

Facilitated Transport of Cr(VI) through a Supported Liquid Membrane with a Carrier

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(Received March 10, 2003 ; Accepted May 12, 2003)

Abstract : This paper has applied a simple model to the mass transfer mechanism of Cr(VI) with crownether in a batch-type, supported liquid membrane module. Concentration at pH 3 are as follows : $0.012 \text{ kmol/m}^3 \leq 18\text{-crown-6} \leq 0.036 \text{ kmol/m}^3$ and $20 \text{ g/m}^3 \leq \text{Cr(VI)} \leq 500 \text{ g/m}^3$. The measured values of forward- and backward-reaction rate constants between Cr(VI) and 18-crown-6 were used to simulate the model with the mass conservation equation and associated boundary conditions. Comparison between the experimental and simulated facilitated factor of Cr(VI) transport led to classification of reaction regions.

Keywords : *facilitated transport, immobilized liquid membrane, Cr(VI), 18-crown-6, mass transfer coefficient.*

1. 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 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 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 which separates a feed from 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

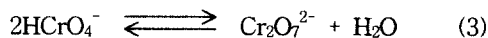
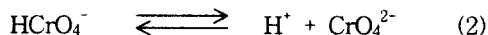
solution interface. Further rate enhancement can be expected by the addition of active carrier, which facilitates transport, to the liquid membrane. Quaternary ammonium salts as a carrier have been shown to be very effective for the removal of chromate ions, such as trioctylamine[4], tri-dodecylamine[6], triisooctylamine[7], and trioctylmethylammonium chloride[5, 8-11], from acid solution in the liquid membrane. Because various chemical species of Cr(VI) in the aqueous solution are formed according to the total concentration of Cr(VI) and pH, several models are used to analyze the transport of Cr(VI) with a carrier. There is little information about the effect of crown ethers as carriers on the extraction of Cr(VI) through a supported liquid membrane with a simple reaction such as $\text{H}_2\text{CrO}_4 + 18\text{-crown-6}$ complex.

In the present work, the extraction of Cr(VI) from aqueous solutions of pH 3 through a SLM with 18-crown-6 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 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 18-crown-6 were used to simulate the extraction model. The reaction regions of the reaction between Cr(VI) and crown ether were classified by comparison of the measured facilitated factors with the simulated ones.

2. Theory

2.1. Chromate chemistry

Cr(VI) may exist in the aqueous solution in different ionic forms as illustrated by the following equilibrium reactions[12].



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:

$$K_1 = \frac{[\text{H}^+][\text{HCrO}_4^-]}{[\text{H}_2\text{CrO}_4]} \quad (4)$$

$$K_2 = \frac{[\text{H}^+][\text{CrO}_4^{2-}]}{[\text{HCrO}_4^-]} \quad (5)$$

$$K_3 = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{HCrO}_4^-]^2} \quad (6)$$

where the brackets refer to the concentration.

Using the mass balance of Cr(VI) and equilibrium constants, various chromate species existing in the aqueous solution can be obtained for given value of pH and total concentration of Cr(VI). Figure 1 shows a typical phase diagram of Cr(VI) species as a function of pH and total Cr(VI) concentration

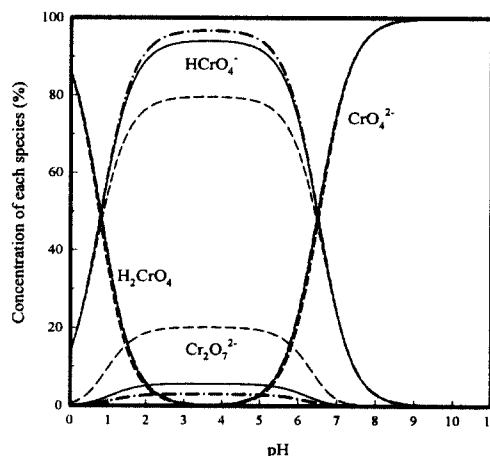


Fig.1. Phase diagram of Cr(VI) species as function of pH and total Cr(VI) concentration at 25 °C. (— : Cr(VI) = 50ppm, - - - : Cr(VI) = 100ppm, : Cr(VI) = 500ppm)

using K_1 , K_2 and K_3 as 0.1585 kmol/m^3 , 0.2239 kmol/m^3 and $33.1131 \text{ m}^3/\text{kmol}$ at 25°C , respectively, as in the literature[12]. 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 basic aqueous solution.

2.2. Modeling of Cr(VI) transport through 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 a 18-crown-6 membrane when NaOH aqueous solution is used a strip solution is shown in Fig. 2.

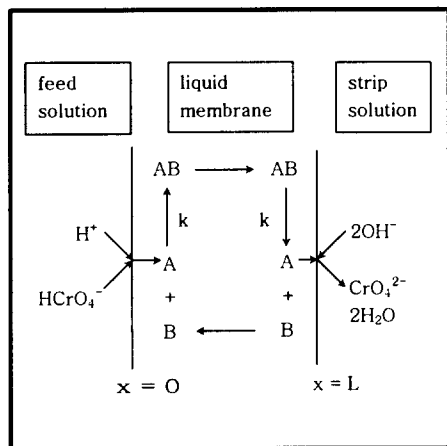
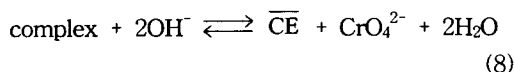
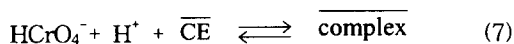


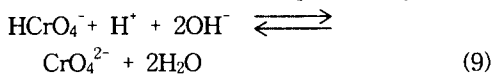
Fig. 2. Mechanism of chromium transport across liquid membrane containing 18 crown-6 as a carrier.

The extraction and stripping reactions are considered to be expressed as follows:

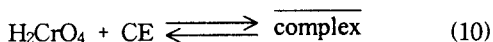


where, $\overline{\text{CE}}$ represents 18-crown-6, and the overbar refers to the membrane phase.

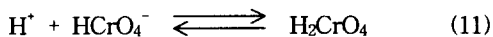
The overall reaction is expressed by



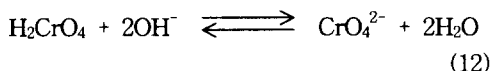
According to this mechanism, HCrO_4^- and H^+ are transported simultaneously from the feed to the strip solution. Although sulfuric acid is extracted by the carrier[6] and transported across the liquid membrane, the transport of sulfuric acid is neglected. When HCrO_4^- and H^+ dissolve in the membrane,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



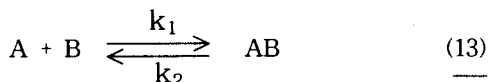
At either side of the membrane, HCrO_4^- in water is in equilibrium with ion pairs, H_2CrO_4 , in the membrane:



At the acid side of the membrane, this equilibrium between ions and pairs can be represented as a shift to the left-hand term. In the stripping alkaline solution, H_2CrO_4 and OH^- react:



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



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

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

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

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

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

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

$$x = 0, \quad C_A = C_{A0}, \quad \frac{dC_B}{dx} = \frac{dC_{AB}}{dx} = 0 \quad (17)$$

$$x = L, \quad C_A = C_{AL}, \quad \frac{dC_B}{dx} = \frac{dC_{AB}}{dx} = 0 \quad (18)$$

where x is a measure of distance(m), and C_{A0} 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

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

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:

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

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

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

$$y = 0 ; a = 1, db/dy = dc/dy = 0 \quad (23)$$

$$y = 1 ; a = a_L, db/dy = dc/dy = 0 \quad (24)$$

$$\int_0^1 (b + c) dy = 1 \quad (25)$$

where a is defined as C_A/C_{A0} , b as C_B/C_{BT} , c as C_{AB}/C_{BT} , a_L as C_{AL}/C_{A0} , y as x/L , δ as $L(k_1 C_{BT}/D_A)^{1/2}$, r as D_{AB}/D_B , q as $D_B C_{BT}/D_A C_{A0}$, and K_{eA} as $(k_1/k_2) C_{A0}$.

The facilitation factor, b , is defined as follows:

$$\beta = -\frac{D_A (dC_A/dx)|_{x=0}}{(D_A/L)C_{A0}} = -\left(\frac{da}{dy}\right)\Big|_{y=0} \quad (26)$$

The solution of the differential equations (Eqs. 20-22) can be obtained by the approximate solution [13].

3. Experimental

Chemicals used in this study were 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/dm³, 0-0.036 kmol/m³ and 0.1-2.0 kmol/m³, respectively. The pH value of the feed solution was fixed at 3.

Aqueous Cr(VI) feed solutions were prepared by dissolving K₂CrO₇ (Junsei Chem. Co., Ltd.) in deionized water, and the pH was adjusted with sulfuric acid. 18-crown-6 (Aldrich Chem. Co., Inc.) dissolved in toluene solvent was used as an organic carrier of Cr(VI). 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 [14]. 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 diphenyl carbazide method [15]. The experimental procedure was the same as those reported earlier [11]. The flat-plate membrane separator module was made of Pyrex glass with inside diameter of 0.1m and height of 0.03m. After setting the impregnated support was set at the center of the module, 0.175 dm³ of aqueous Cr(VI) solution was put into the lower part of the module, and 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 ($1 \times 10^{-3} \text{ dm}^3$) taken from the lower part of the module. The same volume of water was replaced after sampling. The 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 .

4. 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 the reference in [5] are H_2CrO_4 and CrO_4^{2-} , respectively. The diffusivity of Cr(VI) was corrected with the value in reference[5] by the viscosity and molecular weight. The viscosity of toluene solution with an approximate crown ether concentration of $0.012 \sim 0.036 \text{ mol/l}$ was measured by the Ubbelohde viscometer as 0.58 centipoise.

The diffusivity of Cr(VI) in a liquid membrane, D_A , was corrected with that of $2.30 \times 10^{-9} \text{ m}^2/\text{s}$ in water[5], and its value was $3.69 \times 10^{-9} \text{ m}^2/\text{s}$. The diffusivity of 18-crown-6 in toluene was calculated from the Wilke-Chang equation[16] as $1.24 \times 10^{-9} \text{ m}^2/\text{s}$. The diffusivity of Cr(VI) and 18-crown-6 in the membrane liquid were corrected as D_e/t [17], where D was the diffusivity of solute, e and t were the porosity and tortuosity of the supported membrane. Thus, the corrected diffusivity of Cr(VI) and 18-crown-6 were 2.32×10^{-9} and $0.78 \times 10^{-9} \text{ m}^2/\text{s}$, respectively. The diffusivity of the complex in the membrane liquid was assumed to be equal to that of 18-crown-6.

The distribution coefficient of Cr(VI), H_A ,

between the acid aqueous phase and toluene phase was measured by the same procedure as those reported earlier[18], and its value was 0.0165 as the ratio of Cr(VI) concentration in toluene to that 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 18-crown-6 were obtained by the integral method as reported earlier[11], and their values were $645 \text{ m}^3/\text{kmol s}$ and $0.61/\text{s}$, respectively. The membrane thickness was used as the corrected value multiplied by the tortuosity, and its value was $1.96 \times 10^{-4} \text{ m}$.

If the total volume of the organic extractant within the micropores of the membrane is negligible where 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:

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

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

If 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

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

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) concentrations in the feed side in relation to time. Experimental conditions were as follows: $C_{Afo} = 50 \text{ mg/dm}^3$; $[\text{NaOH}]_0 = 1 \text{ kmol/m}^3$ and agitation was at 500 rev/min in the feed- and stripping sides. The experimental feeds also contained 0.012

$\text{kmol/m}^3 [\text{CE}]_{\phi}$. The results are presented in Fig. 3, which shows a semilog plot of C_{A1}/C_{Afo} of Cr(VI) in the feed side against time. A linear relationship between C_{A1}/C_{Afo} and t was found from the experimental data. Therefore, the overall mass transfer coefficients, with and without the carrier, could be obtained from the slopes of the solid line in the Fig. 3, 2.016×10^{-6} , and from Eq. (28), 6.122×10^{-6} m/s. The facilitated factor, 3.04, was obtained as the ratio of the overall mass transfer coefficient with the carrier to that without the carrier.

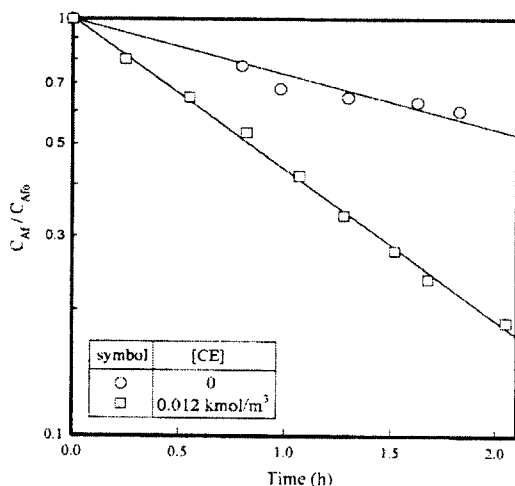


Fig. 3. Dependence of Cr(VI) in feed side on time. ($[\text{Cr(VI)}] = 50\text{ppm}$, $[\text{NaOH}] = 1 \text{ kmol/m}^3$, agitation in feed and stripping side = 500rpm)

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 $C_{Afo} = 50 \text{ mg/dm}^3$; $[\text{CE}]_{\phi} = 0.012 \text{ kmol/m}^3$; and agitation speed of the feed- and stripping-sides of 500 rpm. The overall mass transfer coefficients, which were obtained from slope of the semilog plot of C_{A1}/C_{Afo} vs.

time, are plotted in Fig. 4. K increased sharply with increasing the concentration of NaOH up to 0.5 kmol/m^3 , but it remained almost constant in the higher NaOH concentration range. This means that HCrO_4^- ion in the strip solution is completely consumed by the reaction with 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 as 1 kmol/m^3 in all the experiments.

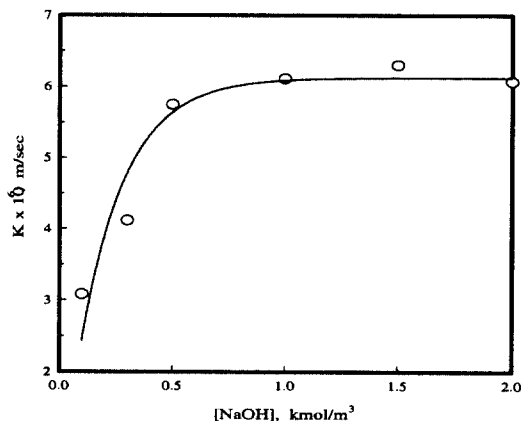


Fig. 4. Effect of NaOH concentration in stripping side on overall mass transfer coefficient. ($[\text{Cr(VI)}] = 50\text{ppm}$, $[\text{CE}] = 0.012 \text{ kmol/m}^3$, agitation in feed and stripping side = 500 rpm)

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 rev/min. Conditions in both experiments were $C_{Afo} = 50 \text{ mg/dm}^3$ and $[\text{CE}]_{\phi} = 0.012 \text{ kmol/m}^3$. K remained constant as the agitation speed in the feed- and the stripping-side were increased, from which the resistance in the feed side can be neglected and independence of K with regard to agitation speed in the

stripping side may be due to the consumption of HCrO_4^- in the strip solution. The agitation speed in the feed- and stripping-sides was fixed as 500 rpm in all experiments.

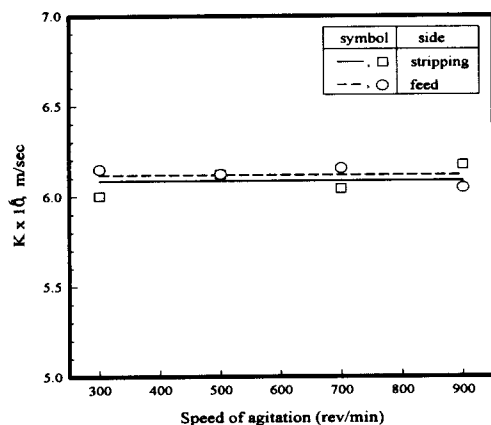


Fig. 5. Effect of agitation speed in feed- and stripping-side on overall mass transfer coefficient. ($[\text{Cr(VI)}] = 50\text{ppm}$, $[\text{CE}] = 0.012\text{ kmol/m}^3$)

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 concentration of Cr(VI) at $[\text{CE}]_0$ of 0.012 kmol/m^3 , 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 range of 20–100 ppm, were in agreement with K of $6.151 \times 10^{-6}\text{ m/s}$ in 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 above the solid line. The concentration of HCrO_4^- , H_2CrO_4 , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ 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 $\text{Cr}_2\text{O}_7^{2-}$ concentration rose from 1.2 to 20.1 % when initial Cr(VI) concentration 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 18-crown-6 in the membrane liquid may be faster than that between H_2CrO_7 and 18-crown-6 due to the differences of the diffusion coefficients and reaction rate constants between each complex (Eq. 13).

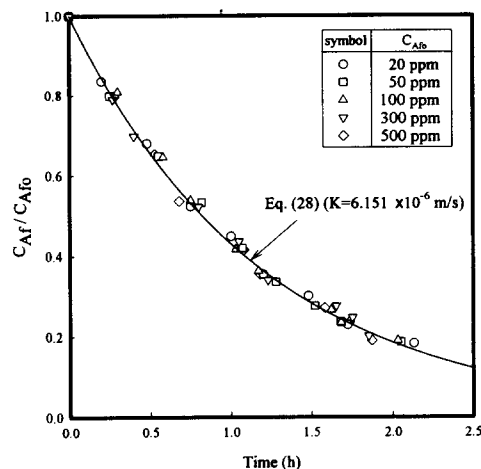


Fig. 6. Time dependent concentration of Cr(VI) in the feed side at various initial concentration of Cr(VI) ($[\text{CE}] = 0.012\text{ kmol/m}^3$)

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-} (%)	$\text{Cr}_2\text{O}_7^{2-}$ (%)
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

The facilitation behavior of Cr(VI) in the liquid film was observed from the concentration profiles of Cr(VI), 18-crown-6 and complex in the membrane liquid that were computed from the approximate solution of Eqs. (20-22) and subjected to Eqs. (23)-(25). Input data were as follows: $D_A = 2.32 \times 10^{-9} \text{ m}^2/\text{sec}$; $D_B = 0.78 \times 10^{-9} \text{ m}^2/\text{sec}$; $k_1 = 645 \text{ m}^3/\text{kmol s}$; $k_2 = 0.61 \text{ /s}$; $\text{Cr(VI)} = 50 \text{ ppm}$; $C_{A0} = 1.529 \times 10^{-5}$; $C_{AL} = 0$; $C_{BT} = 0.012 \text{ kmol/m}^3$; and $L = 1.96 \times 10^{-4} \text{ m}$. The results are presented in Fig. 7 as the dimensionless concentrations. As shown in the figure, Cr(VI) as H_2CrO_4 and 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 concentration of Cr(VI) has a symmetrical form. Near side 1, 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, is consumed. Thus Cr(VI) transport across the film is facilitated by the diffusion of complex.

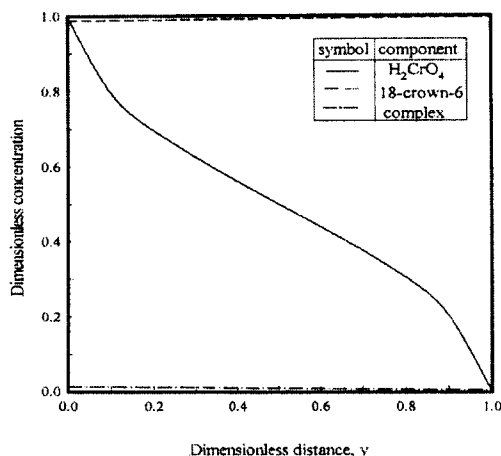


Fig. 7. Dimensionless concentration profile inside liquid membrane. ($[\text{Cr(VI)}] = 50 \text{ ppm}$, $[\text{CE}] = 0.012 \text{ kmol/m}^3$)

To investigate the effect of the carrier on the facilitation of Cr(VI), the concentration of Cr(VI) in the feed side were measured after by the 18-crown-6 concentration were varied from 0 to 0.036 kmol/m^3 . The results are presented in Fig. 8, which shows the facilitated factor against the 18-crown-6 concentration. Facilitated factor increased as the concentration of carrier was increased. The solid line represents the computed values of the facilitated factor that were obtained from the slope of dimensionless concentration profile of component A at $y=0$. As shown in the figure, the calculated values were in a reasonable agreement with the experimental ones.

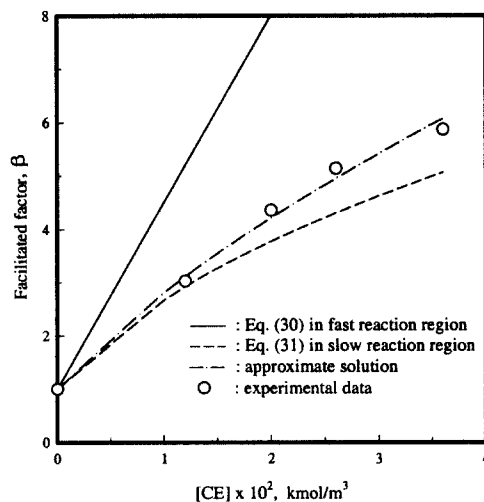


Fig. 8. Effect of concentration of carrier on facilitated factor. ($[\text{Cr(VI)}] = 50 \text{ ppm}$)

Reaction region in the mass transfer accompanied by a chemical reaction is usually classified into fast reaction and slow reaction according to its limiting-step[19]. If the 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:

$$D_A \frac{d^2 C_A}{dx^2} + D_{AB} \frac{d^2 C_{AB}}{dx^2} = 0 \quad (29)$$

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

$$\beta_{\text{exp}} = 1 + \frac{D_{AB} K_e C_{BT}}{D_A (1 + K_e C_{A_0})(1 + K_e C_{AL})} \quad (30)$$

where, K_e is the equilibrium reaction constant as k_1/k_2 .

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

$$\beta_{\text{slow}} = - \frac{L \sqrt{c_3} [B_2 \cosh(\sqrt{c_3} L) + B_1 \sinh(\sqrt{c_3} L)]}{c_1 (C_{AB} - C_{AL})} \quad (31)$$

where, $\overline{C_{AB}} = k_1 C_{BT} (C_{AB} + C_{AL}) / [2k_2 + k_1 (C_{AB} + C_{AL})]$
 ; $\overline{C_B} = C_{BT} - \overline{C_{AB}}$; $c_1 = k_1 \overline{C_B}$; $c_2 = k_2 \overline{C_B}$;
 $c_3 = c_1 / D_A$; $B_1 = c_1 C_{A_0} - c_2$ and $B_2 = [c_1 C_{AL} - c_2 - B_1 \cosh(\sqrt{c_3} L)] / \sinh(\sqrt{c_3} L)$.

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 18-crown-6 is classified into a slow reaction region due to the small change of concentration of the carrier and complex concentrations (Fig. 7).

5. Conclusions

In this work, we investigated the transport of Cr(VI) from aqueous solution of pH 3 through a SLM containing 18-crown-6 dissolved in toluene as a mobile carrier in the $0.012 \text{ kmol/m}^3 \leq 18\text{-crown-6} \leq 0.036 \text{ kmol/m}^3$

and $20 \text{ g/m}^3 \leq \text{Cr(VI)} \leq 500 \text{ g/m}^3$.

The facilitated factor of Cr(VI) transport were obtained as ratio 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 constants in the second-order reversible reaction of Cr(VI) and 18-crown-6 using a batch reactor were obtained experimentally by the integral method. Their values were $645 \text{ m}^3/\text{kmol s}$ and $0.61/\text{s}$, respectively, which were used to simulate the simple model ($\text{H}_2\text{CrO}_4 + 18\text{-crown-6} \rightleftharpoons \text{complex}$) with the mass conservation equation and associated boundary condition.

Based on the comparison between the experimental and simulated facilitated factors of Cr(VI) transport, the reaction between Cr(VI) and 18-crown-6 was classified into the slow reaction region.

Acknowledgements : This work was supported by the Basic Research Program of the Korea Science and Engineering Foundation through the Applied Rheology Center (ARC), Busan Brain 21, and the Research Fund of Pusan National University.

Nomenclature

- A : Cr(VI)
- AB : complex
- a : C_A/C_{A_0}
- B : 18-crown-6
- B_1 : $c_1 C_{A_0} - c_2$ ($\text{kmol/m}^3 \text{ s}$)
- B_2 : $[c_1 C_{AL} - c_2 - B_1 \cosh(\sqrt{c_3} L)] / \sinh(\sqrt{c_3} L)$ ($\text{kmol/m}^3 \text{ s}$)
- b : C_B/C_{BT}
- C_i : concentration of component i (kmol/m^3)

- \overline{C}_{AB} : $k_1 C_{BT}(C_{AB}+C_{AL})/[2k_2+k_1(C_{A0}+C_{AL})]$
 (kmol/m³)
- \overline{C}_B : $C_{BT} \overline{C}_{AB}$ (kmol/m³) C_B/C_{BT}
- c : C_{AB}/C_{BT}
- c_1 : $k_1 \overline{C}_B$ (1/s)
- c_2 : $k_2 \overline{C}_B$ (kmol/m³ s)
- c_3 : c_1/D_A (1/m²)
- D_i : diffusivity of component i (m²/s)
- K : overall mass transfer coefficient
 (m/s)
- K_1 : $[H^+][HCrO_4^-]/[H_2CrO_4]$ (kmol/m³)
- K_2 : $[H^+][CrO_4^{2-}]/[HCrO_4^-]$ (kmol/m³)
- K_3 : $[Cr_2O_7^{2-}]/[HCrO_4^-]^2$ (m³/kmol)
- K_e : k_1/k_2 (m³/kmol)
- K_{eA} : $K_e C_{A0}$
- k_1 : forward reaction rate constant in Eq.
 (13) (m³/kmol s)
- k_2 : backward reaction rate constant in
 Eq. (13) (1/s)
- L : membrane thickness (m)
- CE : 18-crown-6
- q : $D_B C_{BT}/D_A C_{A0}$
- r : D_{AB}/D_B
- S : surface area of the liquid membrane
 (m²)
- t : time (h)
- V : volume of the feed- and stripping
 side (m³)
- x : distance (m)
- y : x/L

Greek symbols

- b : facilitated factor defined by Eq. (26)
- d : $L(k_1 C_{BT}/D_A)^{1/2}$
- e : porosity of the membrane
- t : tortuosity of the membrane

Subscripts

- A : Cr(VI)
- AB : complex
- B : 18-crown-6
- exp : experimental data
- f : feed side
- $fast$: fast reaction
- L : stripping side boundary
- o : feed side boundar
- S : stripping side
- $slow$: slow reaction
- f : initial concentration

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