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Transport of Eu^{3+} through a Bis(2-ethylhexyl)-phosphoric Acid, *n*-Dodecane Solid Supported Liquid Membrane

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Abstract

The coupled transport of Eu^{3+} and H^+ ions through a solid supported liquid membrane consisting of a porous polypropylene film immobilizing an HDEHP solution in *n*-dodecane has been studied as a function of the membrane area, stirring speed of the aqueous solutions, membrane composition, and acidity of the feed solution. The experimental results are in agreement with predictions derived from a theoretical permeability coefficient equation which assumes that membrane diffusion and aqueous film diffusion are the only rate-controlling factors.

INTRODUCTION

In a previous paper (*1*) a permeability coefficient equation for the coupled transport of metal ions through solid supported liquid membranes (SSLM) has been derived considering that (a) diffusion through the aqueous side stagnant layers, (b) interfacial chemical reactions, and (c) membrane diffusion could be simultaneously operative as rate-controlling effects. The equation was derived for the special case of the coupled transport of Cu^{2+} and H^+ ions through liquid membranes containing a β-hydroxy-oxime as carrier. Some literature permeability data were, in fact, available for this system, which could allow one to check in a qualitative way the validity of the derived equation.

In the present investigation the coupled transport of Eu^{3+} and H^+ ions through solid supported liquid membranes consisting of *n*-dodecane solutions of bis(2-ethylhexyl)phosphoric acid, HDEHP, absorbed by microporous polypropylene films, was studied under carefully controlled experimental conditions. The aim of this work was to verify the suitability of the previously derived equation to represent quantitatively experimental permeability data. The system Eu^{3+}, Hcl, water–bis(2-ethylhexyl)phosphoric acid, *n*-dodecane has been chosen because both its equilibrium properties and the mass transfer rate mechanism had been previously investigated in detail (*2*).

EXPERIMENTAL

Reagents and Membranes

Hydrochloric acid solutions were prepared with Ultrex or Baker Instra-Analyzed grade acid (J. T. Baker, Phillipsburg, New Jersey) and ultra-pure water obtained from a milli-Q2 system water purifier (Millipore Corp., Bedford, Massachusetts). All solutions were brought to 1 *M* chloride with Baker Analyzed Reagent sodium chloride.

HDEHP (Eastman Kodak, Rochester, New York) was purified following the method of Ref. *3*. Normal dodecane, 99% pure (Phillips Petroleum, Bartlesville, Oklahoma), was used as the diluent for HDEHP.

Celgard 2500 (Celanese Plastics, Charlotte, North Carolina), a microporous polypropylene film, was used as the solid support. The film is 2.5×10^{-3} cm thick with a nominal porosity of 45% and an effective pore size of 0.04 μm. The support material was stored in a dessicator prior to use. The hydrophobic organic phase (HDEHP in dodecane) was absorbed into the film to produce a solid supported liquid membrane (SSLM).

Apparatus

The experimental apparatus used to measure the permeability coefficient is schematically shown in Fig. 1. The two 250-mL round-bottom flasks are joined with an O-ring joint. A membrane (SSLM) is placed in the O-ring joint to separate the two cells. Solutions are poured into the flasks through the sampling ports. The solutions are stirred with 4-bladed Teflon paddles placed on glass rods which enter through the flask neck. The stirring rods are driven by high precision electric motors. In all experiments, both feed and strip solutions were stirred at the same speed. To maintain constant temperature, the flasks were suspended in a thermally regulated water bath. All experiments have been performed at 25 ± 0.5°C.

Flasks with different O-ring joint diameters have been used to evaluate the dependence of the permeability coefficient on the membrane area, *Q*, and the volume of the aqueous solution, *V*.

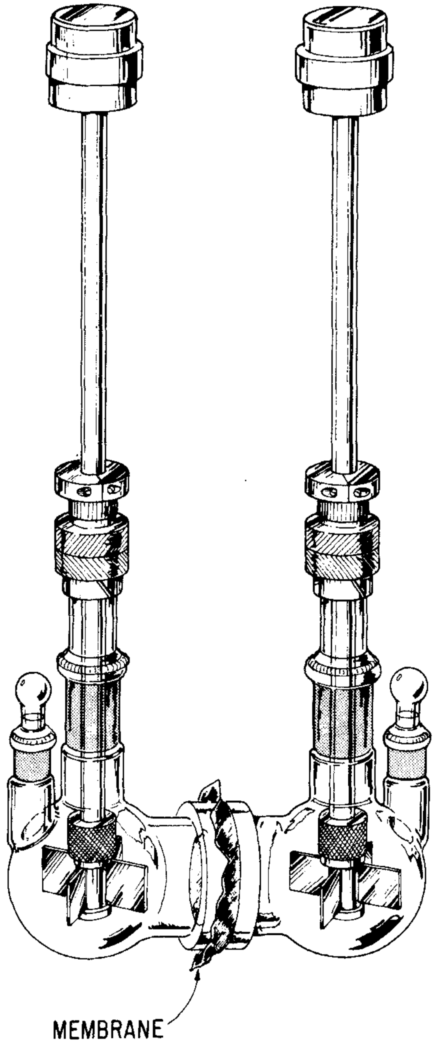

FIG. 1. Experimental apparatus for measuring the permeability coefficients.

Permeability Coefficient Measurements

The permeability coefficient measurements were performed as follows. A Celgard 2500 membrane, which contained absorbed HDEHP in *n*-dodecane solution, was inserted in the O-ring joint of the two-half cells. The two-half cells were then securely clamped. Aqueous solutions having the appropriate

H^+ concentration were poured into the two cells, a spike of $^{152\text{-}154}$Eu introduced into the feed solution, and the stirring motors of the aqueous solutions started. The instant that the motors were started was taken as the initial time of the experiment.

The acidity of the strip solution, initially containing no europium, was kept constant in all experiments at $[H^+] = 1.0\ M$. In this way the distribution ratio, K_d, for europium between the membrane phase and the strip aqueous solution was always kept at much lower values ($K_d = 1.08 \times 10^{-2}$) than that of the feed solution. This condition allows one to neglect the contribution of the membrane–strip solution interface on the overall permeability experiment (*1*). The permeability coefficient, P, of the liquid membrane has been evaluated by sampling the feed and the strip aqueous solutions at time intervals and then counting the $^{152\text{-}154}$Eu gamma activity. By plotting the logarithm of the $^{152\text{-}154}$Eu activity vs time, for either the feed or strip solutions, linear plots were always obtained. The slopes of these straight lines were used to calculate the permeability coefficients. Since it is

$$P = \frac{J}{[\mathrm{Eu}^{3+}]} = -\frac{d[\mathrm{Eu}^{3+}]}{[\mathrm{Eu}^{3+}]dt}\frac{V}{Q} \tag{1}$$

where J = overall flux of europium from feed to strip solution, $[\mathrm{Eu}^{3+}]$ = activity of europium in the feed solution, V = volume of the feed solution, and Q = geometrical membrane area, it follows by integration

$$-\ln\,[\mathrm{Eu}^{3+}] = \frac{Q}{V}Pt + \text{constant} \tag{2}$$

The term $-d\ln[\mathrm{Eu}^{3+}]/dt$ is a function of Q/V; the larger the area of the membrane, the more rapid the decrease in Eu^{3+} concentration in the feed solution. The permeability coefficient, P, is a constant and is independent of Q/V as shown in Fig. 2.

Permeability Equation

An equation describing the permeability of Eu^{3+} ions through solid supported liquid membranes, consisting of an HDEHP in *n*-dodecane solution, can be derived using the same assumptions and limitations as described in Ref. *1*. These are: steady state throughout the system, linear concentration gradients, negligible metal ion concentrations with respect to those of H^+ and the HDEHP carrier, and distribution ratio of the metal between the membrane and feed aqueous phase that are much larger than the strip side. Considering that the membrane flux J_0:

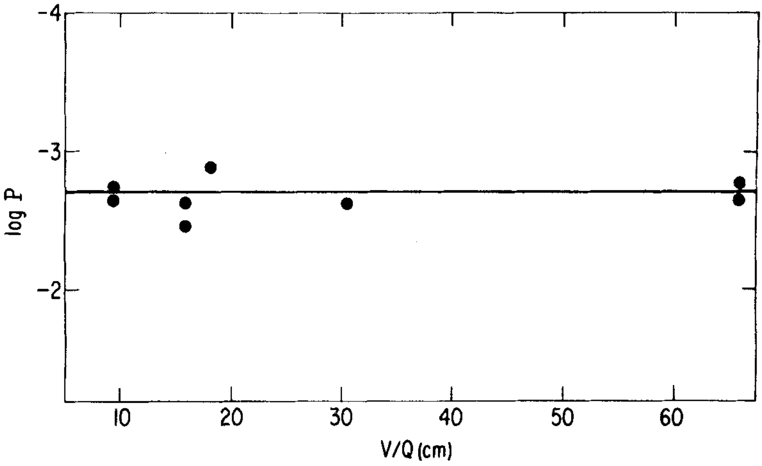

FIG. 2. Permeability coefficient, P (cm/s), vs. the ratio of the feed solution volume over membrane area, V/Q. Feed solution: $[H^+] = 10^{-2}\,M$, $[Cl^-] = 1\,M$. Strip solution: $[HCl] = 1\,M$. Membrane: 0.1 F HDEHP in n-dodecane. Stirring rate: 250 rpm.

$$J_0 = \frac{D_{\bar{m}}}{\delta_0}[\overline{Eu}] \tag{3}$$

the flux through the aqueous diffusional layer J_a:

$$J_a = \frac{D_m}{\delta_a}([Eu^{3+}] - [Eu^{3+}]_i) \tag{4}$$

and the aqueous–membrane interfacial flux, J_i (determined by the rate of the interfacial chemical reactions):

$$J_i = k_1[Eu^{3+}]_i - k_{-1}[\overline{Eu}] \tag{5}$$

have the same value at the steady state, it follows that

$$P = \frac{k_1}{k_1\dfrac{\delta_a}{D_m} + k_{-1}\dfrac{\delta_0}{D_{\bar{m}}} + 1} \tag{6}$$

where $[Eu^{3+}]$ = europium concentration in the bulk aqueous feed solution, $[Eu^{3+}]_i$ = interfacial europium concentration at the aqueous feed solution side, $[\overline{Eu}]$ = europium concentration in the membrane phase at the membrane–aqueous feed solution interphase, δ_a = thickness of the aqueous diffusion film, δ_0 = membrane thickness, D_m = aqueous diffusion coefficient of Eu^{3+}, $D_{\bar{m}}$ = membrane diffusion coefficient of the europium–HDEHP complex, $k_1 = k_1^* a_D^3$ and $k_{-1} = k_{-1}^*[\mathrm{H}^+]^3$ = pseudofirst-order forward and reverse rate constants of the interfacial reaction between europium and HDEHP (*2*)

$$\mathrm{Eu}^{3+} + 3\overline{(\mathrm{HX})_2} \overset{K_e}{\rightleftharpoons} \overline{\mathrm{EuX}_3 \cdot (\mathrm{HX})_3} + 3\mathrm{H}^+ \tag{7}$$

with $\overline{(\mathrm{HX})_2}$ = membrane phase dimer of HDEHP, $\overline{\mathrm{EuX}_3(\mathrm{HX})_3}$ = membrane phase complex between Eu and HDEHP, $K_e = 300$, conditional equilibrium constant of Reaction (7) (*2*). Equation (6) has general validity, i.e., it holds for the permeability of any cation through liquid ion exchange membranes provided the above-mentioned assumptions and limitations are experimentally met and the proper expressions for the pseudofirst-order rate constants are used. In the specific case of the transport of Eu^{3+} ions through a liquid HDEHP membrane, where relatively fast interfacial chemical reactions can be assumed, Eq. (6) becomes

$$P = \frac{\dfrac{D_m}{\delta_a} a_D^3}{a_D^3 + \left(\dfrac{D_m}{D_{\bar{m}}}\right)\left(\dfrac{\delta_0}{\delta_a}\right) K_e^{-1}[\mathrm{H}^+]^3} \tag{8}$$

where a_D is the activity of the HDEHP dimer in *n*-dodecane (*4*). To obtain Eq. (8) from Eq. (6), the relationships

$$K_e = \frac{k_1^*}{k_{-1}^*} = \frac{[\overline{\mathrm{EuX}_3(\mathrm{HX})_3}]\,[\mathrm{H}^+]^3}{[\mathrm{Eu}^{3+}]\,a_D^3} \tag{9}$$

and the approximation

$$k_1\left(\frac{\delta_a}{D_m}\right) + k_{-1}\left(\frac{\delta_0}{D_{\bar{m}}}\right) + 1 \sim k_1\left(\frac{\delta_a}{D_m}\right) + k_{-1}\left(\frac{\delta_0}{D_{\bar{m}}}\right) \tag{10}$$

have been used.

RESULTS

The influence that the rate of stirring of the aqueous solutions has on the permeability coefficient is shown in Fig. 3. Apparently the permeability coefficient, *P*, becomes independent of the stirring rate at 250 rpm. This result may be interpreted either as a complete destruction of the aqueous diffusion films ($\delta_a = 0$) or the reaching of a limiting value for it, independent

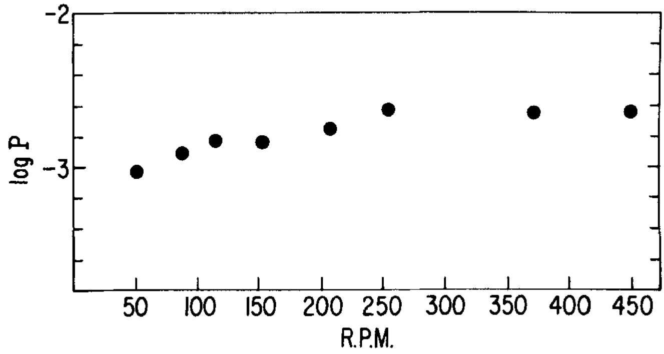

FIG. 3. Permeability coefficient, P (cm/s), vs stirring rate of the aqueous solutions in rpm. Feed solution, strip solution, and membrane compositions are the same as in Fig. 2.

of the hydrodynamic conditions (δ_a = constant). In the former case, the dependence of P on the HDEHP and H$^+$ concentrations should be

$$P = \frac{K_e a_D^3}{\frac{\delta_0}{D_{\bar{m}}}[\mathrm{H}^+]^3} \tag{11}$$

i.e., P should linearly increase with both a_D^3 and $[\mathrm{H}^+]^3$. That this is not the case is shown by the data reported in Figs. 4 and 5, where the logarithmic plots of P vs a_D and $[\mathrm{H}^+]$ are seen to reach limiting values. The result is in agreement with what is expected from Eq. (8) when $\delta_a \neq 0$. Therefore, it can be concluded that when the stirring rate of the aqueous solution exceeds 250 rpm, a constant thickness of the aqueous diffusion film is reached.

The data reported in Figs. 4 and 5, showing the dependence of the permeability coefficient on the membrane carrier activity a_D and the hydrogen ion concentration in the aqueous feed solution, $[\mathrm{H}^+]$, are represented by

$$P = \frac{\alpha a_D^3}{a_D^3 + \beta[\mathrm{H}^+]^3} \tag{12}$$

with $\alpha = (2 \pm 0.2) \times 10^{-3}$ and $\beta = (0.17 \pm 0.03)$. The kind of dependency of P on a_D and $[\mathrm{H}^+]$ is therefore what is expected on the basis of the theoretically derived Eq. (8). Considering that the polymeric solid support has a 45% porosity, a comparison between Eqs. (8) and (12) allows one to calculate the following values of the diffusional parameters: $D_m/\delta_a = 4.4 \times 10^{-3}$ cm/s and $D_{\bar{m}}/\delta_0 = 8.7 \times 10^{-5}$ cm/s. An approximate value for the

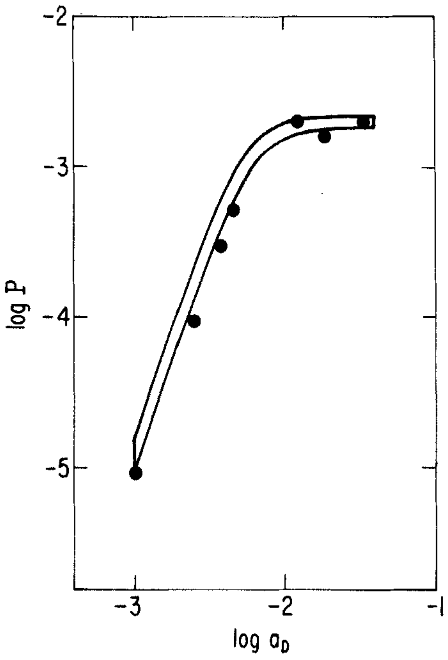

FIG. 4. Permeability coefficient, P (cm/s), vs activity of the HDEHP dimer in the liquid membrane, a_d. Feed solution, strip solution, and stirring rate are the same as in Fig. 2. The continuous lines have been calculated using Eq. (12) with $\alpha = 2.2 \times 10^{-3}$, $\beta = 0.14$ (upper curve) and $\alpha = 1.8 \times 10^{-3}$, $\beta = 0.20$ (lower curve).

thickness of the aqueous side diffusion film, $\delta_a = 1.4 \times 10^{-3}$ cm, is then obtained when the literature value (5) $D_m = 6 \times 10^{-6}$ cm^2/s is used. Further, by assuming that δ_0 is equal to the nominal thickness of the polypropylene membrane film (2.5×10^{-3} cm), a value of $D_{\bar{m}} = 2 \times 10^{-7}$ cm^2/s is calculated. This value is in reasonable agreement with the value 7×10^{-8} cm^2/s evaluated by Horwitz et al. (5) for the Eu(III)–HDEHP complex in undiluted HDEHP. Our $D_{\bar{m}}$ value also falls within the values 4×10^{-6} and 6×10^{-9} cm^2/s, evaluated in Ref. *6* for the membrane diffusion coefficient of the complex formed between uranyl sulfate and the tertiary amine Alamine 336 in the aromatic diluent Aromatic 150.

CONCLUSIONS

The coupled transport of Eu^{3+} and H^+ ions through a solid supported liquid membrane consisting of a porous polypropylene film in which an HDEHP solution in *n*-dodecane is absorbed has been shown to be controlled by both membrane diffusion and by diffusion through membrane–aqueous

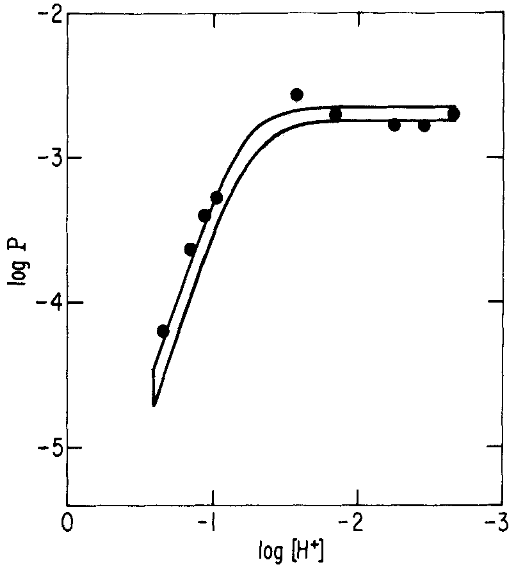

FIG. 5. Permeability coefficient, P (cm/s), vs acidity of the aqueous feed solution, $[H^+]$. The strip solution, membrane composition, and stirring rate are the same as in Fig. 2. The continuous lines have been calculated as in Fig. 4.

solution stagnant layers. The thickness of these layers decreases by increasing the stirring rate of the aqueous solutions separated by the liquid membrane, reaching a constant limiting value when the rate of stirring exceeds 250 rpm. The rate of the interfacial chemical reactions between Eu^{3+} and HDEHP does not influence the rate of permeability.

The results obtained are in agreement with the predictions expected from a permeability coefficient equation derived on the basis of a model which takes into account aqueous diffusion, interfacial chemical reactions, and membrane diffusion as possible simultaneous rate-controlling effects.

Numerical evaluations seem to indicate that in our experimental conditions the limiting thickness of the aqueous diffusion film ($\sim 1 \times 10^{-3}$ cm) is of the same order of magnitude as the membrane thickness (2.5×10^{-3} cm), while the diffusion coefficient of the metal ion–membrane carrier complex is about one order of magnitude lower than that of the aqueous metal cation.

Acknowledgments

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REFERENCES

1. P. R. Danesi, E. P. Horwitz, G. F. Vandegrift, and R. Chiarizia, *Sep. Sci. Technol., 16,* 201 (1981).
2. P. R. Danesi and G. F. Vandegrift, *J. Phys. Chem.,* In Press.
3. J. A. Partridge and R. C. Jensen, *J. Inorg. Nucl. Chem., 31,* 2587 (1969).
4. P. R. Danesi and G. F. Vandegrift, *Inorg. Nucl. Chem. Lett., 17,* 109 (1981).
5. E. P. Horwitz and C. A. A. Bloomquist, *J. Inorg. Nucl. Chem., 34,* 3851 (1972).
6. W. C. Babcock, R. W. Baker, E. D. Lachapelle, and K. L. Smith, *J. Membr. Sci., 7,* 89 (1980).

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