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Effects of a Carrier and Its Diluent on the Transport of Metals across Supported Liquid Membranes (SLM). II. Viscosity Effect

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Effects of a Carrier and Its Diluent on the Transport of Metals across Supported Liquid Membranes (SLM). II. Viscosity Effect

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Abstract

A new model equation was developed which incorporates the solubility and viscosity effects of the diluent and the carrier immobilized in a supported liquid membrane. It was found that these effects influence the system significantly. The negative effect of increased viscosity on diffusivity, accounted for in the theoretical development, was found to give better predictions of the measured fluxes. The theory is so simple that one needs only to specify the maximum point and determine the flux at 100% carrier concentration in order to predict the flux at any other points.

INTRODUCTION

In the preceding paper (*2*) the transport of uranyl ion through supported liquid membranes impregnated with an acidic carrier was described. The driving force for this facilitated transport is provided by the different acidities of the feed and stripping solutions. The predominant interfacial reaction at the feed side in this case was proposed by Base et al. (*3*):

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$$[UO_2^{2+}]_a + [2(HG)_2]_o \rightleftarrows [UO_2(HG_2)_2]_o + [2H^+]_a \qquad (1)$$

while at the strip side the predominant interfacial reaction is assumed to be (*4*):

$$[UO_2(HG_2)_2]_o + [3CO_3^{=}]_a + [2H^+]_a \rightleftarrows [2(HG)_2]_o + [UO_2(CO_3)_3^{4-}]_a \qquad (2)$$

where the subscripts *a* and *o* refer to species soluble only in the aqueous and organic phases, respectively. It can be seen that metal ions move from the feed side to the strip side, and electrical neutrality is maintained by the movements of hydrogen ions in the opposite direction.

A simplified model based on the solubility mechanism was developed in the preceding paper (*2*). An implicit assumption in that model's development was that the effect of many important parameters, such as viscosity of the organic phase and pore size effects, were lumped in the apparent diffusion coefficient. This limitation restricted the application of that model to systems having maxima occurring at carrier concentrations greater than 50%. Babcock et al. (*1*), however, observed a maximum at 30 vol% of Alamine 336 in their study of uranium transport. That interesting observation motivated this work. Babcock et al. (*1*) tried to predict their experimental flux by using Fick's law and the Stokes-Einstein equation. However, the calculated fluxes were as much as five times larger than the experimental values. They attributed part of the discrepancy to hindered diffusion of the uranium complex in the rather small pores of the membrane.

In this model development we modify the simplified model described in the preceding paper (*2*) by incorporating the viscosity effect. In so doing, the Stokes-Einstein equation is modified so that the viscosity will account for the effect of the carrier and the diluent. The inclusion of this modification will qualitatively and quantitatively predict the maximum and the flux very closely.

THEORY

The Stokes-Einstein equation has been shown to be fairly good for describing the diffusion of large spherical particles (*5*). The diffusion coefficient, *D*, is estimated from the Stokes-Einstein equation as

$$D = \frac{kT}{6\pi r\eta} \qquad (3)$$

where k is the Boltzmann constant, T is the absolute temperature, r is the molecular radius of the diffusing species, and η is the viscosity of the organic phase.

If the viscosity of the complexed carriers and the uncomplexed carriers are denoted as η_c and η_u, respectively, then the viscosity of the mixture may be calculated as follows:

$$\eta = \eta_c x + \eta_u(1 - x) \tag{4}$$

where x is the concentration of the carrier. Substitution of Eq. (4) into Eq. (3) gives

$$D = \frac{D_0\eta_0}{[\eta_c x + \eta_u(1 - x)]} \tag{5}$$

where $D_0\eta_0$ is a constant and is equal to $kT/6\pi r$.

Fick's first law of diffusion was defined for the system of the preceding paper (*2*) as

$$J = \frac{D_R}{\delta} K_E M x[\alpha x + \beta(1 - x)] \tag{6}$$

Substitution of Eq. (5) into Eq. (6) gives

$$J = \left(\frac{kT}{6\pi r}\right)\left(\frac{K_E M}{\delta}\right)\left\{\frac{x[\alpha x + \beta(1 - x)]}{\eta_c x + \eta_u(1 - x)}\right\} \tag{7}$$

In order to investigate the behavior of the flux with respect to the carrier concentration, it is only necessary to investigate the following function $f(x)$ derived from Eq. (7):

$$f(x) = \frac{\alpha x + \beta(1 - x)}{\eta_c + \eta_u\left(\dfrac{1 - x}{x}\right)} \tag{8}$$

It is not difficult to show that the function expressed in Eq. (8) exhibits a maximum at $x = x_{\max}$, where $x_{\max}$ is a "real" solution of the following quadratic equation:

$$x_{\max}^2 + 2\left(\frac{\eta_c}{\eta_u} - 1\right)^{-1} x_{\max} + \left(\frac{\alpha}{\beta} - 1\right)^{-1}\left(\frac{\eta_c}{\eta_u} - 1\right)^{-1} = 0 \tag{9}$$

In order for the quadratic equation to possess real solutions, it is necessary that

$$\left(\frac{\eta_c}{\eta_u} - 1\right)^{-2} - \left(\frac{\alpha}{\beta} - 1\right)^{-1}\left(\frac{\eta_c}{\eta_u} - 1\right)^{-1} > 0 \tag{9a}$$

When the quadratic Eq. (9) possesses a real solution $x_{\max}$, the solubility ratio α/β can be expressed as a function of $x_{\max}$ and the viscosity ratio η_c/η_u as follows:

$$\frac{\alpha}{\beta} = 1 + \frac{1/x_{\max}}{\left[\left(1 - \frac{\eta_c}{\eta_u}\right)x_{\max} - 2\right]} \tag{10}$$

With this modification, the model is no longer limited by the dependence of the maximum on the value of the ratio α/β. Evaluating the flux Eq. (7) at 100% carrier concentration gives

$$J|_{x=1} = \left(\frac{kT}{6\pi r}\right)\left(\frac{K_E M}{\delta}\right)\left(\frac{\alpha}{\eta_c}\right) \tag{11}$$

Knowing the flux at 100% carrier concentration, the values of the flux at other carrier concentration can be calculated from

$$\frac{J|_x}{J|_{x=1}} = \frac{x + \frac{\beta}{\alpha}(1 - x)}{\left[1 - \frac{\eta_u}{\eta_c}\left(1 - \frac{1}{x}\right)\right]} \tag{12}$$

Evaluating Eq. (12) at $x_{\max}$ gives

$$\frac{J|_{x_{\max}}}{J|_{x=1}} = \frac{x_{\max} + \frac{\beta}{\alpha}(1 - x_{\max})}{1 - \frac{\eta_u}{\eta_c}\left(1 - \frac{1}{x_{\max}}\right)} \tag{13}$$

Finally, the following algorithm is used to calculate the transport flux at any values of carrier concentration:

(1) Measure $x_{\max}$ at which the flux is maximum
(2) Measure the relative ratio of fluxes obtained at $x_{\max}$ and $x = 100\%$
(3) Solve Eqs. (10) and (13) simultaneously to obtain the ratio (η_u/η_c) and (α/β)
(4) Predict other fluxes by using Eq. (12)
(5) Compare the predicted flux to the experimental values

EXPERIMENTAL

The experimental procedures were the same as described in the preceding paper (*2*).

DISCUSSION

First, the algorithm was applied to Babcock et al.'s (*1*) data. The calculated results are given in Table 1 and presented graphically in Figs. 1 and 2. From Table 1, one can easily see that agreement between the model predictions and the experimental fluxes is far better than that reported in Babcock et al.'s (*1*) paper. The highest percentage relative error is only 28%. When the predicted fluxes were compared to the measured ones as shown in Fig. 1, a good correlation coefficient (R^2) of 0.9745 was obtained. Figure 2 shows how closely the model is capable of

TABLE 1
Comparison between Predicted *J* (model) and *J* (data) Obtained Experimentally by Babcock et al. (*1*)

Carrier concentration (vol%)	*J* (data) (μg/cm^2 · min)	*J* (model) (μg/cm^2 · min)	Relative error (%)
0	2	2	0
10	62	53.86	+13
20	72	72.36	−0.5
30	74	76.52	−3.4
40	68	73.45	−8
50	54	66.22	−22.6
60	44	56.39	−28
100	4	4	0

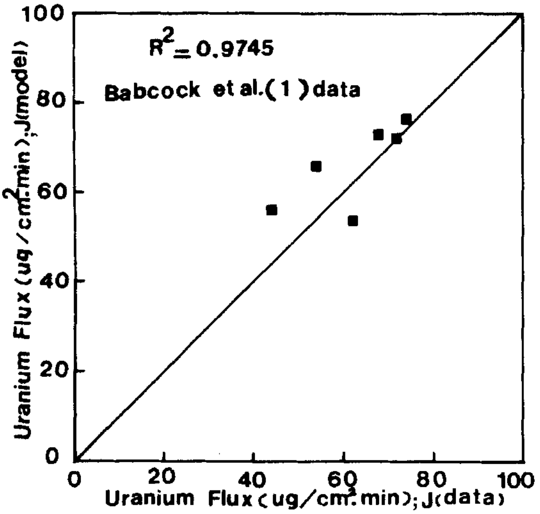

FIG. 1. Comparison between the predicted J (model) and the J (data) obtained experimentally by Babcock et al. (*1*).

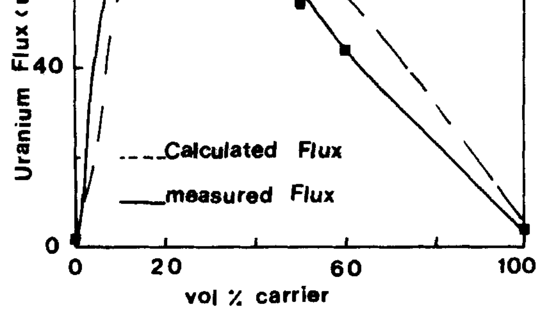

FIG. 2. Effect of carrier concentrations on uranium flux. Data obtained experimentally by Babcock et al. (*1*) for the system membrane:Alamine 336 in Aromatic 150. Feed solution: 2.0 g/L uranium, pH 1.0. Strip solution: pH 4.5 acetate buffer.

predicting the experimental fluxes as a function of carrier concentration. It is important to note that η_u/η_c is equal to 0.17, β/α is equal to 37.74, and $x_{\max}$ is equal to 30%. From this, we can say that the viscosity of the complexed carrier (η_c) is about 5.9 times the viscosity of the uncomplexed carrier (η_u). In their measurements of viscosity using solvent extraction experiments, Babcock et al. (*1*) obtained a ratio (η_c/η_u) of about 2.1 for the 30% carrier concentration. The comparison, if it holds, between the viscosity ratio predicted by our model and the viscosity ratio measured by Babcock et al. (*1*), leads us to conclude that the viscosity effect is more pronounced in small membrane pores than in the solvent extraction analogy. In regard to the solubility effect, we can say that the distribution of the metal into the diluent is about 37 times the distribution of the metal into the carrier. This leads us to conclude that the function of the diluent is to increase the ability of the carrier to exist in monomeric, dimeric, and trimeric forms in equilibrium with each other (*6*) and also to increase its ability to solvate polar molecules (*6*).

Second, the algorithm was applied to our data reported in the preceding paper (*2*). The calculated results of Case A are given in Table 2 and presented graphically in Figs. 3 and 4. The calculated results of Case B are given in Table 3 and presented graphically in Figs. 5 and 6. Also, the data are reported in terms of permeability coefficients rather than fluxes.

For Case A, Table 2 and Figs. 3 and 4 show the system where $\eta_u/\eta_c = 0.73$, $\beta/\alpha = 12.81$, and $x_{\max} = 50\%$. This tells us that the viscosity of the complexed carrier is about 1.4 times the viscosity of the uncomplexed carrier. This can be compared to (a) the Babcock system where $x_{\max} = 30\%$ and where the viscosity of the complexed carrier is about 5.9 times the viscosity of the uncomplexed carrier, and (b) Babcock et al.'s (*1*)

TABLE 2
Comparison between Predicted *P* (model) and *P* (data) Obtained Experimentally in This Work: Case A

Carrier concentration (vol%)	*P* (data) × 10^{-5} (cm/s)	*P* (model) × 10^{-5} (cm/s)	Relative error (%)
0	1.65	1.65	0
5	2.98	2.01	32.6
20	6.99	6.53	6.6
50	9.77	9.78	−0.10
100	2.45	2.45	0

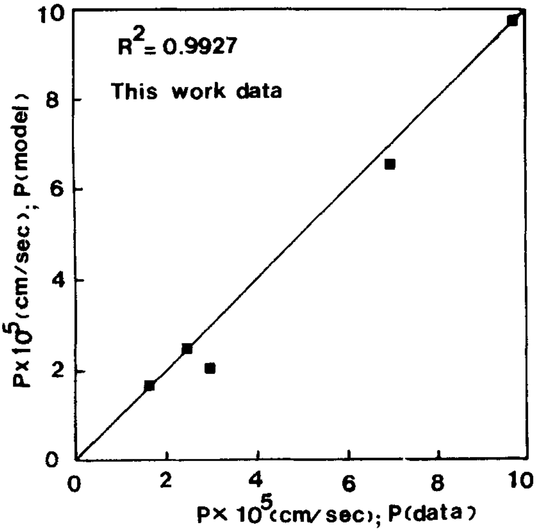

FIG. 3. Comparison between the predicted P (model) and P (data) obtained experimentally in this work (*2*). Case A.

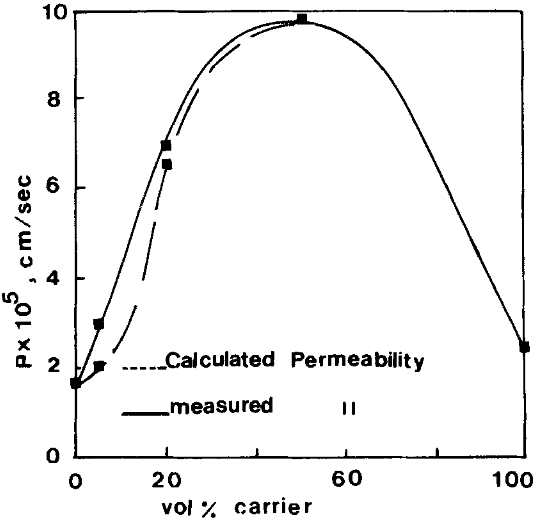

FIG. 4. Effect of carrier concentration on uranium flux. Data obtained experimentally in this work (*2*). Case A.

TABLE 3
Comparison between Predicted P (model) and P (data) Obtained Experimentally in This Work: Case B

Carrier concentration (vol%)	P (data) × 10^{-5} (cm/s)	P (model) × 10^{-5} (cm/s)	Relative error (%)
0	1.70	1.70	0
5	3.29	1.33	59.6
10	3.6	2.63	26.9
20	5.37	5.12	4.7
30	7.38	7.51	−1.8
40	10.28	9.37	8.8
50	12.27	11.16	9.0
70	13.48	12.83	4.8
100	3	3	0

measurements of viscosity using solvent extraction experiments where they obtained an η_c/η_u ratio of about 6.8 for the 50% carrier concentration. This leads us to conclude that the impact of the viscosity effect in Case A is not as severe as comparisons (a) and (b). This may be due to the synergistic and antagonistic behavior of viscosity, diffusivity, and pore size effects. The model also tell us that the distribution of the metal into the diluent in our system is about 13 times the distribution of the metal into the carrier. Thus, one can see that if this is accepted, then the function of the diluent is to attract the metal into the organic phase. When we compare the ratio $\beta/\alpha = 12.81$ of our system to the ratio $\beta/\alpha = 37.74$ of Babcock's system, we will be able to understand the reasons behind the shift of the maximum from 50 to 30% carrier concentrations, respectively. What this says is that when a system's solubility is high, the system is able to achieve maximum flux at a lower percent of carrier concentration. When the predicted permeability is compared to the measured ones, as shown in Fig. 3, a good correlation coefficient (R^2) of 0.9927 is obtained. Figure 4 shows the good agreement between the model predictions.

For Case B, Table 3 and Figs. 5 and 6 show the system with $\eta_u/\eta_c = 4.19$, $\beta/\alpha = 37.62$, and $x_{\max} = 70\%$. Even though the ratio of the distribution of the metal into the diluent to that into the carrier is almost equal to that obtained in Babcock et al.'s (*1*) work, the viscosity of the uncomplexed carrier is about 4 times greater than that of the complexed carrier. In their measurements of viscosity, Babcock et al. (*1*) obtained an η_c/η_u ratio of about 14 for the 70% carrier concentration extraction. While it is doubtful that the viscosity of the uncomplexed carrier is about 4 times the viscosity

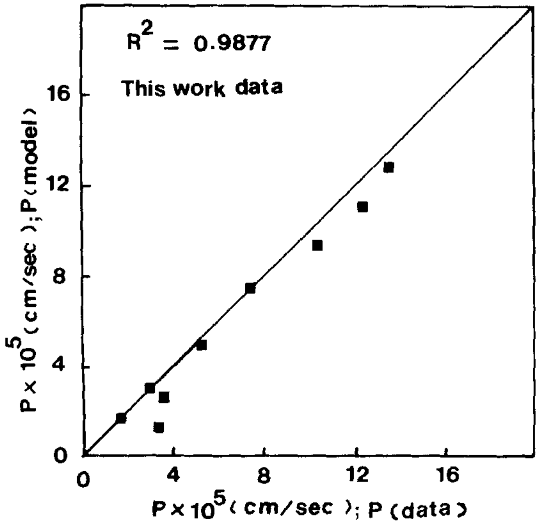

FIG. 5. Comparison between the predicted *P* (model) and *P* (data) obtained experimentally in this work (*2*). Case B.

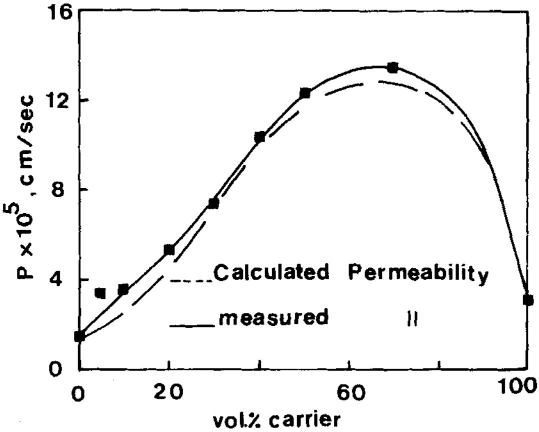

FIG. 6. Effect of carrier concentration on uranium flux. Data obtained experimentally in this work (*2*). Case B.

of the complexed carrier, we tried to look at the causes behind this discrepancy. First, very high metal concentrations above the loading capacities of the organic phase were used. This left many of the metal species uncomplexed and contributed highly to the rise of the viscosity of the uncomplexed phase. This also caused violation of the assumption imposed earlier in the theory that the carrier is capable of complexing all metal ions. Second, a very high distribution of the metal into the diluent to that into the carrier contributed toward the acceptance of many metal ions into the organic phase without being capable of complexing them. Finally, a high stirring rate was used which added to the problem by providing more metal ions to the already crowded organic phase. A good correlation coefficient (R^2) of 0.9877 was obtained when the model permeability was compared to the measured permeability as shown in Fig. 5. Figure 6 shows the comparison between the measured permeability and the calculated values as a function of carrier concentration; a good fit is obtained.

CONCLUSIONS

It has been shown that the negative effect of increased viscosity on diffusivity can be included in the theoretical development to give better prediction of the measured fluxes. In contrast to the preceding paper (*2*), which could only explain maxima occurring at carrier concentrations greater than 50%, the present theory explains all maxima that occurred over the whole range of carrier concentrations.

SYMBOLS

A	membrane area
B2EHHP	bis(2-ethylhexyl) hydrogen phosphate
C	carrier concentration at time t; carrier metal concentration at time t
D	diffusion coefficient
$D_0\eta_0$	$kT/6\pi r$
D_R	diffusivity of the metal–carrier complex
D_{M^*}	diffusivity of the metal in the organic phase
$f(x)$	functional behavior of the flux
J	solute flux

K_E	equilibrium constant for the metal–carrier complex formation reaction
M	concentration of the metal in the aqueous phase
M^*	concentration of the metal in the organic phase
P	membrane permeability
r	molecular radius of diffusing species
R	metal–carrier concentration
T	absolute temperature
U	uranium concentration
V	volume of aqueous feed solution
x	initial concentration of the carrier in the diluent
$x_{\max}$	concentration where flux is maximum

Greek Letters

α	the distribution coefficient in a pure carrier
β	the distribution coefficient in a pure diluent
δ	thickness of the membrane
ε	porosity of the membrane
κ	Boltzmann constant
η	viscosity of the organic phase
η_c	viscosity of the complexed carrier
η_u	viscosity of the uncomplexed carrier

Subscripts

a	aqueous phase
o	organic phase
0	zero thickness of the membrane
δ	δ thickness of the membrane

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