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Transport of Co(II) Ions through Di(2-ethylhexyl) Phosphoric Acid–CCl_4 Supported Liquid Membranes

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Abstract

A liquid membrane transport study of Co(II) using di(2-ethylhexyl) phosphoric acid (D2EPHA) as carrier and CCl_4 as diluent supported on polypropylene microporous film has been carried out. The carrier concentration in the membrane and HCl concentration in the stripping phase have been varied to see the effect on transport of Co(II) ions across the membrane. Maximum flux and permeability values of 1.23×10^{-5} mol · m^{-2} · s^{-1} and 7.66×10^{-11} m^2/s, respectively, at a 0.87 mol/dm^3 carrier concentration in the membrane have been found. At 1 mol/dm^3 HCl concentration in the stripping phase the flux and permeability have maximum values of 1.4 mol · m^{-2} · s^{-1} and 5.27×10^{-11} m^2/s, respectively. The distribution coefficient of Co(II) ions into organic phase has been found to increase with increasing carrier concentration. The diffusion coefficient determined varies from 13.73×10^{-11} to 0.83×10^{-11} m^2/s, which is the reverse order of the values of the distribution coefficient and explains the permeability of the Co(II) D2EPHA complex through the membrane.

1. INTRODUCTION

Liquid membranes, consisting of carrier and diluent supported in microporous films, have been used for the concentration and separation of metal species, and it is an effective device for the extraction of metal ions from solutions. Work has been performed in our laboratories on the transport study of UO_2(II) (*2*, *3*), V(V), Zn(II) and Be(II) (*4*), Zr(IV) (*5*), Hf(IV) (*6*), and Mo(VI) (*7*) by using such membranes. Di(2-ethylhexyl) phosphoric acid (D2EHPA) has been used as a mobile carrier by different

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workers to transport Eu(VI) (*8*), Cu(II), Ni(II), and Co(II) (*9*). The metal ions transport mechanism has been explained in their work under their experimental conditions. They restricted their studies to a lower feed acid concentration and used D2EPHA in heptane and toluene diluent. They did not check the effect of stripping solution acid concentration and the concentration of this carrier in the membrane phase. In the present work CCl_4 has been used as the diluent, and the concentrations of HCl and the carrier were varied in the stripping and membrane phases, respectively, in order to study the effect of these parameters on the flux of Co(II) ions through a liquid membrane. The microporous films used by them had a porosity of 70% and a pore size of the order of 0.45 μm. In the present work the membranes used had a porosity of 38% and a pore diameter of the order of 0.02 μm. The permeability of Co(II) ions through the membrane, the distribution coefficient into the liquid membrane aqueous phase, and the diffusion coefficients have also been determined from the experimental data.

2. EXPERIMENTAL

2.1. Apparatus

2.1.1. Liquid Membrane Cell

The cell was described in Ref. *2*. The two half cells had capacities of 106 cm^3 each with 12.56 cm^2 effective membrane areas.

2.1.2. Membranes

The liquid membrane consisted of D2EPHA, dissolved in CCl_4, supported in polypropylene film from Celanese Corporation USA (trade name Celgard 2400). The film was treated with a carrier solution as explained in Ref. *2*.

2.1.3. Analytical Instruments

A spectrophotometer model UV-120-01 from Shimadzu and a pH meter model 701A digital ion analyzer from Orion Research Co. were used for samples analyses.

2.2. Chemicals and Reagents

2.2.1. Chemicals

Cobalt chloride ($CoCl_2 \cdot 6H_2O$), CCl_4, $CH_3COONa \cdot 3H_2O$, CH_3COOH, and HCl from E. Merck of Extrapure grade or better, D2EPHA, GPR

from BDH, and xylenol orange tetrasodium salts, Pro-analysis grade from E. Merck, were used without further purification for this work. Double distilled deionized water was used for the preparation of all reagents.

2.2.2. *Reagents*

Cobalt and D2EPHA solutions for feed and SLM supported liquid membranes were prepared by dissolving known amounts of salt (0.1% in water) and the carrier (in CCl_4). Xylenol orange solution (0.1%), used for the analysis of Co(II) aqueous solution samples, was prepared by dissolving 0.05 g of this compound in 50 cm^3 of distilled deionized water.

Sodium acetate (0.2 mol/dm^3) was prepared by dissolving 13.61 g of this salt in deionized water in 100 cm^3 of distilled deionized water and adjusting its pH to 6 with a 0.2 mol/dm^3 acetic acid solution.

2.3. Analytical Method

The method was derived from Ref. *16*. A standard calibration line was produced for various known concentrations of a Co(II) solution. 500 μL of the sample solution was added to 1 cm^3 of xylenol orange at pH 6 with 5 cm^3 of acetate buffer solution and diluted with water up to 25 cm^3. The absorbance measured for solutions of known concentration furnished the calibration line, after which the concentration of unknown Co(II) samples was read from the calibration line.

2.4. Flux Measurement

The membrane was fixed in the cell. Feed and strip solutions were placed in the half cells. The solutions in both compartments were stirred continuously at a rate greater than 1500 rpm. All experiments were performed at 33 ± 2°C. Samples of 1 cm^3 volume were taken from the feed solution after definite time intervals and analyzed spectrophotometrically as described above. Different concentrations of HCl were used as the stripping agents. A cobalt solution in distilled water was used as the feed solution.

2.5. Solvent Extraction

Equal volumes of the aqueous cobalt(II) solution and organic solutions were shaken for 15 min in separatory funnels and allowed to stand for 20 min. The aqueous layer was separated from the organic layer and analyzed spectrophotometrically, as described above.

3. RESULTS

The results obtained are given in Figs. 1–5 and Table 1. Figure 1 shows that Co(II) ions can be moved against their concentration gradient. Figure

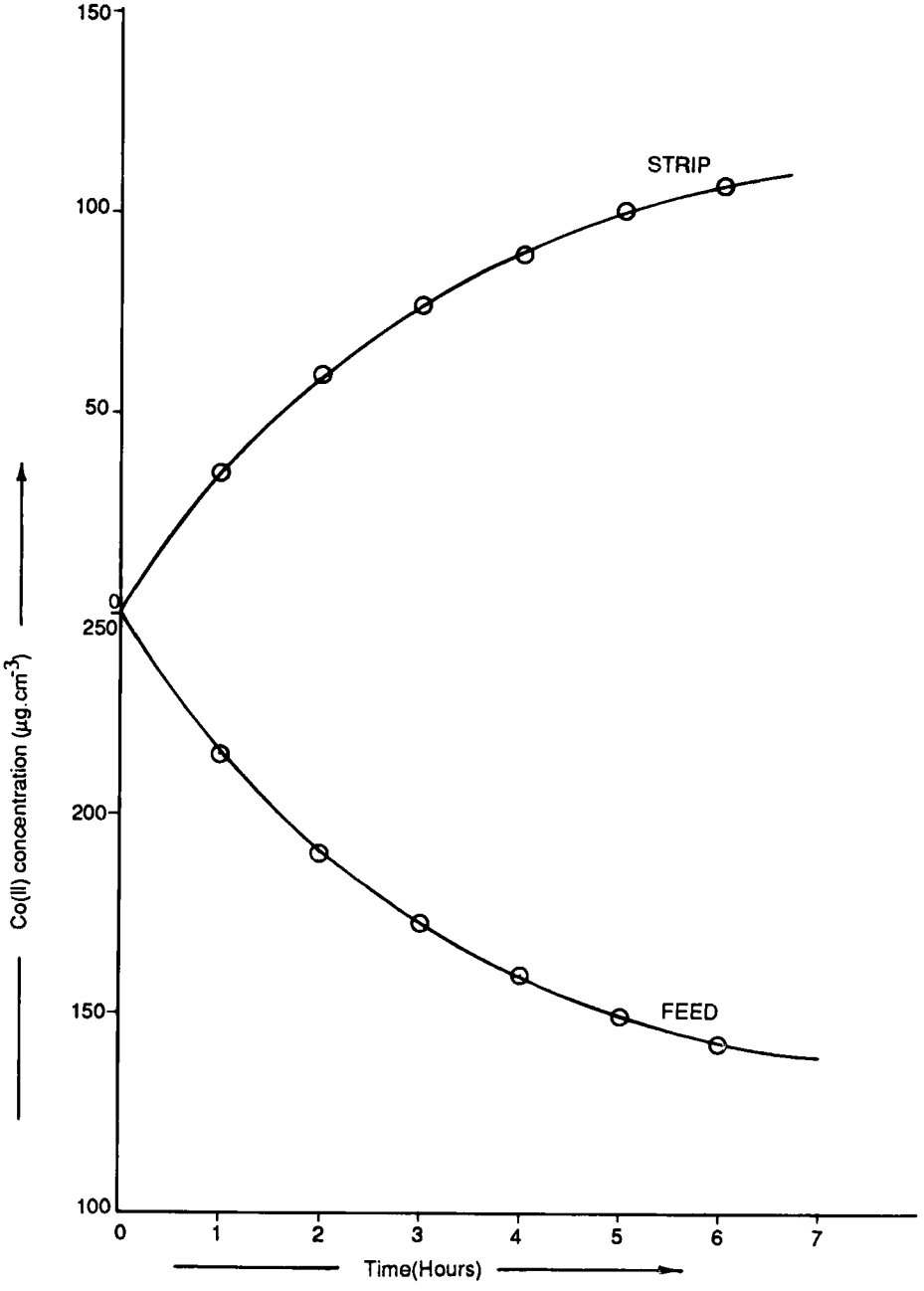

FIG. 1. Co(II) concentration in feed and product solutions as a function of time.

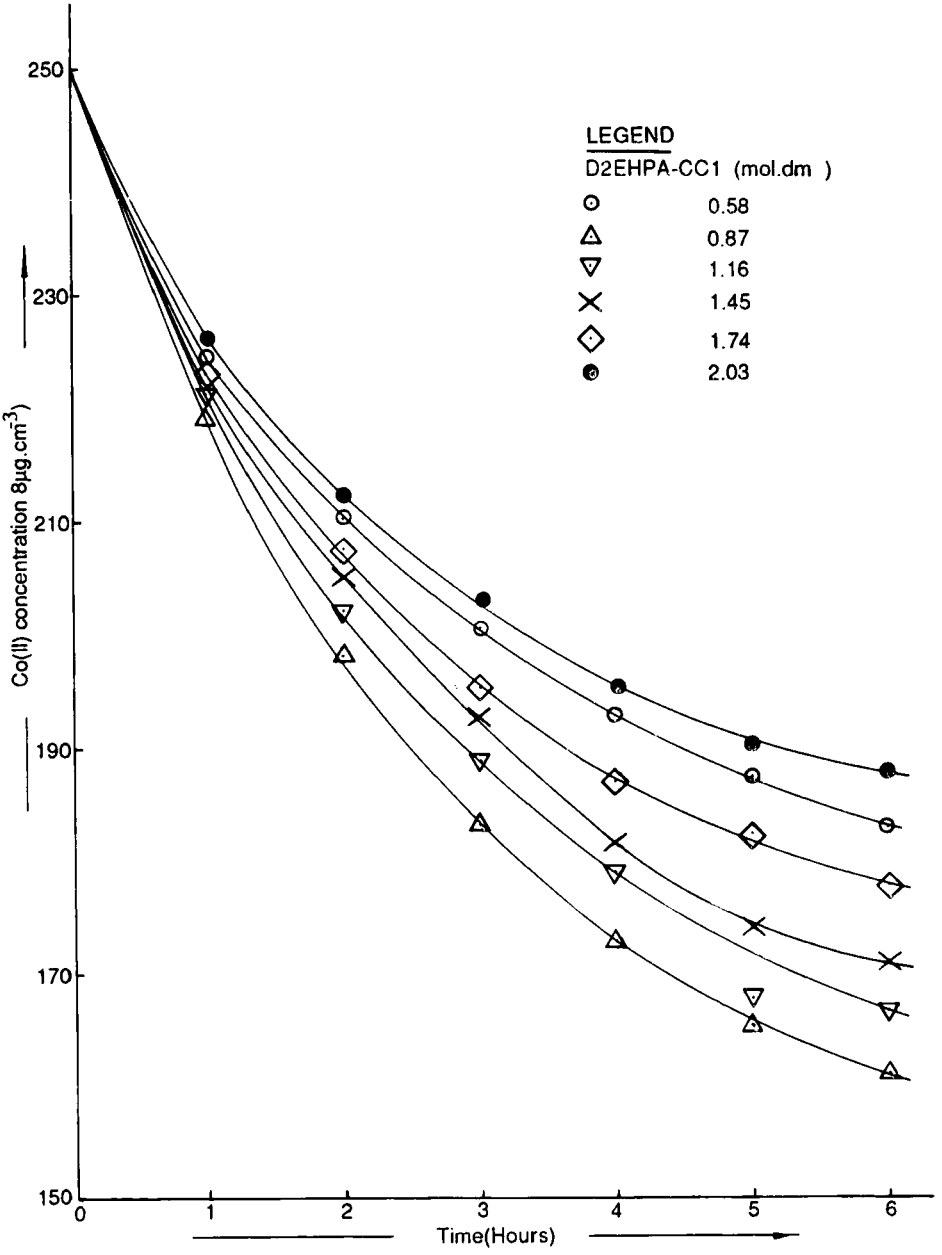

FIG. 2. Plot of Co(II) concentration versus time as a function of D2EHPA concentration in SLM. Feed: 250 μg/cm^3 Co(II), 0.5 *M* HCl.

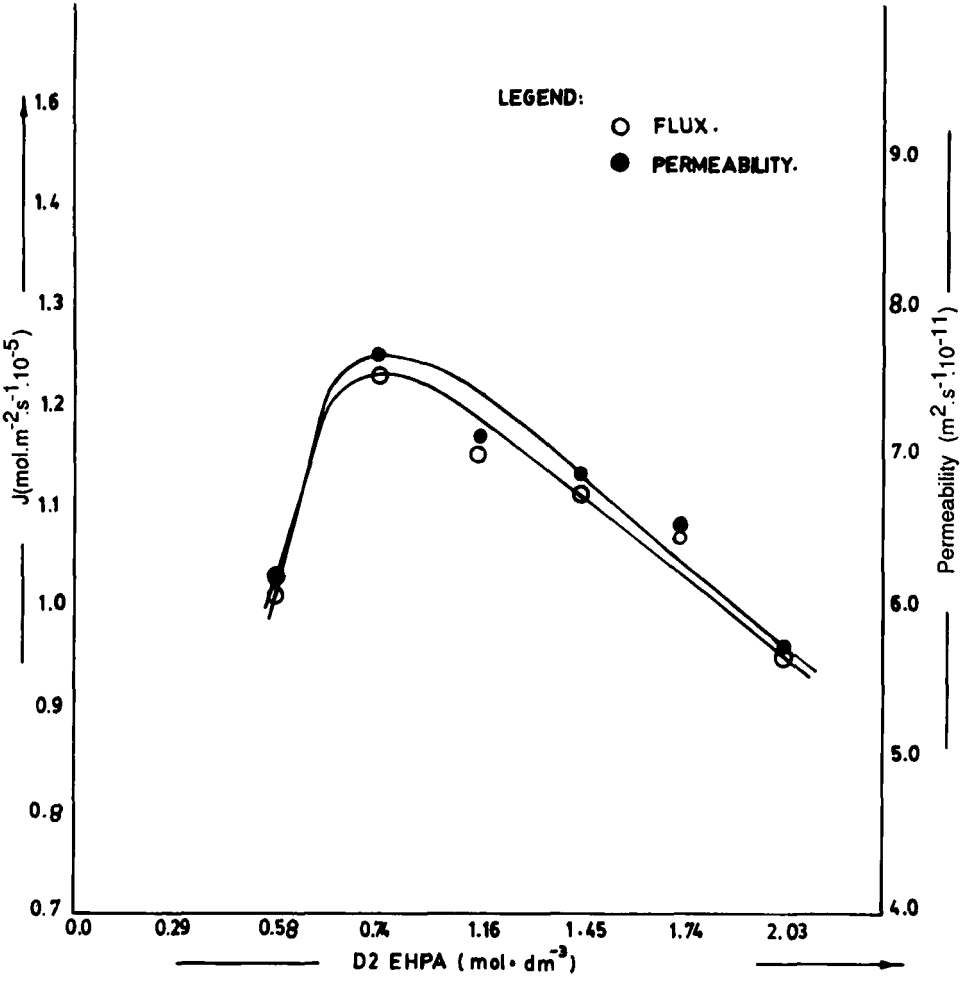

FIG. 3. Plot of Co(II) ions flux (J) and permeability as a function of D2EHPA concentration.

2 depicts the effect of D2EHPA concentration in the membrane on the transport of Co(II) metal ions. Figure 3 shows flux and permeability as a function of carrier concentration. Figure 4 indicates the effect of various concentrations of HCl on the transfer of Co(II) ions across the membrane. Figure 5 presents flux J and permeability P data as a function of HCl concentration in the stripping solution. Figure 6 presents the distribution coefficient (λ) as a function of D2EHPA. Table 1 presents P and D (the diffusion coefficient) as functions of D2EHPA concentration.

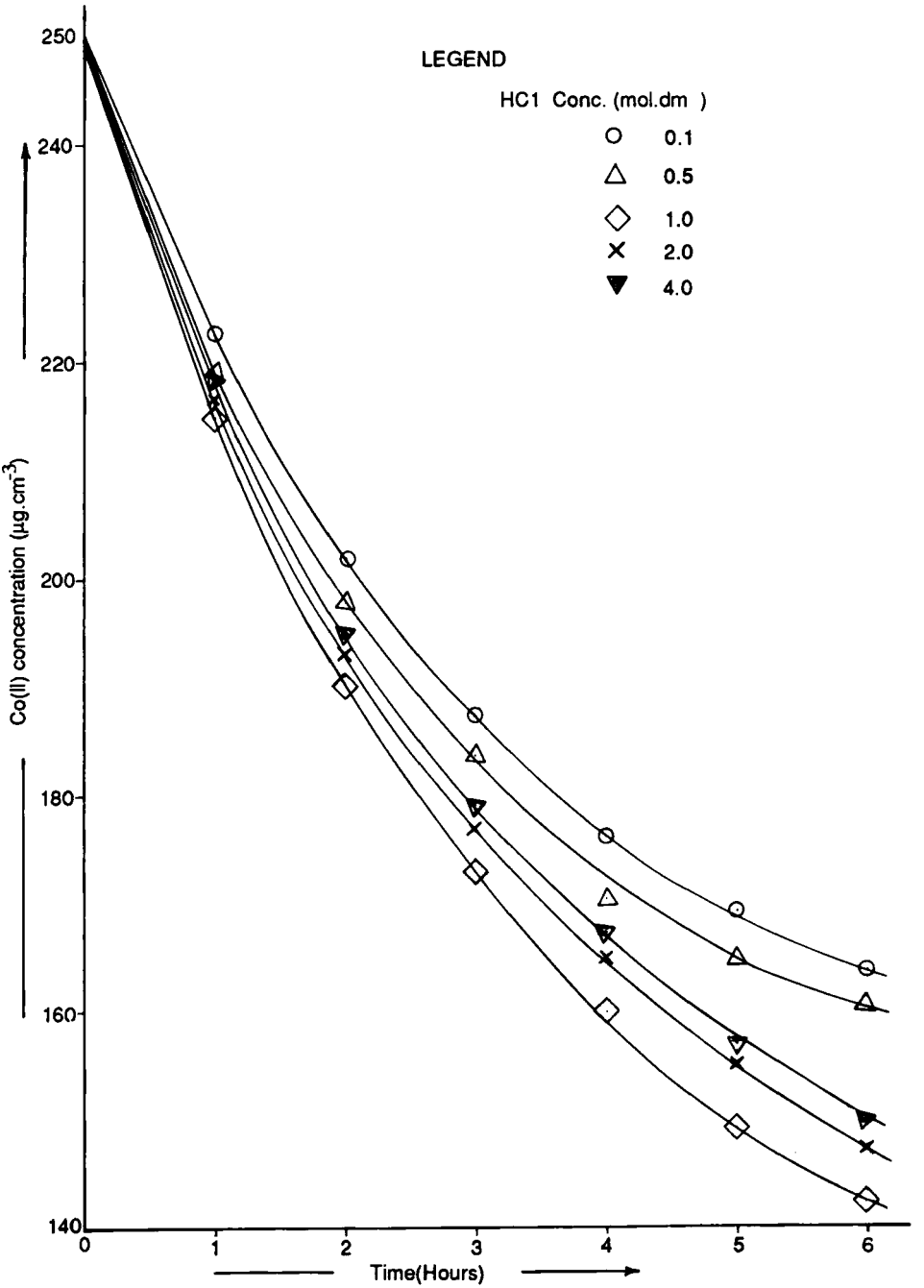

FIG. 4. Plot of Co(II) concentration versus time at various stripping solution HCl concentrations.

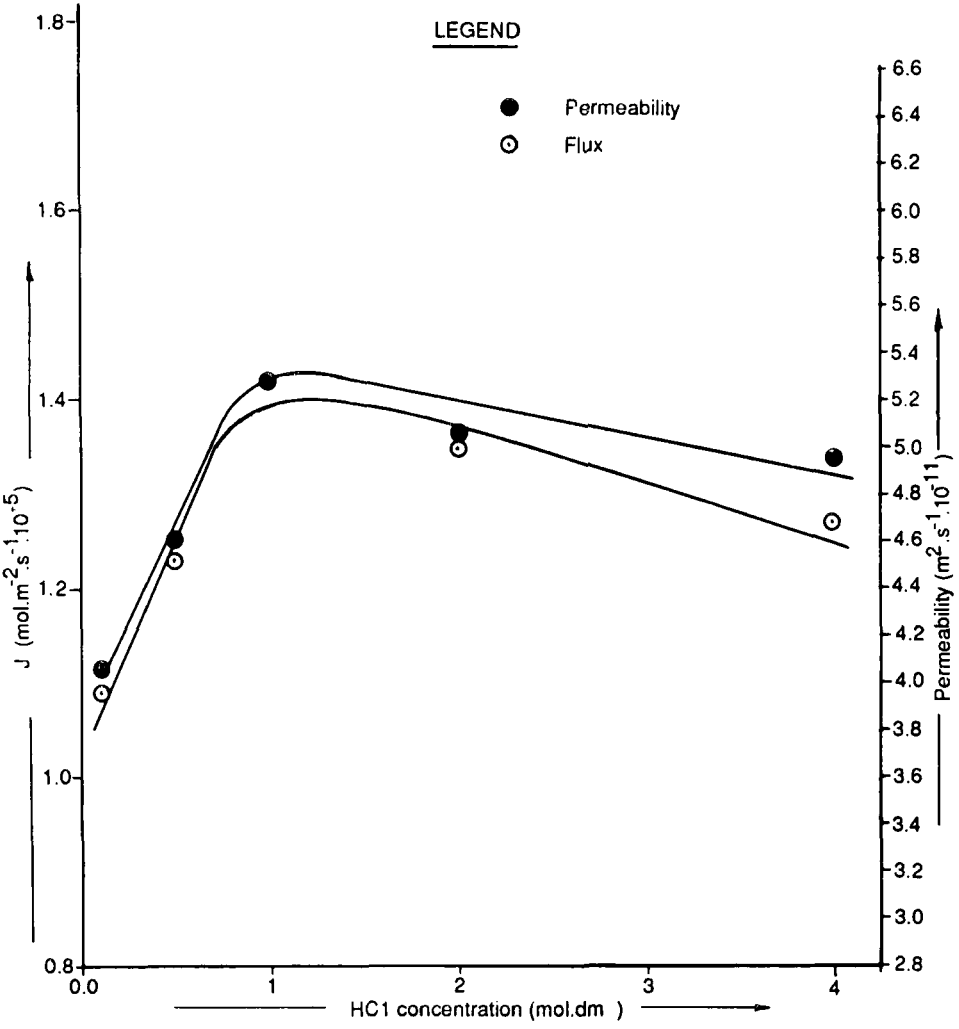

FIG. 5. Plot of flux (J) and permeability as a function of HCl concentration in stripping solution.

4. DISCUSSION

The Co^{2+} ions are extracted into the organic phase after they form a complex with dimeric (*10–15*) D2EHPA through the reaction

$$Co^{2+}_{aq} + 2(HR)_{2\,org} \rightleftharpoons CoR_2(HR)_{2\,org} + 2H^+ \qquad (1)$$

On the stripping side this complex may break to release the $(HR)_2$ carrier dimeric species by reversing Reaction (1). The subscripts "aq" and "org"

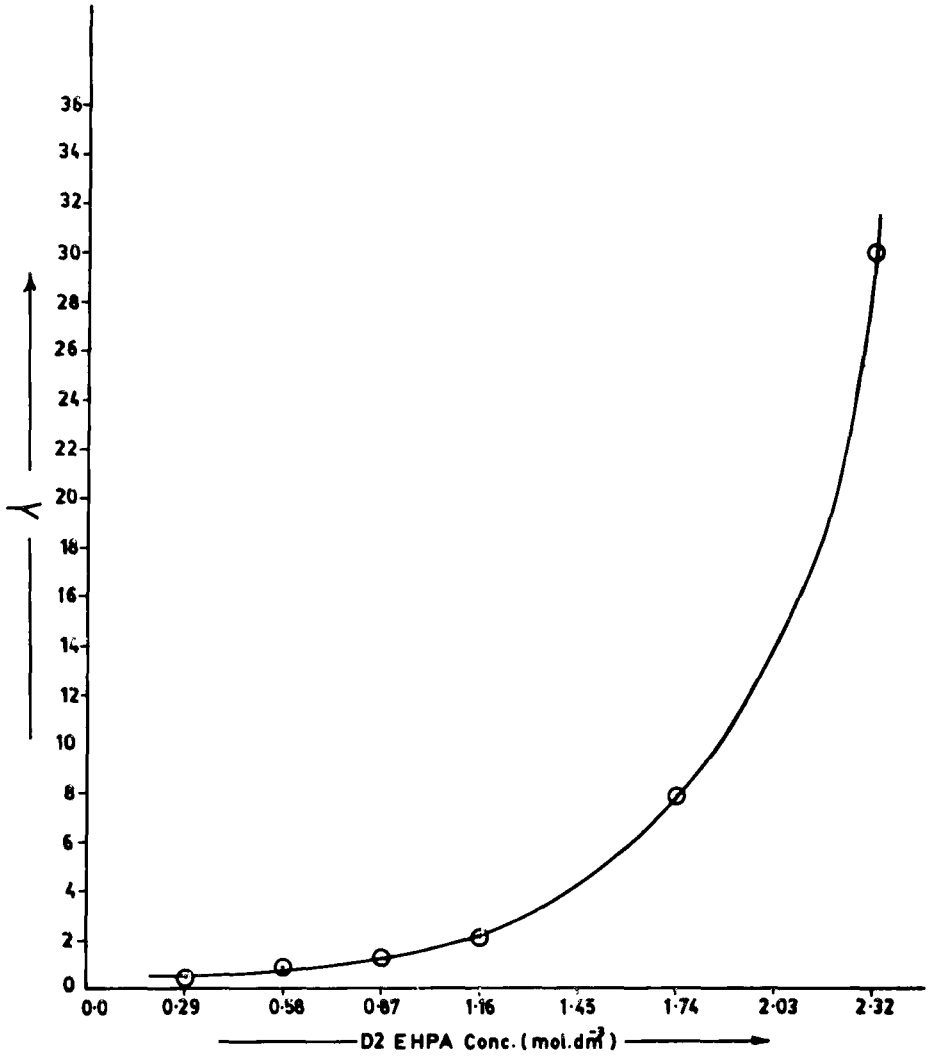

FIG. 6. Plot of distribution coefficient (λ) as a function of D2EHPA concentration.

represent the aqueous and organic phases, respectively. During extraction, aggregates of the metal ions extractant complexes which contain 3–10 molecules of $(HR)_2$ are formed on the average (*16*). It is believed that the metal ions to carrier molecular ratio remains the same in these aggregates. The mechanism of cobalt ions transport is therefore coupled counterion transport with Co(II) and H^+ traveling in the opposite direction, as shown in Fig. 7.

TABLE 1

The Diffusion Coefficient (D) for Co(II) Transport Using the Equation $P = D\lambda$

D2EHPA concentration (mol/dm³)	λ	Permeability ($m^2 \cdot s^{-1} \times 10^{-11}$)	$D = P/\lambda$ ($m^2 \cdot s^{-1} \times 10^{-11}$)
0.58	0.45	6.18	13.73
0.87	0.81	7.66	9.45
1.16	1.30	7.13	5.48
1.45	2.13	6.88	3.23
1.74	7.93	6.56	0.82

The equilibrium constant, K_{Co}, for cobalt can therefore be expressed as

$$K_{Co} = \frac{[CoR_2(HR)_2]_{org} \cdot [H^+]_{aq}^2 \cdot G}{[Co^{2+}]_{aq}[(HR)_2]_{org}^2} \tag{2}$$

where G is a factor based on the activity coefficients of all the involved species. λ, the distribution coefficient for this metal ions distribution in the organic and aqueous phases, is given by

$$\lambda = \frac{[CoR_2(HR)_2]_{org}}{[Co^{2+}]_{aq}} \tag{3}$$

and so

$$K_{Co} = \frac{[H^+]^2 G}{[(HR)_2]^2} \tag{4}$$

By using Fick's law of diffusion and proceeding in the same way as in Ref. *3*, it can be proved that the flux J is given by

$$J = \frac{\epsilon D C_1^\circ [(HR)_2]_{org}^2}{\delta [H^+]_{aq}^2} \tag{5}$$

where D, ϵ, C_1°, and δ represent the diffusion coefficient, the porosity of the membrane, the metal ions [Co(II) ions] concentration in the bulk on the feed solution side, and the membrane thickness, respectively.

By using the Wilke-Change relation, Eq. (5) can be written as

$$J = \frac{\overline{A} T C_1^\circ [(HR)_2]_{org}^2}{\eta [H^+]_{aq}^2} \tag{6}$$

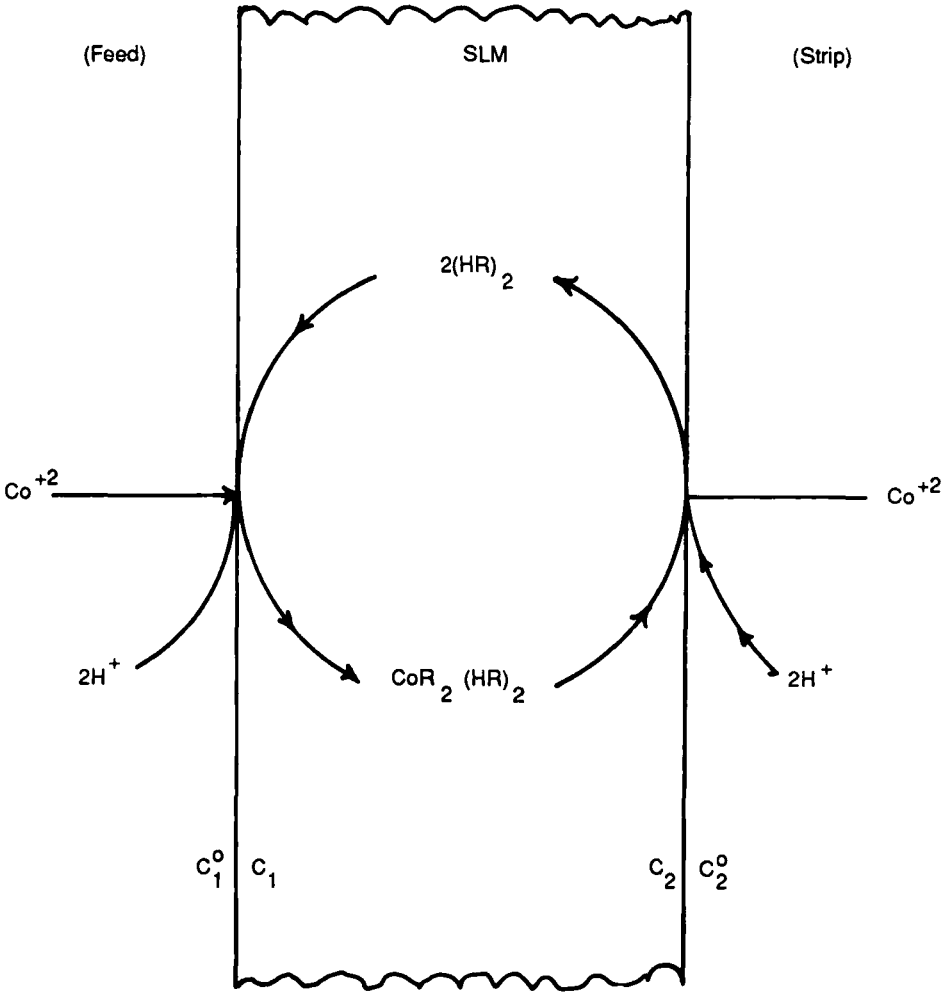

FIG. 7. Possible scheme for Co(II) transport from H_2O to HCl solution through D2EHPA-CCl_4 based supported liquid membrane.

where T and η are the absolute temperature and viscosity of the liquid in the membrane, respectively. $\bar{A}$ is a constant which is dependent on the given membrane thickness and porosity. According to Reaction (1), Eq. (6) will hold and can be written as

$$\log J = \log \bar{A}T - \log \eta + 2 \log [(HR)_2]_{org} - 2 \log [H^+]_{aq} + \log C_1^\circ \quad (7)$$

Equation (7) in a general form may be written as

$$\log J = \log \overline{A}T - \log \eta + n \log [(HR)_2]_{org} - m \log [H^+]_{aq} + \log C_1^\circ \tag{8}$$

where n and m represent the number of D2EPHA dimer and protons, respectively, taking part in the chemical reaction to form the complex responsible for metal ions transport. The metal ions permeability P can be determined by using

$$-\ln \frac{C_{1t}^\circ}{C_1^\circ} = \frac{APt}{V\delta} \tag{9}$$

where C_{1t} and C_1 are the concentrations in the feed at time t and at the start of the experiment, respectively. A, V, and δ are the effective membrane area, the feed cell compartment volume, and the membrane thickness, respectively. By using the relation $P = \lambda D$, the value of the diffusion coefficient can be determined if the distribution coefficient of metal ions for the aqueous feed to the liquid membrane phase is determined.

D2EHPA molecules exist as dimers in the complex formation reaction, and the complex formed diffuses through the membrane and is responsible for the transport of cobalt(II) ions across the liquid membrane, as shown in Fig. 1. The ions can be moved under the influence of the chemical potential difference existing in both the feed and the stripping solutions, and, to be more specific, within the membrane across its thickness. Figure 1 also indicates that the ions can be moved against their concentration gradient, and so the scheme for transporting these ions across the membrane is practical.

The effect of carrier concentration on the transport of metal ions (as shown in Fig. 2) is positive up to 0.87 mol/dm^3 D2EHPA concentration, after which there is a decrease in the flux and permeability of the metal ions.

The practical flux value has been calculated by using

$$J = \frac{V(C_0 - C_t) \times 10^{-6}}{MtA} \tag{10}$$

where J is the flux, C_0 is the initial concentration of the metal ions in the feed solution (μg/cm^3), and C_t is the concentration of metal ions at time t. V is the cell volume for the feed and A is the area of the membrane. M

is the atomic weight or the molecular weight of the species being transported. The permeability has been calculated from a plot of $-\ln C_t^\circ/C_0^\circ$ versus time by using Eq. (9). The flux and permeability values as functions of carrier concentration are given in Fig. 3. The decrease in the flux and permeability values above 0.87 mol/dm^3 concentration of the carrier are explained by the increase in viscosity of the liquid membrane phase. The maximum flux value noted (1.23×10^{-1} mol $\cdot$ m$^{-2} \cdot$ s^{-1}) was obtained at a carrier concentration of 0.87 mol/dm^3 and so is the optimum condition for metal extraction when using this technique.

The effect of HCl concentration in the stripping solution is shown in Figs. 4 and 5. It is positive up to 1 mol/dm^3 ($J = 1.4 \times 10^{-5}$ mol $\cdot$ m$^{-2} \cdot$ s^{-1}; $P = 5.27 \times 10^{-11}$ m$^2 \cdot$ s^{-1}). According to Eqs. (6)–(8), J is indirectly proportional to $[H^+]^2$. Therefore an increase in proton concentration will help reverse the complex formation reaction with the metal ions of the carrier, i.e., they help strip the metal ions. This is why HCl has been selected as the stripping agent. As the concentration of HCl in the stripping phase increases, the stripping rate will increase and reduce the concentration of metal ions on the stripping side in the membrane. After a given concentration, because the transport of metal ions is countercoupled transport, the protons concentration increases in the feed solution with time. Therefore the forward reaction rate may be influenced negatively, resulting in a reduced flux at higher HCl concentration. Another reason for this result may be because protonation of the oxygen atom linked by a double bond with the phosphorus atom reduces the possibility of complex formation of the metal ions.

The distribution coefficient of the metal ions increases with an increase in extraction concentration, as shown in Fig. 6, and this suggests an increase in flux with an increase in carrier concentration. Because $P = D\lambda$, the values of the diffusion coefficient D, recorded in Table 1, show that the value of D is less than the value of λ, so the flux and permeability are influenced as expected. The share of λ for the transport of these metal ions is more compared to D. Therefore the properties of the carrier in extracting the metal ions are very important. The possible mechanism of Co(II) ions transport across the liquid membrane is shown in Fig. 7 and it is of the countercoupled transport type.

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