, it decomposes into Cr(VI). Near side 2, the carrier produced by the backward reaction of Eq. (13) diffuses across the film, and near side 1, it is consumed. Thus, Cr(VI) transport across the film is facilitated by the diffusion of the complex.

To investigate the effect of the carrier on the facilitation of Cr(VI), the concentration of Cr(VI) in the feed side was measured after the QCl concentrations were varied from 0 to 0.035 kmol/m³. The results are presented in Fig. 8, which shows the facilitated factor against the QCl concentration. The facilitated factor increased as the concentration of carrier was increased. The solid lines represent the computed values of the facilitated factor that were obtained from the slope of the dimensionless concentration profile of component A at $y = 0$. As shown in the figure, the calculated values were in reasonable agreement with the experimental ones.

The reaction region in the mass transfer accompanied by a chemical reaction is usually classified as fast or slow according to its limiting step (18). If the

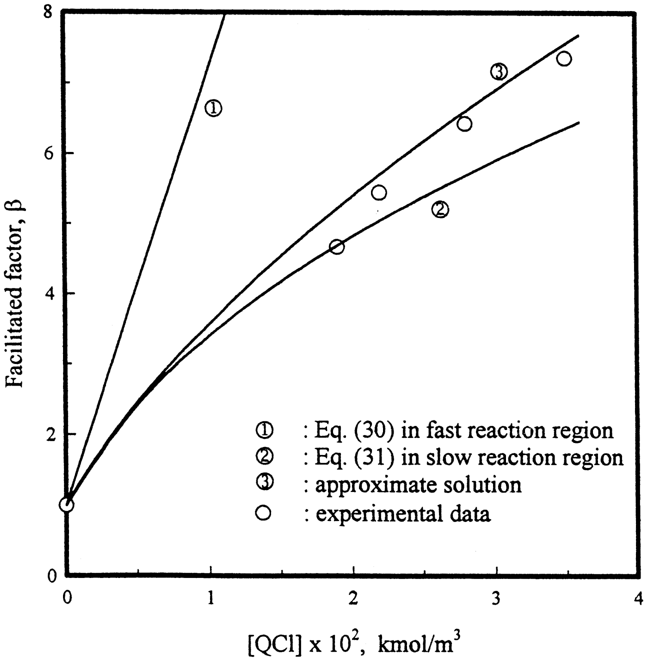

Figure 8. Effect of carrier concentration on facilitated factor. [Cr(VI)] = 50 ppm.

reaction depicted in Eq. (13) is sufficiently fast, reacting species exist in an equilibrium state. Then, it is useful to solve the differential equations (Eqs. 14–16) by adding Eqs. (14) and (16) to get the flux of Cr(VI) as follows:

$$D_{\mathrm{A}}\frac{d^2C_{\mathrm{A}}}{dx^2} + D_{\mathrm{AB}}\frac{d^2C_{\mathrm{AB}}}{dx^2} = 0 \tag{29}$$

The facilitated factor, β_{fast}, is derived from the analytical solution of Eq. (29) subject to Eqs. (17–19) and Eq. (26) as follows:

$$\beta_{\mathrm{fast}} = 1 + \frac{D_{\mathrm{AB}}K_{\mathrm{e}}C_{\mathrm{BT}}}{D_{\mathrm{A}}(1 + K_{\mathrm{e}}C_{\mathrm{Ao}})(1 + K_{\mathrm{e}}C_{\mathrm{AL}})} \tag{30}$$

where K_{e} is the equilibrium reaction constant k_1/k_2.

If the reaction of Eq. (13) is sufficiently slow, the concentrations of the components B and AB are constant as $\overline{C_{\mathrm{B}}}$ and $\overline{C_{\mathrm{AB}}}$ through the liquid film. Equation (14) is solved analytically and the facilitated factor, $\beta_{\mathrm{slow},}$ is derived as follows:

$$\beta_{\mathrm{slow}} = -\frac{\mathrm{L}\sqrt{c_3}[\mathrm{B}_2\cos h\sqrt{c_3}\mathrm{L} + \mathrm{B}_1\sin h(\sqrt{c_3}\mathrm{L})]}{c_1(C_{\mathrm{AB}} - C_{\mathrm{AL}})} \tag{31}$$

where, $\overline{C_{\mathrm{AB}}} = k_1C_{\mathrm{BT}}(C_{\mathrm{AB}} + C_{\mathrm{AL}})\ /\ [2k_2 + k_1(C_{\mathrm{AB}} + C_{\mathrm{AL}})]$; $\overline{C_{\mathrm{B}}} = C_{\mathrm{BT}} - \overline{C_{\mathrm{AB}}}$; $c_1 = k_1\overline{C_{\mathrm{B}}}$; $c_2 = k_2\overline{C_{\mathrm{B}}}$; $c_3 = c_1/D_{\mathrm{A}}$; $\mathrm{B}_1 = c_1C_{\mathrm{Ao}} - c_2$; and $\mathrm{B}_2 = [c_1C_{\mathrm{AL}} - c_2 - \mathrm{B}_1 \cos h(\sqrt{c_3L})]/\sin h(\sqrt{c_3L})$.

The facilitated factors obtained from the approximate solution of the differential equations, Eq. (30) and (31), are presented in Fig. 8. The experimental facilitated factor values were similar to those calculated for a slow reaction. Therefore, the reaction of Cr(VI) with Aliquat 336 is classified into a slow-reaction region due to the small change of carrier and complex concentrations (Fig. 7).

CONCLUSION

In this work, we investigated the transport of Cr(VI) from an aqueous solution of pH 3 through a SLM containing Aliquat 336 dissolved in toluene as a mobile carrier in concentration ranges of 0.019 kmol/m^3 $\leq$ Aliquat 336 $\leq$ 0.035 kmol/m^3 and 20 g/m^3 $\leq$ Cr (VI) $\leq$ 500 g/m^3.

The facilitated factors of Cr(VI) transport were obtained as ratios of the experimental values of the overall mass transfer coefficient with and without the carrier, which were measured from the time dependence of Cr(VI) concentration.

The forward- and backward-reaction rate constant in the second-order reversible reaction of Cr(VI) and Aliquat 336 using a batch reactor were obtained experimentally by the integral method. Their values were 797 m^3/kmol·s and 0.52 per second, respectively, which were used to simulate the simple model H_2CrO_4

+ Aliquat 336 ↔ complex based on the model of Teramoto et al. (4) with the mass conservation equation and associated boundary conditions.

Based on the comparison between the experimental and simulated facilitated factors of Cr(VI) transport, the reaction between Cr(VI) and Aliquat 336 was classified into the slow reaction region.

NOMENCLATURE

A	Cr(VI)
AB	complex
a	C_A/C_{Ao}
B	Aliquat 336
B_1	$c_1 C_{Ao} - c_2$ (kmol/m^3·s)
B_2	$[c_1 C_{AL} - c_2 - B_1 \cos h(\sqrt{c_3} L)]/\sin h(\sqrt{c_3} L)$ (kmol/m^3·s)
b	C_B/C_{BT}
C_i	concentration of component i (kmol/m^3)
$\overline{C}_{AB}$	$k_1 C_{BT}(C_{AB} + C_{AL})/[2k_2 + k_1(C_{Ao} + C_{AL})]$ (kmol/m^3)
$\overline{C}_B$	$C_{BT} - \overline{C}_{AB}$ (kmol/m^3)
c	C_{AB}/C_{BT}
c_1	$k_1 \overline{C}_B$ (per second)
c_2	$k_2 \overline{C}_B$ (kmol/m^3·s)
c_3	c_1/D_A (1/m^2)
D_i	diffusivity of component i (m^2/s)
K	overall mass transfer coefficient (m/s)
K_1	$[H^+][HCrO_4^-]/[H_2CrO_4]$ (kmol/m^3)
K_2	$[H^+][CrO_4^{2-}]/[HCrO_4^-]$ (kmol/m^3)
K_3	$[Cr_2O_7{}^{2-}]/[HCrO_4^-]^2$ (m^3/kmol)
K_e	k_1/k_2 (m^3/kmol)
K_{eA}	$K_e C_{Ao}$
k_1	forward reaction rate constant in Eq. (13) (m^3/kmol·s)
k_2	backward reaction rate constant in Eq. (13) (per second)
L	membrane thickness (m)
QCl	Aliquat 336
q	$D_B C_{BT}/D_A C_{Ao}$
r	D_{AB}/D_B
S	surface area of the liquid membrane (m^2)
t	time (h)
V	volume of the feed- and stripping-side (m^3)
x	distance (m)
y	x/L

Greek symbols

β	facilitated factor defined by Eq. (26)
δ	$L(k_1 C_{BT}/D_A)^{1/2}$
ε	porosity of the membrane
τ	tortuosity of the membrane

Subscripts

A	Cr(VI)
AB	complex
B	Aliquat 336
exp	experimental data
f	feed side
fast	fast reaction
L	stripping side boundary
o	feed side boundary
s	stripping side
slow	slow reaction
ϕ	initial concentration

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