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Kinetics of the Transport of Co(II) from Aqueous Sulfate Solution through a Supported Liquid Membrane Containing Di(2-ethylhexyl) Phosphoric Acid in Kerosene

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Abstract

The permeation rate of Co^{2+} from its aqueous sulfate solution through a solid supported liquid membrane containing di(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene as mobile carrier has been studied as a function of hydrodynamic conditions, concentrations of Co^{2+} (0.17–4.25 mol/m^3) and H^+ (pH 3.5–6.0) in the feed solution, carrier concentration (20–400 mol/m^3) in the membrane, and temperature. It has been observed that Co^{2+} flux across the membrane tends to reach a plateau region at a higher concentration of Co(II) or a lower concentration of H^+ due to carrier saturation within the membrane, leading to a diffusion-controlled process. It is also observed that Co^{2+} flux is about second order with respect to dimerized carrier at a lower D2EHPA concentration (< 150 mol/m^3) and exhibits a lower order (0.6–1.0) at a higher concentration of D2EHPA. Necessary kinetic parameters have been derived from the model equations based on the combination of aqueous film diffusion, interfacial chemical reaction, and membrane diffusion. The low activation energy value suggests that the process is predominantly diffusion controlled.

INTRODUCTION

A considerable amount of investigation has been carried out during the last decade on the use of a liquid membrane with a mobile carrier as one of the most promising techniques for the separation of metal ions from their dilute solutions. Of the two main configurations of liquid membranes, the supported liquid membrane (SLM) has some distinct practical advantages over the W/O/W emulsion-type membrane, such as longer stability, more operational simplicity, and lower solvent and energy consumption (*1*, *2*). Consequently, more attention has been paid to the development of this technique, particularly in the field of extractive met-

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allurgy. Several authors (*1–7*) have discussed this aspect in an elaborate manner, and a large number of references have been cited therein.

Di(2-ethylhexyl) phosphoric acid (D2EHPA) is a widely used reagent in the solvent extraction of metals. Kinetics and mechanisms of the extraction of metals with D2EHPA have been extensively investigated (*8*, *9*). Recently, several authors (*10–12*) have reported the separation of Co(II), Ni(II), and Zn(II) using D2EHPA as the carrier in supported liquid membranes. However, their investigations were carried out either from a nitrate or from a chloride medium using a single homogeneous diluent. In the present work an attempt has been made to elucidate the mechanism of transport of Co(II) from a sulfate medium through a solid supported liquid membrane containing D2EHPA in kerosene as the carrier.

THEORETICAL CONSIDERATIONS

Though the pioneering works of Danesi (*2*) and subsequently of Komasawa et al. (*7*) still form the basis of interpretation of permeation data through an SLM, we are of the opinion that these authors have not been very explicit about the nature of chemical reactions at the feed side of the membrane. This is particularly applicable in the case of D2EHPA which occurs as a dimer in long-chain aliphatic hydrocarbons like kerosene. Komasawa et al. (*13*) reported 31 m^3/mol as the dimerization constant (K_2) of D2EHPA in heptane, while Smelov et al. (*14*) reported 50 m^3/mol in octane. Assuming roughly about 70 m^3/mol as K_2 in kerosene, the concentration of monomer is practically negligible (≈ 0.1 mol/m^3) in the total D2EHPA concentration of 200–400 mol/m^3 used in the present work. Due to the high interfacial reactivity of D2EHPA (*15*, *16*), a dimerized molecule undergoes acid dissociation at the feed side of the membrane. The two-stage combination of partially deprotonated dimer with Co^{2+} is probably the slow step controlling the rate of the interfacial chemical reaction. Permeation of a metal ion through SLM involves at least three major rate-controlling processes: aqueous film diffusion, interfacial chemical reaction, and diffusion through membrane. The resistance due to H^+ diffusion on both sides of the membrane and Co^{2+} diffusion from the stripping side of the membrane are assumed to be negligible.

For aqueous-film diffusion the flux is given by

$$J_w = \frac{D_a}{\delta_a}\{[Co^{2+}]_b - [Co^{2+}]_i\} \qquad (1)$$

The rate of formation of the Co–D2EHPA complex at the feed side of the interface may be derived by applying the following set of reactions (similar to those used for the transport of a metal ion through the aqueous–organic interface in a stirred cell). These are

Step I: Combined effects of monomerization, distribution of monomer between aqueous interface and organic medium and acid dissociation of monomer at the interface, all of which are extremely fast.

$$\overline{(HL)_2} \xleftrightarrow{1/K_2} 2\overline{(HL)} \xleftrightarrow{K_d} 2(HL) \xleftrightarrow{K_a} HL_2^- + H^+$$

Step II: Reaction of Co^{2+} at the interface with ionized D2EHPA.

$$Co^2 + HL_2^- \rightleftharpoons CoHL_2^+$$

Step III: Formation of neutral Co(II) species at the interface.

$$Co(HL)_2^+ + 2(\overline{HL}) \rightleftharpoons CoL_2(HL)_2 + H^+$$

Step IV: Dissolution of the neutral species in the organic medium which is a fast process.

$$CoL_2(HL)_2 \rightleftharpoons [\overline{CoL_2(HL)_2}]$$

Obviously either Step II or Step III is a slow process controlling the overall rate of chemical reaction. It is proposed that at a higher concentration of D2EHPA and at higher pH, the interface is largely saturated with $(\overline{HL})_2$. Step II is a slower process compared to Step III. Conversely, at a lower concentration of D2EHPA (and possibly at lower pH), Step III is a slower process compared to Step II. By combining Steps I and II on one hand and Steps III and IV on the other, it can be shown that for the first case

$$R_0 = \frac{k_1[Co^{2+}][(\overline{HL})_2]}{[H^+]} - k_{-1}[\overline{CoL_2(HL)_2}][H^+] \tag{2}$$

Similarly for the second case, it can also be shown that

$$R_0' = \frac{k_1'[Co^{2+}][(\overline{HL})_2]^2}{[H^+]} - k_{-1}'[\overline{CoL_2(HL)_2}][H^+] \tag{3}$$

However, overlapping of the two rate-controlling steps may occur. Since the Co–D2EHPA complex on the stripping side of the membrane is negligibly small, Co(II) flux across the membrane is given by

$$J_m = \frac{D_{mi}}{\delta_0}[\overline{\mathrm{CoL_2(HL)_2}}] \tag{4}$$

The total analytical concentration of D2EHPA (C_t) within the membrane may be represented as

$$C_t = [\overline{\mathrm{(HL)_2}}] + 2[\overline{\mathrm{CoL_2(HL)_2}}] \tag{5}$$

Since at steady state $J_w = R_0 = J_m = J$, the overall flux equation may be split into three limiting cases on the basis of relative resistances ($1/J$) as suggested by Komasawa et al. (7). (a) Aqueous film-diffusion control:

$$J = \frac{D_a}{\delta_a}[\mathrm{Co^{2+}}] \tag{6}$$

(b) Interfacial chemical reaction control:

$$J = \frac{k_1[\mathrm{Co^{2+}}][\overline{\mathrm{(HL)_2}}]}{[\mathrm{H^+}]} \tag{7}$$

Combining Eqs. (4), (5), and (7), we have

$$J = \frac{\beta C_t \dfrac{D_m}{\delta_0}}{2\beta + \dfrac{D_m}{\delta_0}} \tag{8}$$

or

$$J = \frac{k_1'[\mathrm{Co^{2+}}][\overline{\mathrm{(HL)_2}}]^2}{[\mathrm{H^+}]} \tag{9}$$

Combining Eqs. (4), (5), and (9), we have

$$J = \frac{D_m}{\delta_0}\left\{\frac{D_m}{\delta_0\beta} + 4C_t - \frac{D_m}{\delta_0\beta}\sqrt{1 + \frac{8\beta C_t\delta_0}{D_m}}\right\} \tag{10}$$

(c) Membrane diffusion control:

$$J = \frac{D_m}{\delta_0} \frac{K_{ex}^m[Co^{2}][\overline{(HL)_2}]}{[H^+]^2} \tag{11}$$

Combining Eqs. (4), (5), and (11), we have

$$J = \frac{D_m}{\delta_0} \frac{C_t\alpha}{2\alpha + 1} \tag{12}$$

or

$$J = \frac{D_m}{\delta_0} \frac{K_{ex}^m[Co^{2+}][\overline{(HL)_2}]^2}{[H^+]^2} \tag{13}$$

Combining Eqs. (4), (5), and (13), we have

$$J = \frac{D_m}{8\delta_0} \left\{ \frac{1}{\alpha} + 4C_t - \frac{1}{\alpha}\sqrt{1 + 8\alpha C_t} \right\} \tag{14}$$

In the above equations $\beta = k_1[Co^{2+}]/[H^+]$ and $\alpha = K_{ex}^m[Co^{2+}]/[H^+]^2$, where K_{ex}^m is the equilibrium constant within the membrane and is related to that in the bulk of the solution (K_{ex}) as follows: $K_{ex}^m = K_{ex}/\epsilon$, where ϵ = porosity of the membrane under loaded conditions.

EXPERIMENTAL

Reagents

All the inorganic reagents used, such as $CoSO_4{\cdot}6H_2O$, Na_2SO_4, potassium hydrogen phthalate, sodium acetate, and acetic acid, were of analytical grade. Distilled kerosene (b.p. 170–220°C) was used to dilute D2EHPA (K & K, USA; 99% purity) in the concentration range of 8–400 mol/m^3.

Membrane

Microporous polypropylene membrane Celgard 2500, made by Celanese Separation Products USA, was used as the solid support. As per the specifications provided by the supplier, the membrane has a porosity of 0.45 and a thickness of 0.025 mm.

Method

The two half cells, each having a capacity of 100 cm^3, were separated by a membrane with an effective area (geometric area × ϵ) of 12.37 cm^2. The membrane was impregnated under vacuum with D2EHPA dissolved in kerosene and clamped between the two half cells using PVC gaskets. A small quantity of tributyl phosphate was used as the modifier for the organic phase. An H_2SO_4 solution of ~1 *M* was used as the stripping medium. The solutions in both compartments were kept under agitation by using glass stirrers, and the kinetic run began the moment agitation started. The aqueous feed solution consisted of Co(II) concentration in the range of 0.17 to 4.0 mol/m^3, 0.05 *M* Na_2SO_4, and 5 mL of a suitable buffer solution at the desired pH level. One cubic centimeter of solution was withdrawn alternately from each half cell and analyzed for cobalt content by atomic absorption spectrophotometry (AAS) (Varian, Model 1475AA). The total volume of solution in each compartment was kept constant by replenishing with the corresponding solutions. The entire cell was dipped in a thermostatic bath.

Solvent Extraction

To determine the equilibrium constant of extraction, equal volumes of known concentrations of $CoSO_4$ solution in water and D2EHPA in kerosene were taken in a separating funnel and thoroughly shaken for 20 min at 303 K. After equilibration, Co(II) was estimated in the aqueous phase by AAS and its equilibrium pH value was noted.

RESULTS AND DISCUSSION

The following parameters were studied to elucidate the kinetics and mechanism of the transport of Co(II) across a D2EHPA–kerosene liquid membrane: (a) concentration of Co(II), (b) pH of feed solution, (c) concentration of D2EHPA in the membrane phase, and (d) temperature. It was observed that a change in concentration of Co(II) either in the feed or in the strip solution varies linearly with time for a period of at least 8 h. The slope of the resultant straight line gave the rate of extraction from which the flux (J_{Co}) was calculated according to the following relationship

$$J_{Co} = J = \frac{V}{A}\frac{d[\mathrm{Co(II)}]}{dt}\ \mathrm{mol{\cdot}m^{-2}{\cdot}s^{-1}} \qquad (15)$$

where V = volume of solution in each side of the membrane, m^3
A = effective membrane area, m^2

Effect of Stirring Speed

Of the two types of diffusional resistances encountered during the transport of metal ion across a supported liquid membrane, the resistance due to the liquid boundary layer can be very important. Indeed, in many cases of membrane separation the magnitude of boundary layer resistance is comparable to or even greater than the membrane resistance (*17*). Conventionally, the resistance due to the boundary layer is qualitatively estimated from the effect of stirring on the permeation flux of the metal ion. Figure 1 shows that Co(II) flux increases linearly from 100 to 400 rpm and then slowly up to 500 rpm, above which no appreciable increase in Co(II) flux is observed. It may therefore be reasonably concluded that diffusional resistance due to the boundary layer is minimum above 500 rpm for a particular concentration difference $\{[Co^{2+}]_b - [Co^{2+}]_i\}$. At high concentrations of $[Co^{2+}]$ the difference is indistinguishable with respect to $[Co^{2+}]_b$ as the carrier concentration reaches saturation. Therefore, the appearance of a plateau region does not necessarily mean the elimination of the aqueous diffusion layer, although the resistance due to it is minimized. A simple plot of J against a low concentration of Co^{2+} shows a good linear relationship passing through the origin (figure not shown). The slope has a value of 0.67×10^{-6} m/s as the value of D_a/δ_a. All subsequent investigations were therefore carried out at a stirring speed of 500 rpm.

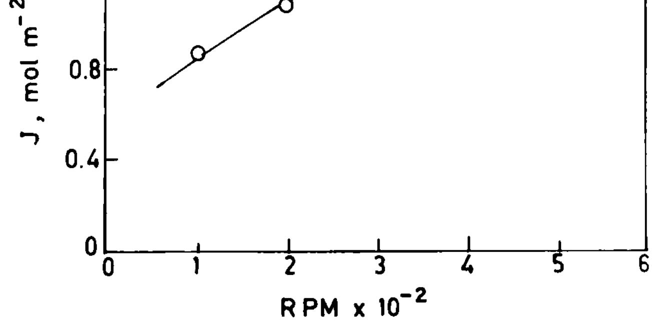

FIG. 1. Variation of J with increase in the stirring rate of solution.

Effect of H^+ Concentration

Figure 2 depicts the log-log plot of J vs $[H^+]$ for the two D2EHPA concentrations 400 and 200 mol/m^3. It may be noted that the slope of the initial linear behavior at lower pH gradually diminishes to zero at a pH higher than 5.5–6.0 depending upon the concentration of D2EHPA in the membrane. The initial linear rise in flux is due to the increased formation of the Co–D2EHPA complex according to the principle of extraction equilibrium. The resultant decrease in the concentration of free D2EHPA is compensated for by the increase in stripping rate which, however, attains a maximum due to the relatively lower diffusion rate of the Co–D2EHPA complex. The low slope values (0.18–0.25) in the initial linear region therefore suggest that the rate is controlled by diffusion of the metal ion either through the aqueous film layer or through the membrane or by a combination of both.

In this connection it is worthwhile to note that no extraction of Co(II) takes place at pH < 3.0. Komasawa and Otake (*18*) suggested that the hydrated metal ion combines with anions of the complexing agent to form an outer-sphere complex which then replaces the coordinated water molecules to form an inner-sphere complex. It is well known that the kinetics of the homogeneous substitution reaction depends mainly on the nature of the metal ion and not much on the nature of the ligand (*8*). At pH <

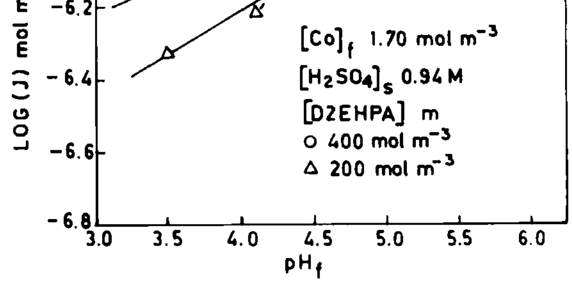

FIG. 2. Change in J with increase in pH of feed solution. The broken line shows the change in flux values calculated from Eq. (8) at a D2EHPA concentration of 400 mol/m^3.

3.0 the hydration energy of cobalt is stronger than that of the Co–D2EHPA complex, thereby preventing the formation of the latter complex.

In order to derive kinetic parameters from the data in Fig. 2, the case of diffusion through the aqueous boundary layer and interfacial chemical reaction were considered. Since the flux values were obtained at a D2EHPA concentration above 200 mol/m^3 (or $[\overline{(HL)_2}] = 100$ mol/m^3), Eqs. (17) and (18) are applicable for this range of concentration of D2EHPA (as shown in the latter sections of this paper). Therefore, combining Eqs. (6) and (7) and rearranging we have

$$\frac{[Co^{2+}]}{J} = \frac{\delta_a}{D_a} + \frac{[H^+]}{k_1[\overline{(HL)_2}]} \tag{16}$$

Figure 3 shows the plot of $[Co^{2+}]/J$ vs $[H^+]$ for the two different concentrations of D2EHPA. The figure demonstrates that a good linear relationship is obtained at pH above 4.10, particularly for a D2EHPA concentration of 200 mol/m^3. From the slopes and intercepts of the two

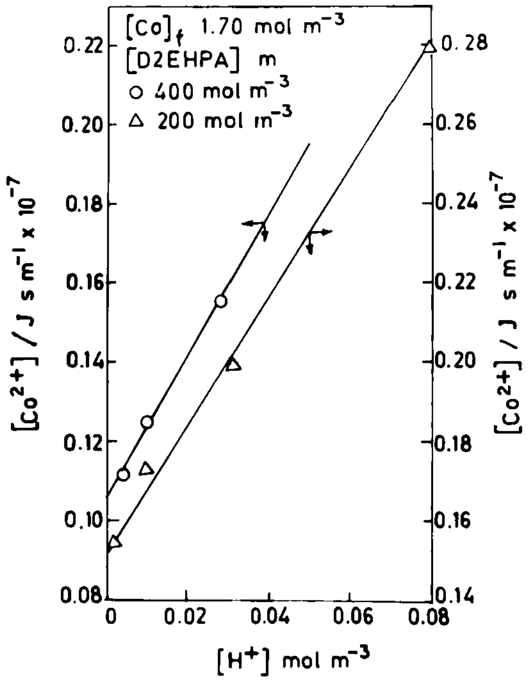

FIG. 3. Plot of $[Co^{2+}]/J$ versus $[H^+]$ according to Eq. (16), using the data in Fig. 2.

TABLE 1
Kinetic Parameters for the Permeation of Co(II) through a Solid Supported D2EHPA–Kerosene Liquid Membrane

	Model				
	Δ_a (s/m)	Δ_0 (s/m)	k_1 ($m^4 \cdot mol^{-1} \cdot s^{-1}$)	K_{ex} (—)	k_{-1} (= k_1/K_{ex}^m) ($m^4 \cdot mol^{-1} \cdot s^{-1}$)
				7.88×10^{-9a}	4.76×10^{-2}
				3.00×10^{-9b}	5.60×10^{-2}
Limit:					
$\log C_f \to \propto$	1.046×10^6				
$\log H^+ \to -\alpha$					
Eq. (6)	1.428×10^6				
Eq. (16)	1.50×10^{6a}		6.25×10^{-10a}		
	1.05×10^{6b}		2.80×10^{-10b}		
Eq. (17)		2.26×10^7			
Eq. (18)	0.945×10^6	2.06×10^7			

[a] Measurement in potassium phthalate buffer.
[b] Measurement in acetate buffer.

straight lines, two different values of k_1 and δ_a/D_a (or Δ_a) are obtained. This suggests that kinetic parameters obtained from the present model are *not unique* in nature but depend upon the experimental conditions. The results are shown in Table 1.

Effect of Co(II) Concentration

Figure 4 illustrates the log-log relationship between the metal flux (J) and the feed concentration of Co(II). A linear relationship is observed for low concentrations of Co(II) with a slope of about unity. However, with an increase in the concentration of Co(II), a gradual decrease in the slope values occurs and finally a limiting plateau region is obtained due to complete saturation of D2EHPA with Co^{2+}. Under this limiting condition the total concentration of $[\overline{(HL)_2}]$ becomes equivalent to $[\overline{CoL_2(HL)_2}]$ and Eq. (11) or Eq. (13) reduces to

$$J_{\text{lim}} = \frac{D_m}{\delta_0} \frac{[\overline{CoL_2(HL)_2}]}{n} = \frac{C_t}{\Delta_0 n} \tag{17}$$

where n is the stoichiometric coefficient of the reaction. This relationship is demonstrated in Fig. 5 where log (J_{lim}) is plotted against log (D2EHPA). The slope of the resulting straight line is 0.82, which is close to unity, and from the intercept more than one value of $1/\Delta_0$ can be obtained depend-

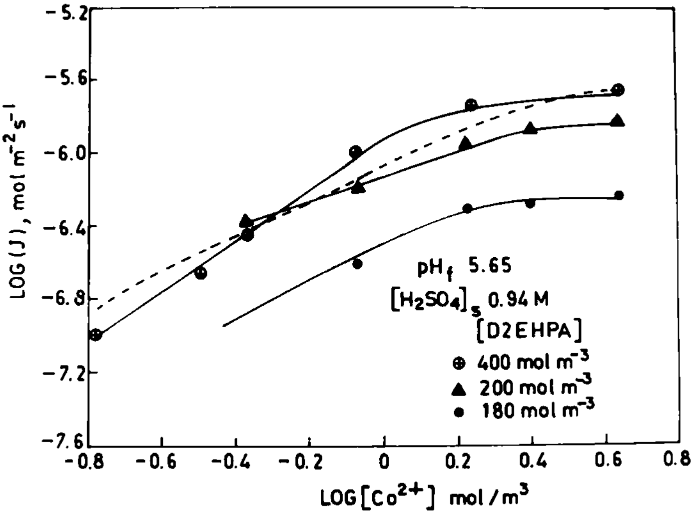

FIG. 4. Log-log plot of J versus feed concentration of Co^{2+}. The broken line shows the flux values calculated from Eq. (6) for a D2EHPA concentration of 400 mol/m^3.

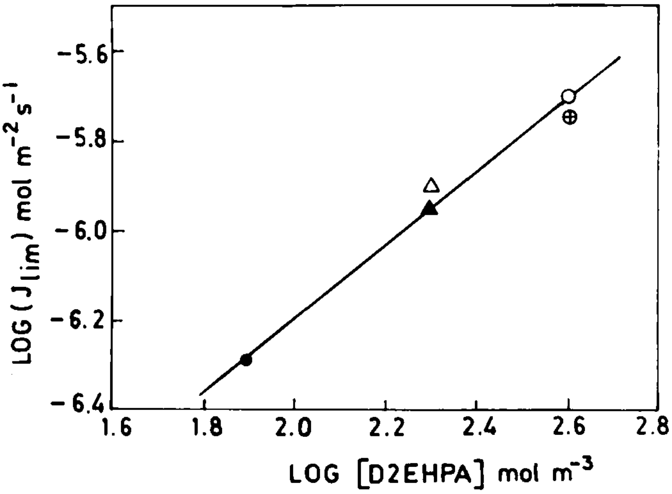

FIG. 5. Relationship between limiting values of J and total monomer concentration. Limiting values of J were obtained from Figs. 2 and 4.

ing upon the stoichiometry of the reaction. If *n* is taken as 2, the value is 3.54×10^{-8} m/s whereas for $n = 2.5$ the value is 4.42×10^{-8} m/s. This aspect is further discussed in dealing with the determination of the equilibrium constant.

Effect of the Concentration of D2EHPA

The effect of the concentration of D2EHPA in its dimeric form $[\overline{(HL)_2}]$ on Co(II) flux is illustrated in Fig. 6 in the form of a log-log relationship. The figure shows that at an $\overline{(HL)_2}$ concentration below 50 mol/m^3 the slope of the linear relationship is 1.8 and above this concentration the slope is 0.65. At a very low concentration of D2EHPA, deviation occurs as the membrane becomes saturated with the Co–D2EHPA complex with the limited availability of free dimer. Similar results were obtained by Komasawa et al. (7) and Imato et al. (6) for the separation of Cu by LIX65N. This shows that the total stoichiometric coefficient with respect to $\overline{(HL)_2}$ is about 2.5 up to the limiting stage of metal flux.

In order to confirm the order of the Co(II) flux rate with respect to $\overline{(HL)_2}$ concentration for a diffusional controlled process, the function of $[Co^{2+}]/J[H^+]$ is plotted against $1/[\overline{(HL)_2}]$ or $1/[\overline{(HL)_2}]^2$ in Fig. 7. It can be seen that a better linear relationship is obtained for the reciprocal of $[\overline{(HL)_2}]$, indicating that the average stoichiometry is 2 and conforming to

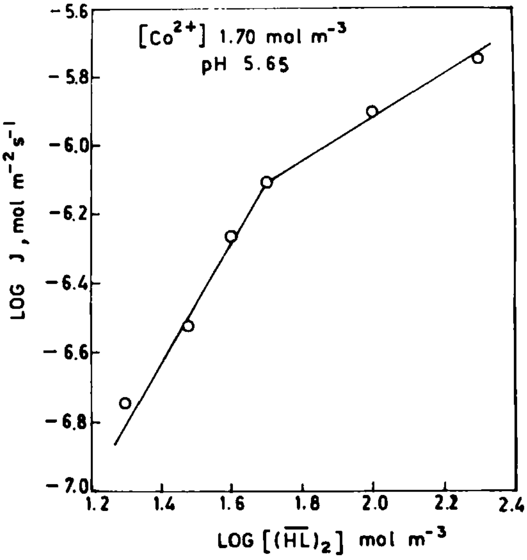

FIG. 6. Log-log relationship between *J* and concentration of dimer.

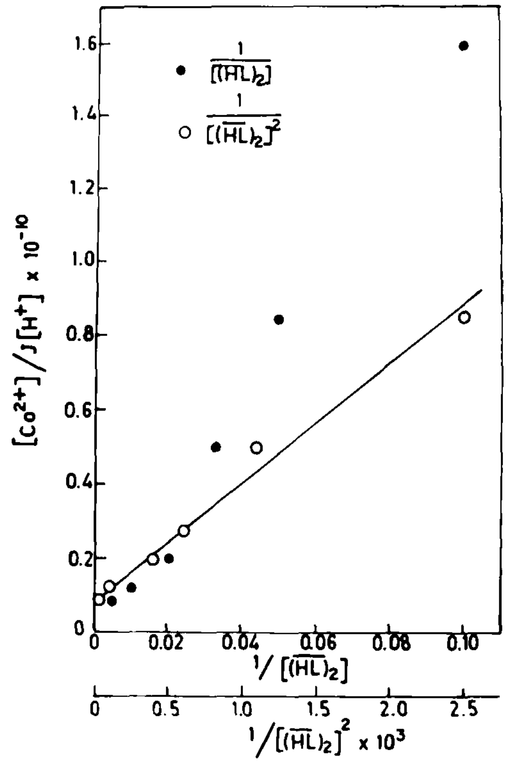

FIG. 7. Plot of $[\mathrm{Co}^{2+}]/J[\mathrm{H}^+]$ versus $1/[\overline{(\mathrm{HL})_2}]$ or $1/[\overline{(\mathrm{HL})_2}]^2$ using the values in Fig. 6. The sharp break in the slope of the initial linear behavior at $1/[\overline{(\mathrm{HL})_2}]$ above 0.02 indicates a sharp change in the kinetic order with respect to $\overline{(\mathrm{HL})_2}$.

the combined Eqs. (6) and (13):

$$\frac{[\mathrm{Co}^{2+}]}{[\mathrm{H}^+]J} = \frac{\Delta_a}{[\mathrm{H}^+]} + \frac{[\mathrm{H}^+]\Delta_0}{K_{\mathrm{cx}}^{m}[\overline{(\mathrm{HL})_2}]^2} \tag{18}$$

From the slope and intercept of this plot, Δ_a and Δ_0 are determined by knowing the equilibrium constant of the reaction which was determined by the solvent extraction method. Figure 8 shows plots of log D against log $\{[\overline{(\mathrm{HL})_2}]/[\mathrm{H}^+]\}$ in both phthalate and acetate buffer media. Extraction is generally lower in phthalate than in acetate medium; as a result, a higher slope value (≈ 3.0) is obtained. In acetate medium the slope value is around 2.6, which is closer to the overall stoichiometric value of 2.5 observed in

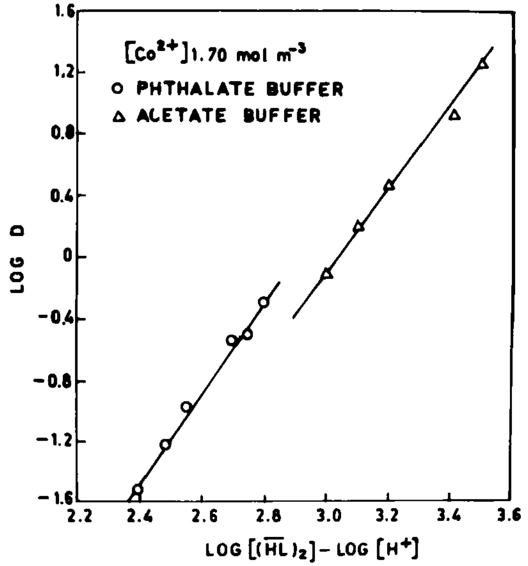

FIG. 8. Log-log plot of the distribution coefficient (D) of Co^{2+} versus $[\overline{(HL)_2}]/[H^+]$ in two types of buffer medium.

Fig. 6. The extraction constant obtained from the intercept in the acetate medium is 7.88×10^{-9}.

Effect of Temperature

The effect of temperature on Co(II) flux through a D2EHPA-kerosene liquid membrane is illustrated in the form of an Arrhenius plot in Fig. 9. An activation energy value of about 23.0 kJ/mol indicates that permeation of Co(II) is predominantly controlled by the diffusion process, possibly through the aqueous film boundary as well as through the membrane. Our general analysis of the data is in agreement with this suggestion. However, very little information is available from the literature on the activation energy of the permeation of a metal ion through an SLM. Consequently, verification could not be carried out.

Kinetic Model

Using the parameters given in Table 1, an attempt was made to fit the flux data to an appropriate model equation. To determine the concentration of organic species in the membrane phase, it is necessary to evaluate the porosity of the membrane under solvent-loaded conditions. This was done

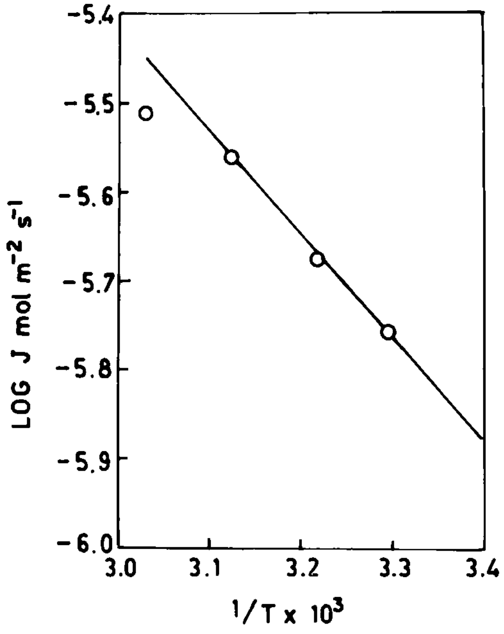

FIG. 9. Arrhenius plot of log *J* versus 1/*T*.

by impregnating a piece of membrane with kerosene under vacuum. The difference in weight between the dry and the wet membrane gives the volume of kerosene (density 0.808 g/cm^3). The ratio between the volume of kerosene adsorbed and the total volume of the membrane (area × thickness) yields a porosity value of 0.60. Imato et al. (*6*) found a similar value (0.57–0.59) for Duragard 2500, which is exactly identical to Celgard 2500 from its adsorption of LIX65N. Thus, the bulk organic concentration of any species gives the corresponding concentration in the membrane phase when multiplied by 0.60. Since most of the permeation experiments were carried out at a D2EHPA concentration at 200 mol/m^3 or higher, either Eq. (6) or Eq. (8) or Eq. (12) or a combination of more than one of these is found to fit most of the data within a reasonable limit of accuracy. Thus, for the variation of Co(II) concentration, the flux is controlled by the aqueous boundary film diffusion. On the other hand, the H$^+$ concentration is controlled predominantly by the interfacial chemical reaction only at pH values above 4.5.

NOMENCLATURE

J	Co(II) flux mol (m^2/s)
k_1, k_1'	forward reaction rate constant (m^4·mol^{-1}·s^{-1})

C_t	total concentration of D2EHPA in membrane
k_{-1}	backward reaction rate constant ($m^4 \cdot mol^{-1} \cdot s^{-1}$)
K_{ex}	equilibrium constant
K_{ex}^m	equilibrium constant in membrane
D_a	diffusion coefficient of cobalt in the aqueous phase (m^2/s)
δ_0	thickness of the membrane (m)
ϵ	porosity of the membrane
t	time (s)
D_m	diffusion coefficient of the cobalt complex in the organic phase (m^2/s)
δ_a	thickness of aqueous diffusion layer (m)
$\overline{(HL)_2}$	dimerized D2EHPA
Δ_a	δ_a / D_a
Δ_0	δ_0 / D_m

Subscripts

b	bulk concentration
i	feed aqueous solution or the species adjacent to the interface between the feed solution and the membrane

Superscript

—	species in organic medium

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