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Permeation of Lanthanum through Supported Liquid Membranes

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ABSTRACT

The mechanism of lanthanum transport through a supported liquid membrane is presented. The membrane consisted of a Teflon millipore membrane with a kerosene solution of di(2-ethylhexyl) phosphoric acid (HDEHP) as a mobile carrier held within the pores by capillary forces. Interposing the liquid membrane between two aqueous solutions with different pH values, lanthanum was transported and concentrated from the high pH solution to the low pH solution across the liquid membrane. The effects of HDEHP concentration in the membrane solution and of the lanthanum concentration and pH in the aqueous phases on the permeation rates of lanthanum were investigated. It was observed that the permeation rates decrease drastically by the addition of surfactant to the membrane phase. The permeation rates of lanthanum can be explained by a permeation model which includes the extraction and the stripping reaction at the membrane interfaces and the diffusion process of the complex formed between lanthanum and HDEHP through the membrane in addition to the diffusion process of lanthanum in the aqueous film adjacent to the membrane.

Key Words. Extraction; Supported liquid membrane; Lanthanum; HDEHP; Permeation mechanism; Active transport

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INTRODUCTION

The liquid membrane separation technique has been found to be an attractive method for the separation and concentration of different solutes. Liquid membranes containing carriers which possess the potential for fast and selective permeation by the active transport mechanism have been widely applied to the recovery and concentration of metal ions. The first commercial liquid membrane permeation plant was built in Austria in 1986 for zinc separation from the wastewater of the artificial fiber industry (1).

Rare earth metals, which are essential elements in the electronic and magnetic industries, have been separated and enriched by solvent extraction and ion exchange. The demand for them has drastically increased, so the development of more efficient separation methods is desirable. There have been many papers on the application of the liquid membrane technique to the separation and concentration of rare earth elements (2–13). However, the mass transfer mechanism for permeation through a liquid membrane, which is of practical importance in selective separation and concentration, has not been sufficiently clarified (14–18). In particular, there have been very few reports on the permeation mechanism of lanthanum (16).

In this work the separation and concentration of lanthanum using supported liquid membranes impregnated with di(2-ethylhexyl) phosphoric acid (HDEHP) as a carrier has been studied to clarify the permeation mechanism. The experiments were carried out to investigate the effects of a number of operating conditions on the permeation rates of lanthanum. The experimental results are then compared with a permeation model for concentrating lanthanum across a liquid membrane. The effect of surfactants on the permeation rate is also discussed.

PERMEATION MODEL

It has been shown that a reaction between lanthanum ion and HDEHP (HR) occurs at the organic–aqueous interface, and the kinetics of this reaction is described as follows (19):

$$\mathrm{La^{3+}} + 3\mathrm{(HR)_2} \rightleftarrows \mathrm{LaR_3{\cdot}3HR} + 3\mathrm{H^+} \quad (A + 3B \rightleftarrows C + 3H) \tag{1}$$

$$K_{\mathrm{ex}} = (CH^3/AB^3)_{\mathrm{eq}} \tag{2}$$

$$r_{\mathrm{f}} = k_{\mathrm{f}}\{AB^3/H^3 - (C/K_{\mathrm{ex}})\} \tag{3}$$

$$r_{\mathrm{r}} = k_{\mathrm{r}}\{C - (K_{\mathrm{ex}}AB^3/H^3)\} \tag{4}$$

The schematic concentration profile for lanthanum permeation through a supported liquid membrane containing HDEHP is shown in Fig. 1. Lanthanum ion, A, in the feed solution diffuses toward the feed–membrane interface ($x = 0$), where complex formation between A and HDEHP, B, occurs. The lanthanum–HDEHP complex, C, diffuses in the membrane. On reaching the stripping–membrane interface ($x = l$), hydrogen ion, H, in the stripping solution reacts with the complex to liberate lanthanum ion. This step regenerates the carrier, B, which then diffuses back to the feed side of the membrane and the entire process is repeated. Thus, lanthanum ion can be pumped from a lower concentration solution into a higher concentration solution through the HDEHP liquid membrane because its flow is coupled to a flow of hydrogen ions in the opposite direction.

The permeation rate of lanthanum through the liquid membrane is therefore influenced by the above elementary steps. The rates of these steps at steady state are as follows:

1. Diffusions of lanthanum and hydrogen ions in the aqueous film of the feed solution:

$$J_{AF} = k_A(A_F - A_0) \tag{5}$$

$$J_{HF} = k_H(H_0 - H_F) \tag{6}$$

2. Forward reaction at the feed–membrane interface:

$$J_f = k_f\{A_0 B_0^3/H_0^3 - (C_0/K_{ex})\} \tag{7}$$

3. Diffusions of the carrier and complex through the liquid membrane:

$$J_B = (D_B/\tau l)(B_l - B_0) \tag{8}$$

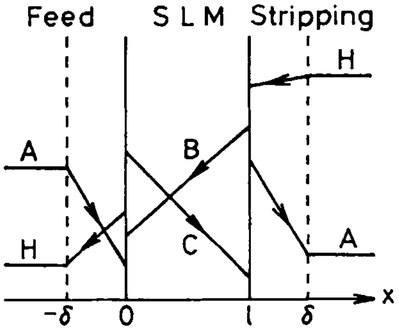

FIG. 1 Permeation model for the supported liquid membrane.

$$J_C = (D_C/\tau l)(C_0 - C_l) \tag{9}$$

4. Stripping reaction at the stripping–membrane interface:

$$J_r = k_r\{C_l - (K_{ex}A_lB_l^3/H_l^3)\} \tag{10}$$

5. Diffusions of lanthanum and hydrogen ions in the aqueous film of the stripping solution:

$$J_{AS} = k_A(A_l - A_S) \tag{11}$$

$$J_{HS} = k_H(H_S - H_l) \tag{12}$$

where k_A and k_H are the mass-transfer coefficients of lanthanum and hydrogen ions in the aqueous film and are assumed to be the same for the feed and stripping sides. l is the thickness of the supporting membrane and τ is a constant factor that allows for the diffusion of species through the tortuous pore within the membrane.

The dissolution of the carrier and the complex in the aqueous phases is negligibly small, so the total amount of the carrier is conserved in the membrane phase:

$$B_T = \int_0^l (B + 3C)dx/l = \{B_0 + B_l + 3(C_0 + C_l)\}/2 \tag{13}$$

At steady-state the following equality also holds:

$$J_{AF} = J_{HF}/3 = J_f = J_B/3 = J_C = J_r = J_{AS} = J_{HS}/3 \tag{14}$$

If the mass transfer and reaction parameters are known, the flux of lanthanum ion can be obtained from Eqs. (5)–(14), and the change of lanthanum concentration with time in the feed solution can be computed from the following equation:

$$dA_F/dt = -(S/V)J_{AF} \tag{15}$$

where S is the membrane area and V the volume of the feed solution.

In the limiting case when the permeation rate is controlled by the diffusion of lanthanum ion in the aqueous film of the feed solution, the time-dependent concentration of lanthanum in the feed solution is expressed by

$$A_F/A_F^0 = \exp\{-(S/V)k_At\} \tag{16}$$

where A_F^0 is the initial lanthanum concentration of the feed solution.

The parameters used for computing the permeation rate are summarized in Table 1. The mass-transfer coefficient, k_A, was calculated from the following correlation (20):

$$k_Ad/D_A = 0.158(\mu/\rho D_A)^{1/3}(Nd^2\rho/\mu)^{0.63} \tag{17}$$

TABLE 1
Parameters Used for Computing the Permeation Rate of Lanthanum

$k_A = 7.1 \times 10^{-6}$ m/s (1.4 rps)
$k_A = 9.0 \times 10^{-6}$ m/s (2.0 rps)
$D_B = 3.84 \times 10^{-10}$–$2.76 \times 10^{-10}$ m^2/s[a]
$D_C = 1.98 \times 10^{-10}$–$1.41 \times 10^{-10}$ m^2/s[a]
$k_f = 1.5 \times 10^{-6}$ m/s
$K_{ex} = 0.35$
$\tau = 5.0$

[a] Variation with the carrier concentration.

where d is the diameter of the impeller, N is the rotational speed of the impeller, and ρ and μ are the density and viscosity of the aqueous solution, respectively. The diffusivity, D_A, in the aqueous phase was estimated by the Nernst equation (21), and those of the carrier and complex, D_B and D_C, in the membrane phase were estimated from the Wilke–Chang equation (22). The forward reaction rate constant, k_f, is a value reported by Imai and Furusaki (19), and the equilibrium constant, K_{ex}, was measured in this study as is described later. The membrane constant, τ, is a value obtained in a previous paper (20).

EXPERIMENTAL

Membrane and Reagents

A Teflon millipore membrane filter which has a thickness of 125 μm, a porosity of about 68%, and a pore size of 10 μm was used as the solid support membrane in this study. The pores within the solid support membrane were filled with the HDEHP carrier by immersion in kerosene for about 2 hours and then in the membrane solution for about 15 hours. The membrane solution was prepared by diluting HDEHP with kerosene and washing the resultant solution two times with hydrochloric acid solution and then two times with distilled water. When the effect of surfactant on the permeation rate was investigated, Span 80 or ECA4360J (polyamine) was added to the membrane solution.

The feed solution was aqueous lanthanum chloride solution which was adjusted to an ionic strength of 0.3 kmol/m^3 and the desired pH with sodium chloride–hydrochloric acid buffer. Sulfuric acid solutions of 0.5 to 2 kmol/m^3 were used as a stripping solution. All aqueous solutions were prepared using distilled water saturated with HDEHP–kerosene solution.

Extraction Equilibria

A known volume of aqueous lanthanum solution with 0.3 kmol/m^3 ionic strength was equilibrated with an equal volume of kerosene solution containing HDEHP in a separatory funnel by shaking the two phases at 298 K. The distribution ratio of lanthanum was measured as a function of the aqueous pH and the concentration of HDEHP. The lanthanum concentration in the aqueous phase was determined by chelate titration with 10 mol/m^3 EDTA standard solution, and that in the organic phase was obtained from the mass balance. The concentration of HDEHP was determined by titration with sodium hydroxide solution. The experiments were also carried out for the organic phase containing Span 80.

Permeation Rates

The experimental apparatus for a supported liquid membrane, which is shown in Fig. 2, and the experimental procedures were the same as described in previous papers (15, 23). The membrane was clamped between two glass half-cells of 8 cm i.d. The turbine impellers of 4 cm diameter with six flat-blades were driven with variable-speed motors in both cells. The volume of the solution in each cell was 370 cm^3, and the membrane area was 33.2 cm^2.

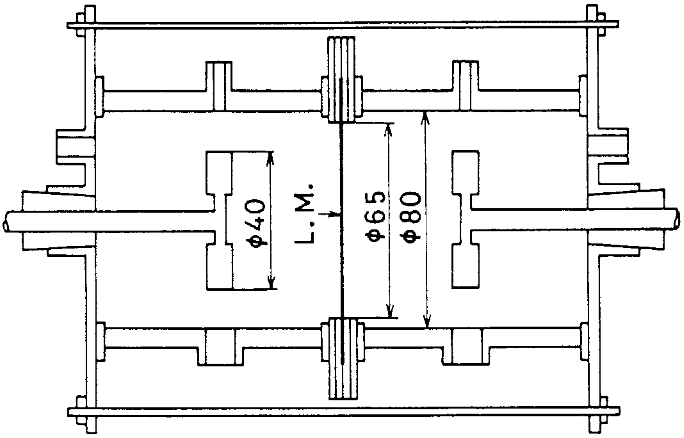

FIG. 2 Permeation apparatus.

The feed solution was carefully transferred into the left cell and the stripping solution into the right cell without causing a difference in the liquid level across the membrane. The motors were started as soon as each cell was filled with its respective aqueous solution. Unless otherwise specified, the experiments were carried out at a stirring speed of 1.4 $\sec^{-1}$. To determine the lanthanum concentration in the feed solution as a function of time, about 5 cm^3 of samples were taken with a syringe at intervals as the original aqueous solution was added in order to maintain the original volume of the cell solution.

RESULTS AND DISCUSSION

Extraction Equilibria

Figure 3 shows the distribution ratio of lanthanum, C/A, obtained for different concentrations of lanthanum (A^0) and HDEHP (B_T) at different pH values. The values of C/A were plotted logarithmically as a function of B/H value. A linear relationship with a slope of 3 between C/A and B/H holds. The equilibrium relation can therefore be expressed by Eq. (2), and an equilibrium constant K_{ex} value of 0.35 was obtained. This value is a little smaller than a value of 0.66 obtained by using Shellsol-K as a diluent (24).

The effect of the surfactant, Span 80, which was added to the organic phase, on the extraction equilibrium is shown in Fig. 4. The solid line is the same line as in Fig. 3, and the experimental data nearly lie on it. The equilibrium relation is not affected by the addition of Span 80 up to 4 vol%.

Permeation Rates

Effects of Carrier Concentration and Stirring Speed

The permeation rates of lanthanum were measured by varying the HDEHP carrier concentration, B_T, at an initial La concentration of $A_F^0 = 1$ mol/m^3 and pH 2.1 in the feed solution and an initial sulfuric acid concentration of $H_S^0 = 1$ kmol/m^3 in the stripping solution. The variation of La concentration with time in the feed solution is shown in Fig. 5. In all experiments the pH of the feed solution after 6 hours was about 2, almost unchanged from the initial value. The solid lines represent the values computed for each B_T value at 1.4 rps by using the parameters

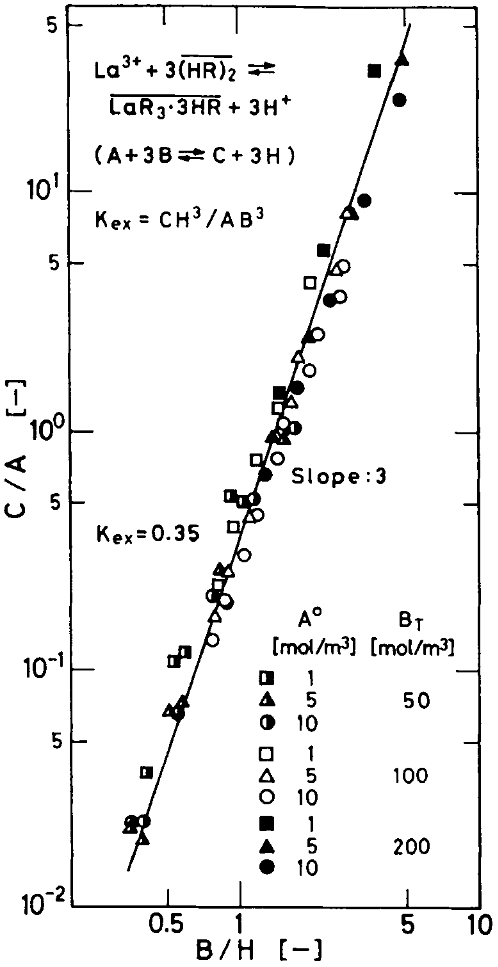

FIG. 3 Equilibrium relation of lanthanum extraction with HDEHP in kerosene.

shown in Table 1. The agreement between computed and experimental values for different carrier concentrations is very good.

In order to check the validity of the evaluation of the mass-transfer coefficient, k_A, by Eq. (17), a similar experiment was carried out for a stirring speed of $N = 2.0$ rps at a B_T of 392 mol/m³. The time-dependent concentration of La in the feed solution is also shown in Fig. 5. The computed values from Eq. (16) with a k_A value estimated by Eq. (17) are

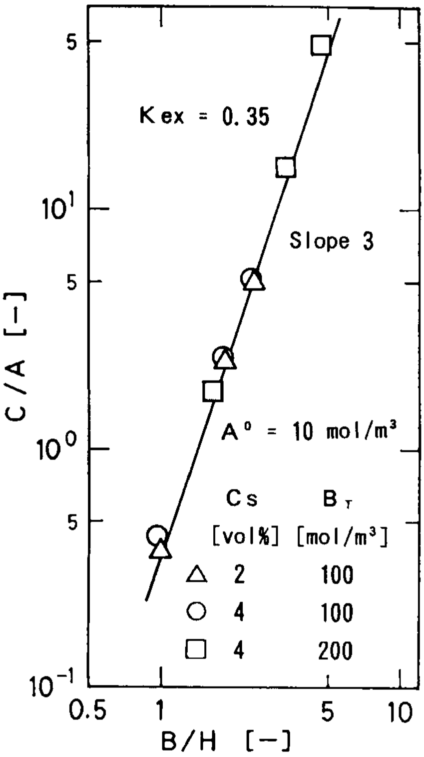

FIG. 4 Effect of Span 80 on the extraction equilibrium of lanthanum.

represented by the broken line in the figure and are in close agreement with the observed values. Therefore, the mass-transfer coefficient, k_A, is satisfactorily evaluated by Eq. (17).

Effect of Sulfuric Acid Concentration

Figure 6 shows the La concentration of the feed phase as a function of time when the initial concentration of sulfuric acid in the stripping phase, H_S^0, was changed. It is seen that the permeation rates of La are not affected by sulfuric acid concentrations above 0.5 kmol/m³.

Effect of pH of the Feed Solution

It is valuable to examine the validity of the k_f value used in this study. The experiment was therefore carried out with the pH value changed from

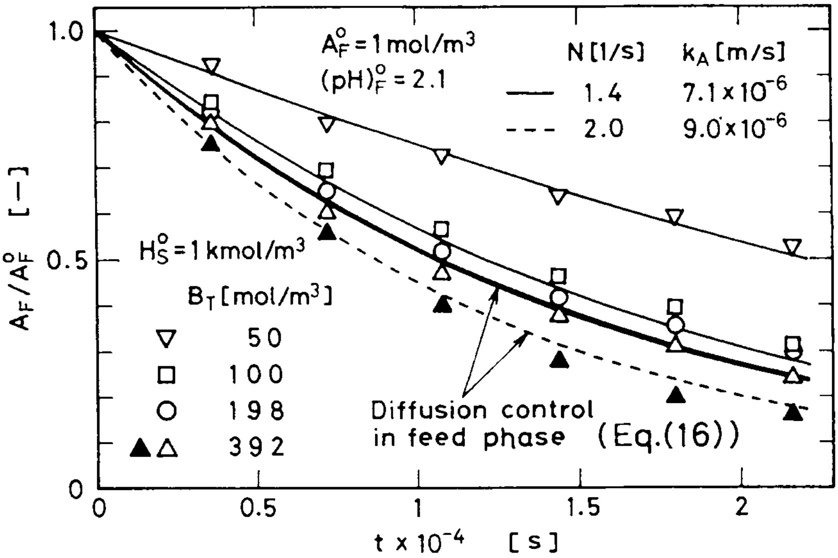

FIG. 5 Effect of HDEHP concentration and stirring speed on the permeation rate.

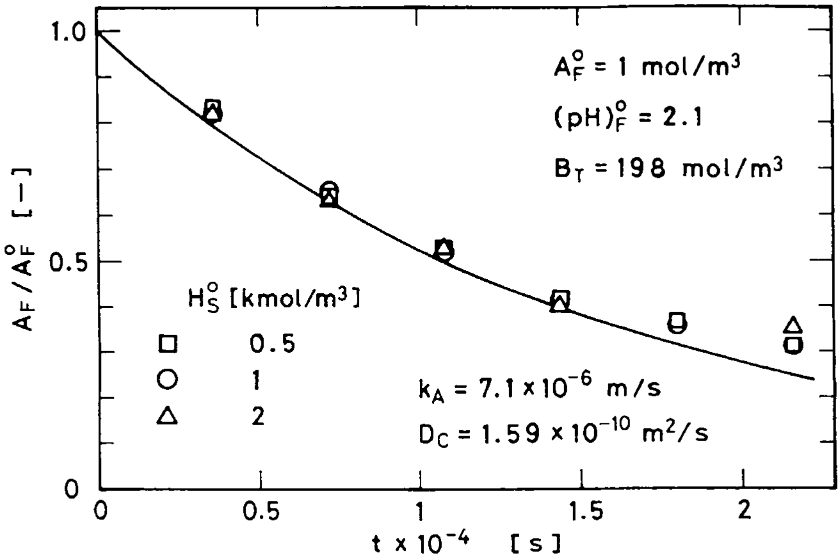

FIG. 6 Effect of sulfuric acid concentration on the permeation rate.

2.1 to 1.1 because the pH in the feed phase influences the reaction rate at the feed–membrane interface, i.e., the permeation rate of La is strongly influenced. The result is shown in Fig. 7. The permeation rate at pH 1.1 is very slow compared to that at 2.1, which is well expressed by model computations using the k_f value in Table 1.

Effect of Initial La Concentration in the Feed Solution

Figure 8 shows the variation of La concentration with time for different initial La concentrations in the feed phase. For each La concentration the computed values nearly agree with the observed values.

Effect of Initial La Concentration in the Stripping Solution

Next, permeation experiments were carried out under conditions where the stripping solution initially contained lanthanum 10, 97, and 760 times the initial feed concentration of $A_F^0 = 1\ \mathrm{mol/m^3}$. The results are shown in Fig. 9. The time-dependent concentrations of La in the feed phase are not influenced by the La concentration of the stripping solution, A_S^0, and lie on the computed line for the case of $A_S^0 = 0$. It is seen that even under conditions in which lanthanum exists in high concentration in the stripping

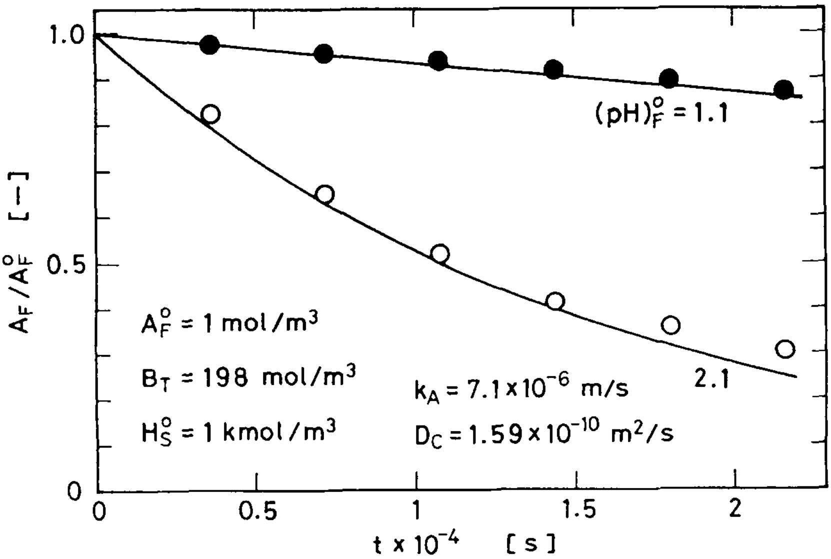

FIG. 7 Effect of pH in the feed solution on the permeation rate.

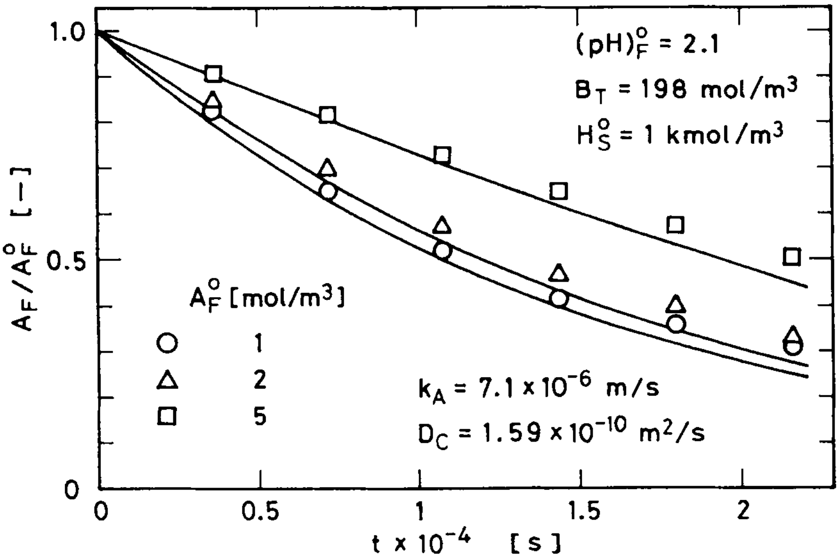

FIG. 8 Effect of initial lanthanum concentration in the feed solution on the permeation rate.

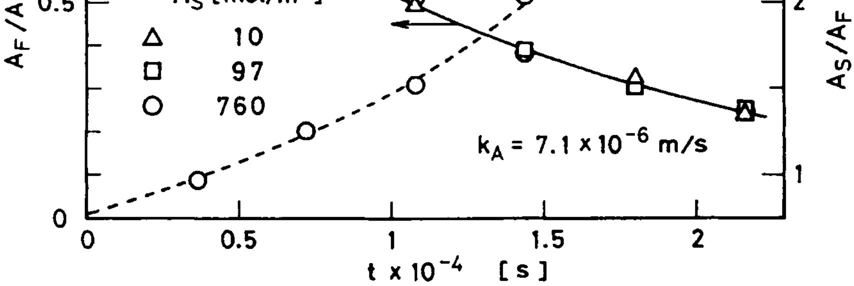

FIG. 9 Effect of initial lanthanum concentration in the stripping solution on the permeation rate.

solution, it permeates from the feed to the stripping phase at the same speed as in the case of $A_S^0 = 0$.

For A_S^0 of 760 mol/m^3, the ratio of La concentration in the stripping phase to that in the feed phase is also plotted as a function of time in Fig. 9. Its value starts from 760 and after 6 hours reaches to about 3200. Thus, lanthanum can be successfully pumped from the lower to the higher concentration phase.

Effect of Surfactant

The effect of addition of surfactant to the membrane phase on the permeation rate of La was investigated. Figure 10 shows the time-dependent concentrations of La measured by adding either Span 80 or ECA4360J. The addition of surfactant decreases the permeation rate remarkably, and ECA4360J produces a larger effect than Span 80. For both surfactants, however, there is no difference as the amount of addition goes from 1 to 4 vol%. On the assumption that such a decrease of the permeation rate is due to the effect of surfactant on the extraction reaction rate, the reaction rate constants, k_f, were obtained by fitting the model computation with the observed values. As is shown in the figure, the k_f values for Span 80 and ECA4360J decrease to about a thirtieth and a hundred-fortieth, respectively, of that without surfactant.

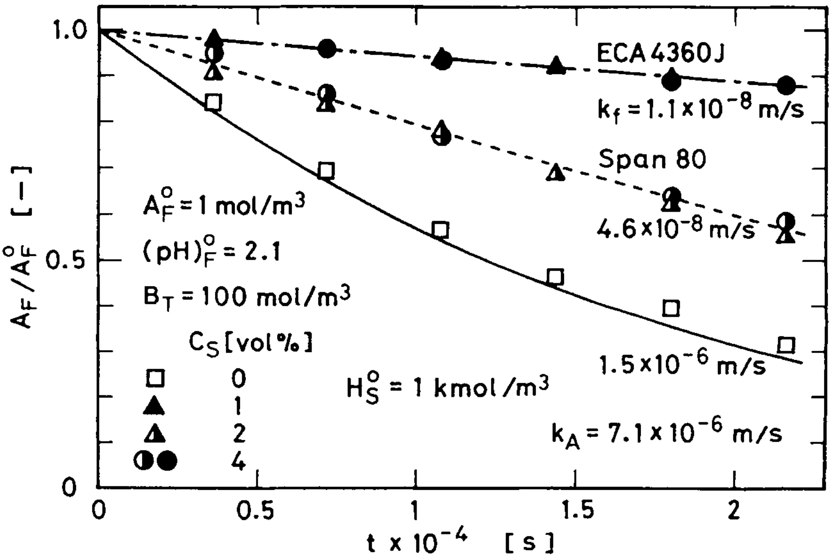

FIG. 10 Effect of surfactants in the membrane solution on the permeation rate.

The effect of Span 80 on the extraction rate of La has been investigated using a stirred cell with a flat liquid–liquid interface by Imai and Furusaki (19). From their results, a k_f value of 5.3×10^{-7} m/s was obtained for Shellsol-K diluent above a 1 wt% Span 80 concentration. The k_f value evaluated in this study is therefore less than a tenth of their value. The reason is not clear, but the difference may be due to the form of contact between the aqueous feed and the organic membrane solution. Attention should be paid to this phenomenon in La permeation by liquid surfactant membranes.

CONCLUSION

The permeation rates of lanthanum using a supported liquid membrane containing HDEHP were investigated to clarify the mechanism of lanthanum transport through the liquid membrane. Lanthanum permeates through the membrane from the feed solution to the stripping solution by means of extraction at the interface $x = 0$ and stripping at the interface $x = l$.

Lanthanum can be transported against its concentration gradient from the high pH solution to the low pH solution across the liquid membrane. The permeation rates of lanthanum can be explained by the permeation model which includes the extraction and the stripping reaction at the membrane interfaces, the diffusion process of the complex formed between lanthanum and HDEHP through the membrane, and the diffusion of lanthanum in the aqueous film adjacent to the membrane. The permeation rates decrease remarkably by the addition of surfactant to the membrane phase, and there is a difference in the effect of the surfactants Span 80 and ECA4360J. The results presented here provide fundamental and significant information on the practical application of liquid membranes to lanthanum separation and concentration.

NOTATIONS

A	concentration of lanthanum
B	concentration of dimer of HDEHP
B_T	initial concentration of dimer of HDEHP
C	concentration of complex
C_S	concentration of surfactant
D	diffusivity
d	diameter of impeller
H	concentration of hydrogen ion
J	flux

J_f	forward reaction rate at the feed–membrane interface
J_r	stripping reaction rate at the stripping–membrane interface
K_{ex}	extraction equilibrium constant
k	mass transfer coefficient
k_f	forward reaction rate constant
k_r	stripping reaction rate constant
l	thickness of supporting membrane
N	rotational speed of impeller
r_f	forward reaction rate
r_r	stripping reaction rate
S	membrane area
t	time
V	volume of the feed solution
x	distance from the feed–membrane interface
μ	viscosity of the aqueous solution
ρ	density of the aqueous solution
τ	membrane constant

Subscripts

A	lanthanum
B	dimer of HDEHP
C	complex
F	feed phase
H	hydrogen ion
l	interface at $x = l$
S	stripping phase
0	interface at $x = 0$

Superscript

0	initial

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