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Rate-Controlling Mechanism of Cobalt Transport through Supported Liquid Membranes Containing Di(2-ethylhexyl)phosphoric Acid

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ABSTRACT

In this paper the permeation process of trace cobalt(II) through supported liquid membranes using di(2-ethylhexyl)phosphoric acid as a mobile carrier was modeled and the rate-controlling mechanism was examined. The permeation rate equations were derived considering diffusion of metal ions across the aqueous stagnant layers toward the membrane, chemical reaction at the feed–membrane interface, and diffusion of extractant and its metal complex in the membrane phase. The application of the measured permeation rates for determining the kinetic parameters of the solvent extraction reaction was also investigated. It was found that the calculated rates were in good agreement with the measured ones (average standard error, 12%).

INTRODUCTION

A liquid membrane process has recently been proposed as a novel and effective method for the selective separation and concentration of various species from dilute solutions, such as metal ions, weak acids and bases, hydrocarbons or biologically important compounds, and gaseous mixtures (1–3). The so-called "uphill transport" or "pumping effect" in particular has received much attention as a possible alternative to solvent extraction of metal ions.

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Supported liquid membranes (SLMs), which use a porous membrane support impregnated with complexing carriers to separate the feed and strip phases, represent one of the feasible types of liquid membranes. They have been applied to study the transport of individual species (1–10) as well as the separation of multicomponent mixtures (1–3, 11, 12).

The permeation of metal species through SLMs is generally considered to be a combination of extraction and stripping processes. The metal extraction chemistry is identical to that found in solvent extraction, but the overall process is governed by kinetic rather than equilibrium parameters, i.e., occurring under nonequilibrium conditions (3). Consequently, the kinetic parameters of solvent extraction reactions can be evaluated from the measured permeation rates through SLMs as long as a suitable permeation model is available.

Di(2-ethylhexyl)phosphoric acid (D2EHPA, HR) has been widely used to extract and separate a number of metals such as Cu(II), Co(II), Ni(II), and Zn(II), as well as Fe(III), In(III), Y(III), Zr(IV), and U(VI), in a wide range of operating conditions due to its chemical stability, high selectivity for metal species, and extremely low aqueous solubility (13–21). As has been stated in previous kinetic studies of solvent extraction (14–19), the extraction process for some divalent metals such as Cu(II), Co(II), and Zn(II) by D2EHPA is not wholly controlled by the complex formation reaction at the aqueous–organic interface, but more or less by diffusion of the metal complex in the organic stagnant layer, or by diffusion of metal ions in the aqueous stagnant layer, or by a combination of these steps. For example, Brisk and McManamey (14) studied the extraction kinetics of Cu(II) and Co(II) by an equilibrium extraction technique. They found the interfacial reaction resistance is between 30 and 75% of the total mass transfer resistance. Ihm et al. (15) also indicated that the resistance of interfacial reaction is less than 50% of the total resistance for the extraction of Cu(II) from nitrate solution. The remainder of the resistance is ascribed to diffusion near the interface. However, Komasawa and Otake (16) found that the rates of extraction of Cu(II), Co(II), and Ni(II) from nitrate solutions are entirely controlled by the interfacial chemical reaction. Accordingly, it would be difficult and questionable to directly determine the rate constants of complex formation between metal ions and D2EHPA only from the kinetic results of solvent extraction.

The transport of Co(II) ions through SLMs containing D2EHPA has been frequently examined (8–11). However, less work has been done on elucidating the nature of complex formation at the feed–membrane interface (8). Furthermore, most authors have assumed that contributions due to interfacial chemical reaction or aqueous film diffusion are negligible (4, 9). In this paper the permeation rates of Co(II) ions through SLM containing D2EHPA were measured, and the rate-controlling steps during the permeation process were quantitatively identified. In addition, the application of the measured rates for determining the kinetic parameters of solvent extraction reactions was investigated.

MODELING OF THE PERMEATION RATES

Extraction Chemistry

The reaction stoichiometry of divalent metals extraction with D2EHPA has been extensively studied (15–21). The extraction equilibrium of Co(II) at relatively low organic loading can be represented by the following reaction:

$$Co^{2+} + 2\overline{(HR)_2} \rightleftharpoons \overline{CoR_2(HR)_2} + 2H^+ \tag{1}$$

Also, the extraction equilibrium constant K_{ex} is given by

$$K_{ex} = [\overline{CoR_2(HR)_2}][H^+]^2/\{[Co^{2+}][\overline{(HR)_2}]^2\} \tag{2}$$

where $[\overline{(HR)_2}]$ represents the dimer concentration of D2EHPA in the organic phase. The value of K_{ex} is found to be 3.02×10^{-5} in the extraction of Co(II) from 5×10^1 mol/m^3 Na_2SO_4 aqueous media with kerosene solutions of D2EHPA (20).

It is worth noting that, based on equilibrium studies of Co(II) extraction with *n*-heptane solutions of D2EHPA at 25°C, the stoichiometry expressed by Eq. (1) is applicable only over a range of loading ratio, defined as $[\overline{CoR_2(HR)_2}]/[\overline{(HR)_2}]_0$, less than 0.12 (21).

Based on the fact that the kinetic data of solvent extraction cannot be explained by an interfacial reaction mechanism but are successfully modeled by an interfacial diffusion with an aqueous reaction mechanism, Dreisinger and Cooper (19) proposed that complex formation between Co(II) ions and D2EHPA probably occurs in the aqueous layer adjacent to the organic–aqueous interface. From the nature of D2EHPA, such as its interfacial activity and extremely low aqueous solubility, however, most researchers have indicated that the formation of metal–D2EHPA complexes is very likely to be interfacial (14–18).

As has been justified by Miyake et al. (18), complex formation between Cu(II) ions and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, another well-known organophosphorus compound, proceeds mainly at the aqueous–organic interface. This conclusion was reached based on comparison of the resistance of the chemical reaction at the interface to that in the aqueous stagnant layer if the chemical reactions in the aqueous phase and at the aqueous–organic interface obey Eigen's mechanism (18, 22). Consequently, the rate for the formation of the Co(II)–D2EHPA complex at the interface, J_f, can be expressed as

$$J_f = k_1[\mathrm{Co}^{2+}][\overline{(\mathrm{HR})_2}]^{1/2} - k_{-1}[\overline{\mathrm{CoR}_2(\mathrm{HR})_2}][\mathrm{H}^+]^2[\overline{(\mathrm{HR})_2}]^{-3/2}, \qquad K_{\mathrm{ex}} = k_1/k_{-1} \tag{3}$$

where k_1 and k_{-1} are the forward and backward reaction rate constants, respectively, for the extraction reaction of Eq. (1).

Permeation Model in SLMs

The concentration profile of each species through SLMs using D2EHPA as a mobile carrier is illustrated in Fig. 1. In the present permeation model, the following steps are taken into account: 1) diffusion of Co(II) ions across the aqueous stagnant layer of feed solution, 2) chemical reaction between Co(II) ions and D2EHPA at the feed–membrane interface, and 3) diffusion of D2EHPA (dimer) and its Co(II) complex in the membrane phase. The permeation rates of these steps are:

1. Diffusion of Co(II) ions in the feed solution toward the membrane:

$$J_1 = k_{\mathrm{Co}}([\mathrm{Co}^{2+}]_f - [\mathrm{Co}^{2+}]_{f,i}) \tag{4}$$

2. Forward interfacial reaction at the feed–membrane interface:

$$J_2 = J_f = k_1([\mathrm{Co}^{2+}]_{f,i}[\overline{(\mathrm{HR})_2}]_{f,i}^{1/2} - K_{\mathrm{ex}}^{-1}[\overline{\mathrm{CoR}_2(\mathrm{HR})_2}]_{f,i}[\mathrm{H}^+]_{f,i}^2[\overline{(\mathrm{HR})_2}]_{f,i}^{-3/2}) \tag{5}$$

3–4. Diffusion of the complex and carrier through the liquid membrane:

$$J_3 = k_{\overline{\mathrm{CoR}_2(\mathrm{HR})_2}}([\overline{\mathrm{CoR}_2(\mathrm{HR})_2}]_{f,i} - [\overline{\mathrm{CoR}_2(\mathrm{HR})_2}]_{s,i}) \tag{6}$$

$$J_4 = k_{\overline{(\mathrm{HR})_2}}([\overline{(\mathrm{HR})_2}]_{s,i}) - ([\overline{(\mathrm{HR})_2}]_{f,i}) \tag{7}$$

In the description of the permeation process, the following assumptions were made: 1) interfacial reaction resistance between H^+ ions and $\overline{\mathrm{CoR}_2(\mathrm{HR})_2}$ at the strip side of the membrane phase was ignored, 2) resistances of the diffusion of Co^{2+} ions in the strip stagnant layer and those of H^+ ions in both aqueous stagnant layers were also neglected, and 3) the diffusion processes could be described by Fick's diffusion equations. In addition, in the membrane phase it is assumed that free D2EHPA exists as dimers due to intermolecular hydrogen bonding, especially in the low polar or nonpolar diluents like kerosene (20).

At steady state the following equality holds:

$$J_1 = J_2 = J_3 = J_{\mathrm{Co}} \tag{8}$$

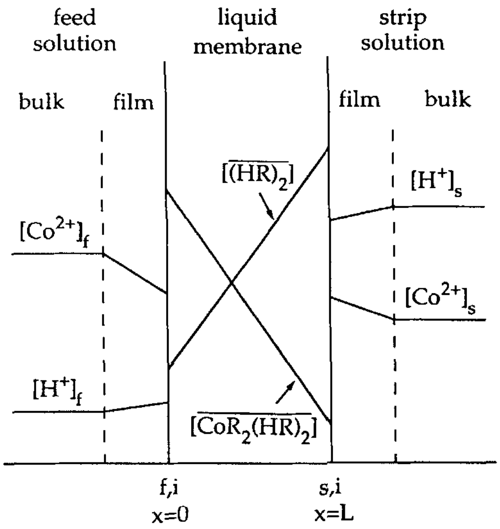

FIG. 1 Concentration profile of each species through SLMs containing D2EHPA as a mobile carrier.

In addition, because counterdiffusion does occur in the membrane phase, the continuity of the total flux of D2EHPA is expressed by

$$J_3 = (1/2)J_4 \tag{9}$$

The solubility of D2EHPA in acidic aqueous solution is considered to be negligibly small (15–21), so the total amounts of D2EHPA in the membrane phase is kept constant:

$$[\overline{(HR)_2}]_0 = (1/L)\int_0^L \{[\overline{(HR)_2}] + 2\,[\overline{CoR_2(HR)_2}]\}\,dx \tag{10}$$

If a linear concentration profile of each species present in the membrane phase is established, Eq. (10) becomes

$$[\overline{(HR)_2}]_0 = (1/2)\{[\overline{(HR)_2}]_{f,i} + [\overline{(HR)_2}]_{s,i}\} + [\overline{CoR_2(HR)_2}]_{f,i} + [\overline{CoR_2(HR)_2}]_{s,i} \tag{11}$$

Because of the relatively high concentration of H^+ ions in the strip solution, the concentration of $\overline{CoR_2(HR)_2}$ at the strip side interface of the membrane, $[\overline{CoR_2(HR)_2}]_{s,i}$, is neglected for simplicity compared to that at the feed side interface, at least at the early stage of the permeation process (7, 10, 20).

Now, substituting Eqs. (4) and (6) into Eq. (5), we obtain

$$J_{\mathrm{Co}} = k_1\{([\mathrm{Co}^{2+}]_f - J_{\mathrm{Co}}/k_{\mathrm{Co}})[\overline{(\mathrm{HR})_2}]_{f,i}^{1/2} - K_{\mathrm{ex}}^{-1}(J_{\mathrm{Co}}/k_{\overline{\mathrm{CoR_2(HR)_2}}})[\mathrm{H}^+]_f^2[\overline{(\mathrm{HR})_2}]_{f,i}^{-3/2}\} \tag{12}$$

Moreover, by substituting Eq. (9) into Eq. (11) we have

$$[\overline{(\mathrm{HR})_2}]_{f,i} = [\overline{(\mathrm{HR})_2}]_0 - (1/k_{\overline{(\mathrm{HR})_2}} + 1/k_{\overline{\mathrm{CoR_2(HR)_2}}})J_{\mathrm{Co}} \tag{13}$$

Provided that the mass transfer coefficients are obtained, it is possible to calculate k_1 from Eqs. (12) and (13) from the measured permeation data. Furthermore, the physical meaning of Eq. (12) can be understood more clearly if it is rewritten as follows:

$$J_{\mathrm{Co}} = \frac{[\mathrm{Co}^{2+}]_f}{(1/k_{\mathrm{Co}}) + (1/k_1)[\overline{(\mathrm{HR})_2}]_{f,i}^{-1/2} + (1/k_{\overline{\mathrm{CoR_2(HR)_2}}}K_{\mathrm{ex}})[\mathrm{H}^+]_f^{-2}[\overline{(\mathrm{HR})_2}]_{f,i}^2} \tag{14}$$

Once the value of k_1 is known, the permeation rate J_{Co} can be calculated from Eqs. (13) and (14) by the trial-and-error method if the values of $[\mathrm{Co}^{2+}]_f$, $[\mathrm{H}^+]_f$, and $[\overline{(\mathrm{HR})_2}]_0$ are given.

It should be noted that the three terms in sequence in the denominator of the right side by Eq. (14) represent the resistances of aqueous layer diffusion, interfacial chemical reaction, and membrane diffusion. The sum of these three types of resistances denotes the overall resistance to the permeation process. In this work, the ratio of each resistance to the overall resistance, designated as R_a, R_c, and R_m, respectively, can be easily obtained, and hence the rate-controlling steps are quantitatively identified.

EXPERIMENTAL

Apparatus and Membrane

The apparatus used in this study is illustrated in Fig. 2. It consists of two chambers (left A and right B), each of about 2.20 × 10^{-4} m^3, separated by a membrane support of 9.62 × 10^{-4} m^2 area sandwiched between two 2-mm thick Teflon spacers. The two chambers were synchronously stirred at 350 rpm with a Cole–Parmer variable-speed agitator driven by a Master Servodyne system. The entire cell was immersed in a thermostat controlled at 25°C.

A microporous polypropylene membrane, Celgard 2500, made by Celanese Separation Product Co., was used as the solid support. It had a nominal thickness of 25 μm and a typical porosity of 0.59. In this work,

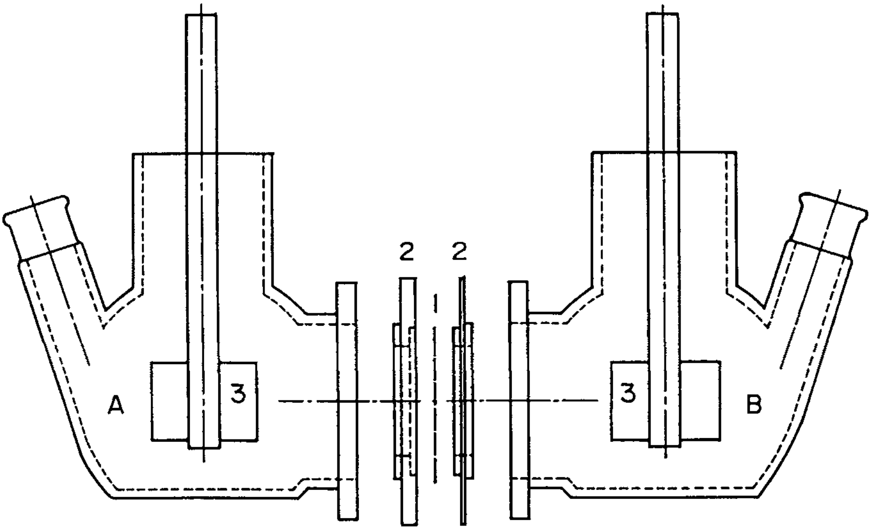

FIG. 2 Permeation cell used in the permeation experiments: (1) supported liquid membrane, (2) Teflon spacer, and (3) stirrer.

the aim of the use of this relatively thin membrane support was to reduce the contribution of resistance due to the membrane diffusion process, and hence it probably increases the extent of resistance due to the interfacial chemical reaction to the overall permeation process (5, 6).

Reagents and Solutions

D2EHPA was the product of Merck Co. and had a purity of about 98.5% as determined by potentiometric titration of an 80 vol% ethanol solution of the acid with 1×10^2 mol/m^3 NaOH in ethanol. It was further purified following a method reported elsewhere (7, 21). The diluent kerosene, from Union Chemical Works Ltd., Hsinchu, Taiwan, was washed twice with 20 vol% H_2SO_4 to remove aromatics and then with distilled water several times. All other inorganic chemicals were supplied by Merck Co. as analytical reagent grade.

The membrane phase was prepared by diluting D2EHPA with kerosene and presaturating two times with the metal-free aqueous phase. The initial concentration of dimeric D2EHPA in the membrane phase ranged from 2×10 to 2×10^2 mol/m^3. The pores in the membrane support were filled with D2EHPA carrier under vacuum as reported previously (7, 10–12), and the resulting liquid membranes were immersed in the membrane phase before use.

The feed phase was prepared by dissolving $CoSO_4$ in distilled water, to which 5×10^1 mol/m^3 Na_2SO_4 was added to maintain the ionic strength constant. The feed pH was adjusted by adding a small amount of acetate buffer solutions. The initial concentration of Co(II) varied from 0.19 to 4.65 mol/m^3, and the feed pH was in the range of 3.45 to 5.94. The strip phase contained about 1×10^3 mol/m^3 H_2SO_4. All aqueous phases were presaturated with kerosene.

Procedure

At the beginning of each run the membrane impregnated with D2EHPA was first clamped, and the apparatus was assembled as shown in Fig. 2. Then the feed and strip solutions were introduced into the left and the right chambers, respectively, and the agitator was immediately started at 350 rpm.

When steady state was reached (about 30 minutes), a sample (1–2 cm^3) was taken from the strip solution at preset intervals and the original strip solution was added to in order to maintain the volume unchanged. The feed pH was measured with a Radiometer pH meter (Model PHM82). The concentration of Co(II) in the sample was analyzed with a Perkin-Elmer atomic absorption spectrophotometer (Model 5100 PC) at a wavelength of 240.7 nm, and corrections due to volume replacement were made. The permeation rate was thus obtained according to

$$J_{Co} = (V_s/A)\{d[Co^{2+}]_s/dt\} \tag{15}$$

RESULTS AND DISCUSSION

Evaluation of the Mass Transfer Coefficients

It has been shown that the value of k_{Co} can be evaluated from permeation data under extreme conditions of low metal concentration, high feed pH, and high carrier concentration when an acidic carrier is employed, and in which the diffusion of metal ions in the feed stagnant layer was rate-controlling (5–7). That is, the resistances of both the interfacial chemical reaction and membrane diffusion are negligible compared to that of aqueous layer diffusion. Consequently, from Eq. (14) we have

$$J_{Co} = k_{Co}[Co^{2+}]_f \tag{16}$$

In this study, the value of k_{Co} was found to be 9.52×10^{-7} m/s at a stirring speed of 350 rpm when $[Co^{2+}]_f = 0.19$ mol/m^3, $[H^+]_f = 1.15 \times 10^{-3}$ mol/m^3, and $[\overline{(HR)_2}]_0 = 8 \times 10^2$ mol/m^3 (not shown). This result roughly agrees with that obtained by Huang and Tsai (12) in SLMs experiments using the same permeation cell.

In fact, the diffusivity of Co(II) ions in the aqueous phase containing 5 × 10^1 mol/m^3 Na_2SO_4 can be estimated to be 6.62 × 10^{-10} m^2/s (23), and a reasonable thickness of the aqueous stagnant layer of about 7 × 10^{-4} m is hence obtained (7, 11, 12).

Moreover, the value of $k_{\overline{CoR_2(HR)_2}}$ was determined from the flux obtained in the experiment by using the diffusion cell where Co(II) was transported from an organic phase loaded with trace Co(II) to the strip phase through the same membrane support as employed in SLMs. Also, the value of $k_{\overline{(HR)_2}}$ was estimated from $k_{\overline{CoR_2(HR)_2}}$ by the relation between the diffusivity and molar volume (24). In this estimation, the diffusivities of D2EHPA dimer ($\overline{(HR)_2}$) and its Co(II) complex ($\overline{CoR_2(HR)_2}$) in the bulk kerosene phase can be evaluated as 7.45 × 10^{-10} and 4.76 × 10^{-10} m^2/s, respectively, at 25°C by the Hayduk and Minhas correlation (24) on the basis of a viscosity of pure kerosene of 1.20 × 10^{-3} Pa·s. Also, the molar volume of D2EHPA dimer at its boiling point is taken to be 810 cm^3/mol by the Schotte method (25), and that of the Co(II)–D2EHPA complex was assumed to be twice that of D2EHPA dimer (18). The parameters obtained and used in this work for the calculation of permeation rates are compiled in Table 1.

Determination of the Reaction Rate Constants

The possibility of the application of permeation data through SLMs for determining the kinetic parameters of solvent extraction reactions was examined. As has been indicated previously (8–10), the permeation of divalent metals, including Co(II) ions, through SLMs containing D2EHPA was predominantly controlled by the diffusion process, possibly through the aqueous stagnant later as well as through the liquid membrane. This

TABLE 1
Values of Parameters Used for the Calculation of Permeation Rates in This Work

Parameter	Co(II)–D2EHPA	Reference
Extraction equilibrium constant:		
K_{ex}	3.02 × 10^{-5}	20
Reaction rate constant:		
k_1	1.69 × 10^{-7} $(m^5/mol\cdot s^2)^{1/2}$	This work
k_{-1}	5.60 × 10^{-3} $(m^5/mol\cdot s^2)^{1/2}$	This work
Mass transfer coefficient:		
k_{Co}	9.52 × 10^{-7} m/s	This work
$k_{\overline{CoR_2(HR)_2}}$	4.63 × 10^{-8} m/s	This work
$k_{\overline{(HR)_2}}$	7.27 × 10^{-8} m/s	This work

means that it is difficult to perform the permeation runs under the extreme conditions in which the interfacial chemical reaction is the unique rate-controlling step, although a relatively thin membrane support was employed in this work.

Accordingly, unlike the determination of the value of k_{Co}, the value of k_l was necessarily evaluated from the permeation data obtained when the role of the interfacial chemical reaction became more important. This corresponds to the conditions of higher pH in the feed solution and lower extractant concentration in the membrane phase (5, 6, 8). Here, the value of k_l was determined to be 1.69×10^{-7} (m^5/mol·s^2)$^{1/2}$ when $[Co^{2+}]_f$ = 1.86 mol/m^3, $[H^+]_f = 1.15 \times 10^{-3}$ mol/m^3, and $[\overline{(HR)_2}]_0 < 4 \times 10^1$ mol/m^3.

The Calculated Permeation Rate and Rate-Controlling Steps

Figures 3–5 show the relationships between the permeation rate of Co(II) and the concentrations of H^+ and Co(II) ions in the feed solution

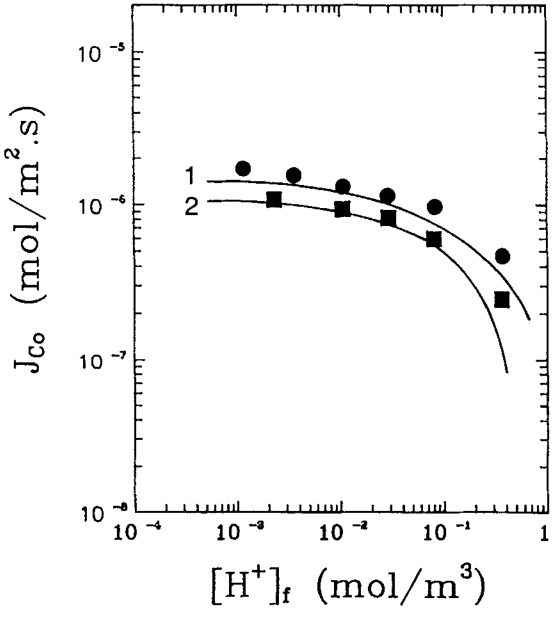

FIG. 3 Effect of hydrogen ion concentration in the feed solution on the permeation rate. The solid curves are calculated by the permeation model. $[Co^{2+}]_f$ = 1.86 mol/m^3, $[\overline{(HR)_2}]_0$ = 2×10^2 (●, Curve 1) and 1×10^2 (■, Curve 2) mol/m^3.

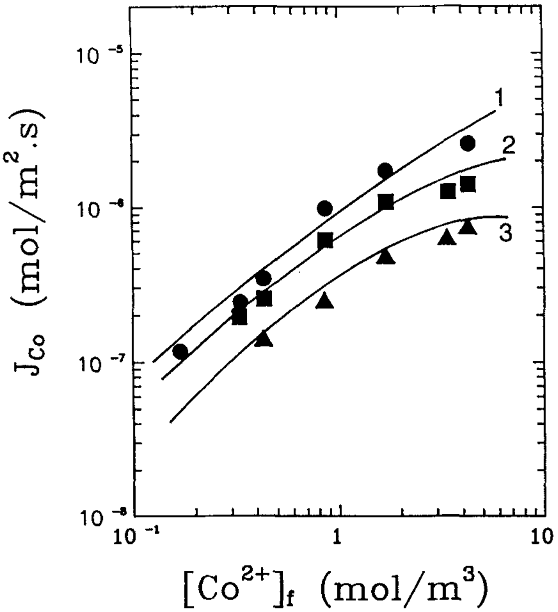

FIG. 4 Effect of Co(II) ion concentration in the feed solution on the permeation rate. The solid curves are calculated by the permeation model. $[H^+]_f = 1.15 \times 10^{-3}$ and $[\overline{(HR)_2}]_0 = 2 \times 10^2$ mol/m^3 (●, Curve 1), $[H^+]_f = 2.29 \times 10^{-3}$ and $[\overline{(HR)_2}]_0 = 1 \times 10^2$ mol/m^3 (■, Curve 2), and $[H^+]_f = 1 \times 10^{-2}$ and $[\overline{(HR)_2}]_0 = 4 \times 10$ mol/m^3 (▲, Curve 3).

and that of D2EHPA in the membrane solution, respectively. The solid curves are calculated by the present permeation model, i.e., from Eqs. (13) and (14), by the trial-and-error method. It is found that the calculated fluxes compare well with the measured values (average standard error, 12%).

It is worth noting that in this calculation $k_{\overline{CoR_2(HR)_2}}$ is found to be the most sensitive parameter, which implicitly implies that the nature of the membrane support, such as the porosity, tortuosity, and thickness, plays an important role on the rate and mechanism of SLMs permeation process.

The values of R_a, R_c, and R_m under various experimental conditions are listed in Table 2. Basically, two data sets (No. 1–5 and 6–9) show the effect of feed pH on these resistance ratios, three data sets (No. 5, 10–12; 13–15; and 16, 17, 20) show the effect of $[Co^{2+}]_f$, and two data sets (No. 4, 9, 18–21; and 2, 7, 22–25) show the effect of $[\overline{(HR)_2}]_0$. As exactly stated above, the role of aqueous layer diffusion becomes more significant under the conditions of low $[Co^{2+}]_f$, high pH_f, and high $[\overline{(HR)_2}]_0$. On the other hand, membrane diffusion becomes rate-controlling at low pH_f and

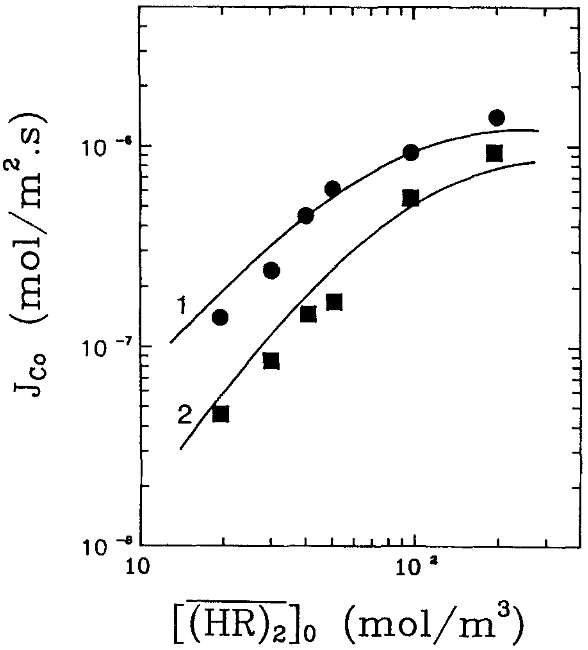

FIG. 5 Effect of initial D2EHPA concentration in the membrane solution on the permeation rate. The solid curves are calculated by the permeation model. $[Co^{2+}]_f = 1.86$ mol/m³, $[H^+]_f = 1 \times 10^{-2}$ (●, Curve 1) and 7.94×10^{-2} (■, Curve 2) mol/m³.

$[\overline{(HR)_2}]_0$, as seen from two data sets (No. 4, 9, 18–21; and 2, 7, 22–25). Under the conditions of trace $[Co^{2+}]_f$ studied, this approximately corresponds to the cases of $pH_f < 4.10$ and $[\overline{(HR)_2}]_0 < 1 \times 10^2$ mol/m³.

However, the value of R_c is surprisingly found to be relatively large under the conditions of high pH_f and low $[\overline{(HR)_2}]_0$. Furthermore, the higher the value of $[Co^{2+}]_f$, the larger the value of R_c, as observed from the data set No. 16, 17, 20. The findings that the contribution of the resistance due to interfacial chemical reaction is not necessarily negligible are different from those observed in previous works (9, 10). This may partially be attributed to the use of a different and relatively thin membrane support in this work, as demonstrated above. It should be noted that Plucinski and Nitsch (6) studied the transport of Zn(II) through SLMs containing dithizone. They found that only for a forward reaction rate constant lower than 4×10^{-7} m/s can the reaction play a role in the permeation mechanism through SLMs, although such a comparison is groundless since the permeation cell geometry and the membrane support used, as well as the related chemical reaction, are different.

TABLE 2
Values of R_a, R_c, and R_m under Various Experimental Conditions

No.	$[\mathrm{Co}^{2+}]_f$ (mol/m^3)	pH$_f$	$[\overline{(\mathrm{HR})_2}]_0$ (mol/m^3)	R_a	R_c	R_m
1	1.86	3.45	200	0.16	0.07	0.77
2	1.86	4.10	200	0.57	0.25	0.18
3	1.86	4.55	200	0.67	0.30	0.03
4	1.86	5.00	200	0.68	0.31	0.01
5	1.86	5.94	200	0.69	0.31	Nil
6	1.86	3.49	100	0.06	0.03	0.91
7	1.86	4.10	100	0.33	0.21	0.46
8	1.86	4.51	100	0.51	0.35	0.14
9	1.86	5.00	100	0.58	0.41	0.01
10	0.19	5.94	200	0.71	0.29	Nil
11	0.93	5.94	200	0.70	0.30	Nil
12	4.65	5.94	200	0.65	0.35	Nil
13	0.47	5.64	100	0.63	0.37	Nil
14	3.72	5.64	100	0.53	0.47	Nil
15	4.65	5.64	100	0.49	0.51	Nil
16	0.93	5.00	40	0.47	0.52	0.01
17	3.72	5.00	40	0.29	0.65	0.06
18	1.86	5.00	20	0.26	0.66	0.08
19	1.86	5.00	30	0.35	0.62	0.03
20	1.86	5.00	40	0.40	0.58	0.02
21	1.86	5.00	50	0.46	0.53	0.01
22	1.86	4.10	20	0.04	0.06	0.90
23	1.86	4.10	30	0.08	0.09	0.83
24	1.86	4.10	40	0.12	0.12	0.76
25	1.86	4.10	50	0.17	0.15	0.68

CONCLUSIONS

The kinetics of the permeation of trace Co(II) from 5×10^1 $\mathrm{Na_2SO_4}$ solutions through SLMs containing D2EHPA have been studied at 30°C. The following results were obtained.

1. The permeation model presented considers the aqueous layer diffusion of Co(II) ions toward the membrane, the chemical reaction between Co(II) ions and D2EHPA at the feed–membrane interface, and the membrane diffusion of D2EHPA and its Co(II) complex. The mass transfer coefficients of Co(II) ions and the Co(II)–D2EHPA complex were also determined using the same permeation cell.
2. The rate-controlling mechanism of the present permeation process was quantitatively examined by comparing the calculated values of R_a, R_c, and R_m as listed in Table 2. In addition, the evaluation of the

kinetic parameters of a solvent extraction reaction would be possible from the permeation data through SLMs as long as the role of interfacial chemical reaction is relatively significant and the mass transfer coefficients for the relevant geometry are known.

NOMENCLATURE

A	effective membrane area (m^2)
$(HR)_2$	dimeric form of D2EHPA
J	permeation flux ($mol/m^2 \cdot s$)
k	mass transfer coefficient (m/s)
k_1	forward reaction rate constant defined in Eq. (3) $(m^5/mol \cdot s^2)^{1/2}$
k_{-1}	backward reaction rate constant defined in Eq. (3) $(m^5/mol \cdot s^2)^{1/2}$
K_{ex}	extraction equilibrium constant
L	membrane thickness (m)
R_a	ratio of the aqueous layer diffusion resistance to the overall resistance
R_c	ratio of the interfacial chemical reaction resistance to the overall resistance
R_m	ratio of the membrane diffusion resistance to the overall resistance
t	time (s)
V	volume (m^3)
x	distance from the feed–membrane interface (m)
$[\ ]$	molar concentration of species in the brackets (mol/m^3)

Subscripts

f, s	feed and strip phases, respectively
i	aqueous–membrane interface
0	initial

Superscript

—	species in the membrane or organic phase

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