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Carrier-Mediated Transport of Rare Earth Ions through Supported Liquid Membranes

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Abstract

Fluxes of rare earth ions (Sc^{3+}, Y^{3+}, La^{3+}, Sm^{3+}, and Lu^{3+}) across supported liquid membranes using mixtures of nitrophenyl octyl, heptyl, or phenyl ethers and tris(2-*n*-butoxyethyl) phosphate (TBEP) as solvents and some β-diketones as carriers were determined. The effects of membrane composition, pH of the source phase, and carrier concentration on the flux are demonstrated. The effect of membrane composition is further discussed from the values of the membrane potential and the viscosity and electrical conductivity of the solvents. A maximal flux of lanthanum is observed for the membranes by using mixtures consisting of equal volumes of the nitrophenol derivative and TBEP. The fluxes of the rare earths, except scandium, decrease rapidly with decreasing pH difference between the source and receiving phases. The difference in flux among the rare earths, except scandium, is small. The flux increases in the carrier order benzoyl- > thenoyl- > furoyltrifluoroacetones. The lanthanum flux is proportional to the carrier concentration.

INTRODUCTION

In previous work (*1*) the effect of plasticizers on the carrier-mediated transport of zinc ion through cellulose triacetate (CTA) membranes was examined. When mixtures of nitrophenyl alkyl or phenyl ethers and tris(2-*n*-butoxyethyl) phosphate (TBEP) or ethyl benzoate were used as plasticizers of the CTA membrane, high fluxes of zinc ion were observed. This effect has also been confirmed by permeation experiments of rare earth ions (*2*) and phenylalanine (*3*) through the CTA membranes.

In the present work the nitrophenol derivative-TBEP mixtures mentioned above were used as solvents of liquid membranes supported by a microporous film, and the fluxes of trivalent rare earth ions (Sc^{3+}, Y^{3+}, La^{3+}, Sm^{3+}, and Lu^{3+}) across the liquid membranes were determined using some β-diketone carriers. To elucidate the effect of membrane composition on the flux, the membrane potential and the viscosity and electrical conductivity of the solvents were measured. In addition, the effects of pH and carrier concentration on the flux were discussed. This paper describes the ionic permeability of liquid membranes consisting of the mixed solvents.

EXPERIMENTAL

Supported Liquid Membranes

A microporous polypropylene film (Celgard 2400, Celanese Plastics Co.) was used as the support. The film is 25 μm thick and has a porosity of about 35% and an average pore size of 0.02 × 0.2 μm^2. A nitrophenol derivative-TBEP mixture containing a given concentration of carrier was immobilized within the pores of the microporous film by the method previously described (*4*). The nitrophenol derivatives used were *o*-nitrophenyl *n*-octyl ether (ONPOE) obtained from Dojindo Lab., *o*-nitrophenyl phenyl ether (ONPPE) from Eastman Kodak Co., and *p*-nitrophenyl *n*-heptyl ether (PNPHE) from Tokyo Kasei Kogyo Co. The TBEP was obtained from Aldrich Chemical Co. The carriers used were benzoyltrifluoroacetone (HBTA), thenoyltrifluoroacetone (HTTA), and furoyltrifluoroacetone (HFTA). These compounds were obtained from Tokyo Kasei Kogyo Co.

Permeability Measurements

The permeability cell consisted of two cylindrical glass compartments which were separated by the membrane. The two compartments containing source and receiving phases are hereafter referred to as Compartments I and II, respectively. In most experiments a cell consisting of equal volumes (30 mL) of two compartments was used. In the only experiments testing the effect of carrier concentration on the flux, the volumes of Compartments I and II used were 150 and 30 mL, respectively. The effective membrane areas of these two types of cells were 7.07 cm^2. The cell was placed in a water bath adjusted to 25 ± 0.1°C. The two compartments were stirred at 180 rpm using a pair of stirrers.

The supported liquid membrane was fixed between the two compartments, and two aqueous solutions were added to the compartments. Except in the case of the experiments testing the effect of carrier concentration, Compartment I initially contained 1.0 m*M* rare earth nitrate and 0.1 *M* sodium acetate buffer (pH 4.0 to 6.1), and Compartment II contained 1.0 m*M* rare earth nitrate and 0.05 *M* sulfuric acid. The rare earth concentrations in the two compartments were determined as a function of time by the xylenol orange method (*2*, *5*) after a small volume of the aqueous solutions had been pipetted off. In the experiments testing the effect of carrier concentration, Compartment I initially contained 5.0 m*M* lanthanum nitrate and 0.1 *M* sodium acetate buffer of pH 6.1, and Compartment II contained 0.05 *M* sulfuric acid. In this case, the lanthanum concentration in Compartment II was determined as a function of time by the same method described above.

Membrane Potential Measurements

The membrane potentials were measured using a Keithley Model 610C or 614 electrometer as described elsewhere (*6*).

Viscosity Measurements

Viscosities of the membrane solvents were measured at 25°C using an Ostwald viscometer. Each value of the viscosity was calculated from its relative value obtained by the measurements, using the value of ethylene glycol, 17.33 cP (*7*).

Electrical Conductivity Measurements

Electrical conductivities of the solvents were measured at 25°C using a TOA Electronics Model CG-7001PL electrode connected to a Yokogawa-Hewlett-Packard Model 4255A bridge.

RESULTS AND DISCUSSION

Effect of Membrane Composition

Plots of lanthanum concentrations in the two compartments against time for the supported liquid membranes using the mixtures of various proportions of ONPOE and TBEP and 50 m*M* HBTA are shown in Fig. 1. The membrane potential against time curves for these membranes are shown in Fig. 2. The shapes of the lanthanum concentration or membrane potential against time curves for the membranes using

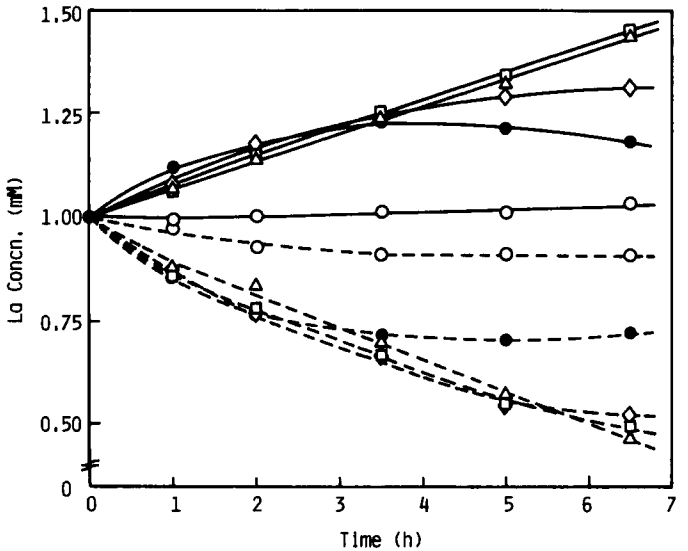

FIG. 1. Plots of lanthanum concentrations in the two compartments against time for the membranes using ONPOE–TBEP mixtures and 50 m*M* HBTA. Volume fraction of TBEP in the ONPOE–TBEP mixture: (○) 0, (△) 0.25, (□) 0.50, (◇) 0.75, (●) 1.00. The dash and solid lines represent the concentration curves in Compartments I and II, respectively.

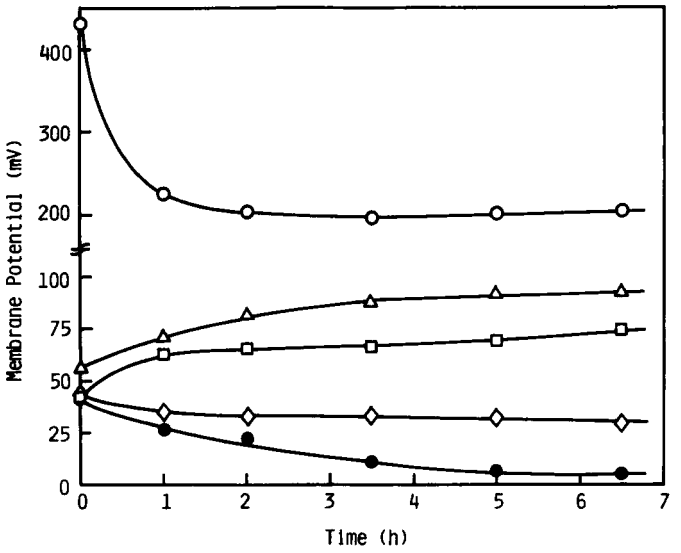

FIG. 2. Plots of membrane potential against time for the transport of lanthanum through the membranes using ONPOE-TBEP mixtures and 50 m*M* HBTA. Volume fraction of TBEP in the ONPOE-TBEP mixture: (○) 0, (△) 0.25, (□) 0.50, (◇) 0.75, (●) 1.00. The polarity of the membrane potential was positive in Compartment I with respect to Compartment II.

mixtures of ONPPE or PNPHE and TBEP were roughly similar to those shown in Figs. 1 or 2. From these concentration against time curves, the lanthanum fluxes across the membranes were calculated. The results obtained are presented in Fig. 3. In this case the flux is expressed as a mean value in the transport process for 6.5 h. The values of the membrane potentials at 1 and 6.5 h after the start of the lanthanum transport are listed in Table 1.

The lanthanum flux for the membrane using the nitrophenol derivative alone was very small, and a high membrane potential was observed throughout the transport process. On the other hand, the lanthanum concentration in Compartment II for the membrane using TBEP alone increased initially and then decreased with time. In this case the membrane potential decreased rapidly with time. The decreases in lanthanum concentration and membrane potential are likely due to the penetration of water into the membrane. In fact, the transparent membrane became whitely turbid in the permeation experiment. For the membranes using the nitrophenol derivative-TBEP mixtures, high fluxes of lanthanum were observed. However, the white turbidity often appeared

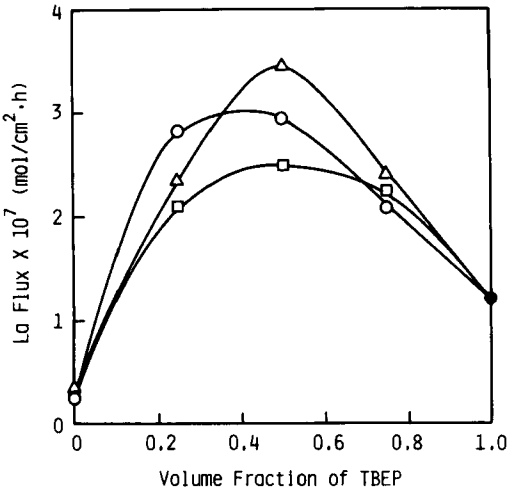

FIG. 3. Plots of lanthanum flux against volume fraction of TBEP for the membranes using nitrophenol derivative-TBEP mixtures: (○) ONPOE-TBEP, (△) ONPPE-TBEP, (□) PNPHE-TBEP. The carrier used was HBTA and its concentration was 50 m*M*. The flux is expressed as a mean value in the transport process for 6.5 h.

TABLE 1

Membrane Potentials 1 and 6.5 h after the Start of the Lanthanum Transport for Membranes Using the Nitrophenol Derivative-TBEP Mixtures[a]

Nitrophenol derivative	Time (h)	Membrane potential (mV)[b] Volume fraction of TBEP 0	0.25	0.50	0.75	1.00
ONPOE	1	223	71	62	35	26
	6.5	202	91	75	29	4
ONPPE	1	120	95	65	36	26
	6.5	123	68	37	31	4
PNPHE	1	223	95	47	36	26
	6.5	198	108	41	35	4

[a]The mixture contained 50 m*M* HBTA.

[b]The polarity of the membrane potential was positive in Compartment I with respect to Compartment II.

on the membranes using the mixtures containing TBEP above 50%. The increase in TBEP content brings about the penetration of water. Consequently, the flux may gradually decrease during the transport process.

The results of the measurements of viscosity and electrical conductivity of the solvents are presented in Figs. 4 and 5, respectively. The viscosity decreased with increasing volume fraction of TBEP in all cases. The diffusion coefficient of the carrier, D, in the membrane is defined by the following Stokes-Einstein equation:

$$D = kT/6\pi r\eta \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, r is the molecular radius of the complexed carrier, and η is the viscosity of the solvent. Since, as will be mentioned later, the flux is approximately proportional to the diffusion coefficient at a constant carrier concentration (from Eq. 1), it is inversely proportional to the viscosity. Hence,

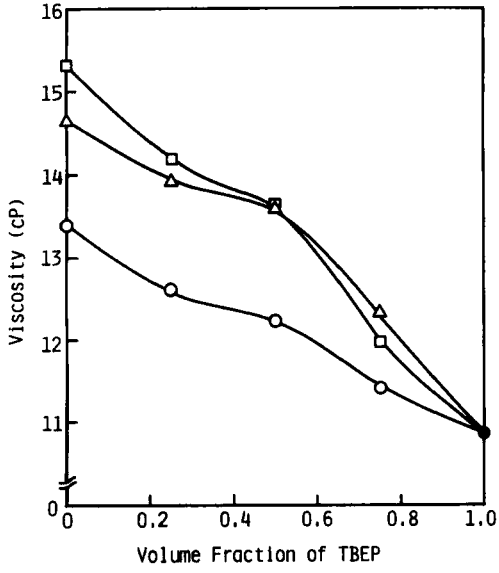

FIG. 4. Plots of viscosity against volume fraction of TBEP for nitrophenol derivative-TBEP mixtures: (○) ONPOE-TBEP, (△) ONPPE-TBEP, (□) PNPHE-TBEP.

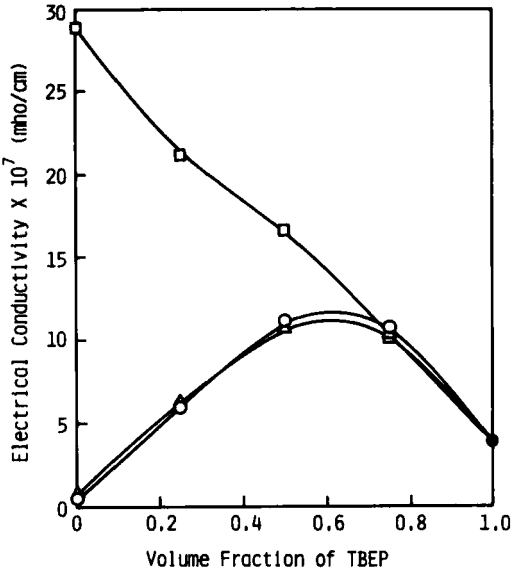

FIG. 5. Plots of electrical conductivity against volume fraction of TBEP for nitrophenol derivative-TBEP mixtures: (○) ONPOE-TBEP, (△) ONPPE-TBEP, (□) PNPHE-TBEP.

the decrease of the viscosity caused by the addition of TBEP may contribute somewhat to the increase in lanthanum flux.

On the other hand, the electrical conductivity for ONPOE and ONPPE showed a maximal value at a volume fraction of TBEP near 0.6. For PNPHE, it decreased with an increasing volume fraction of TBEP. The value for PNPHE alone was much higher than that for ONPOE or ONPPE alone. In the case of PNPHE, the membrane potential at an early stage of the membrane transport decreased with an increasing volume fraction of TBEP (Table 1) in spite of the decrease in electrical conductivity of the solvent (Fig. 5). This is because the electrical conductivity of the membrane containing HBTA increases by the transport of ions; that is, the increase in lanthanum flux. In other words, the distribution ratio of lanthanum between the membrane and the aqueous phase on the side of Compartment I increases by the addition of TBEP. Similarly, a decrease in membrane potential was observed for ONPOE- or ONPPE-TBEP mixtures. In these cases the electrical conductivity of the solvent was lower than that for PNPHE in the range of volume fraction of TBEP of 0 to 0.5. Therefore, an additional increase of the distribution ratio of lanthanum can be expected.

Effect of pH

The fluxes of rare earths using HBTA, HTTA, and HFTA as carriers were determined at pHs 4.0, 5.1, and 6.1 of the source phase. The results obtained are listed in Table 2. In all cases the membrane solvent used was the ONPOE-TBEP 3:1 mixture, and the carrier concentration was 50 m*M*.

The fluxes of rare earths except scandium decreased rapidly with a decreasing pH difference between both the aqueous phases. In the case of scandium, the difference in flux between pHs 4.0 and 6.1 was small. The transport of scandium may occur at lower pHs of the source phase than that of the other rare earths. No appreciable difference in flux among the rare earths, except scandium, was observed. The flux also increased in the carrier order HBTA > HTTA > HFTA. These tendencies are similar to those previously obtained for the CTA membranes (*2*).

Effect of Carrier Concentration

Plots of the lanthanum concentration in Compartment II against time for the membranes containing various concentrations of HBTA are

TABLE 2
Fluxes of Rare Earths at pHs 4.0, 5.1, and 6.1 for the Membranes Containing β-Diketones

		Flux × 10^7 (mol/cm^2 · h)[b]				
β-Diketone	pH[a]	Sc	Y	La	Sm	Lu
HBTA	4.0	1.6	0.7	0.4	1.0	0.7
	5.1	1.9	1.8	1.2	2.1	1.9
	6.1	1.9	2.7	2.8	3.1	2.8
HTTA	4.0	0.9	0.5	0.2	0.4	0.4
	5.1	1.1	1.3	1.0	1.3	1.2
	6.1	1.2	1.7	1.6	1.9	1.6
HFTA	4.0	0.1	0.1	0.1	0.1	0.2
	5.1	0.2	0.4	0.3	0.4	0.2
	6.1	0.2	0.4	0.4	0.5	0.4

[a]pH values of the source phase (Compartment I).
[b]Mean values in the transport process for 6.5 h.

shown in Fig. 6. The membrane solvent used was the ONPOE-TBEP 3:1 mixture. A similar relation was obtained for the membranes containing HTTA or HFTA, though the lanthanum concentrations in Compartment II were lower than those in the case of HBTA. Since the data of the lanthanum concentration against time gave approximately linear plots in the range 0.5 to 2 h, the lanthanum fluxes were calculated from the increments in lanthanum concentration in this range. The results obtained are presented in Fig. 7.

At the membrane-aqueous phase interface, the rare earth ion, M^{3+}, reacts with the β-diketone, HA, to form the complex, MA_3, inside the membrane as follows:

$$M^{3+} + 3HA = MA_3 + 3H^+ \quad (2)$$

The equilibrium constant, K, of the above reaction is given by

$$K = [MA_3][H^+]^3/[M^{3+}][HA]^3 \quad (3)$$

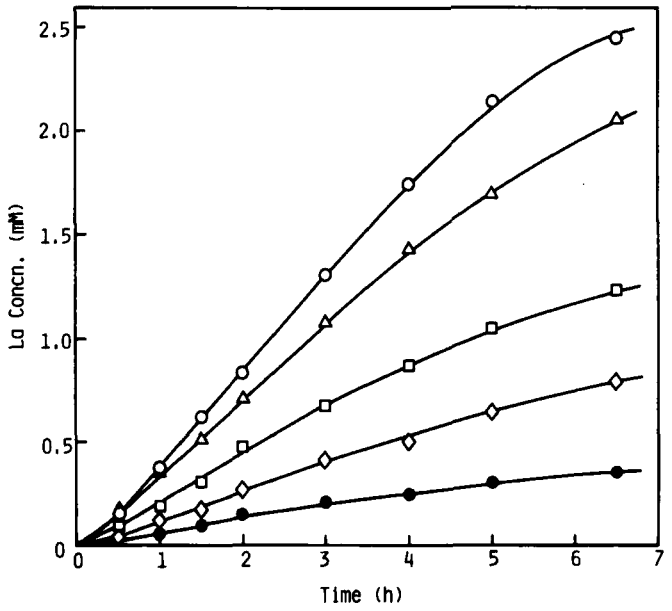

FIG. 6. Plots of lanthanum concentration in Compartment I against time for membranes containing various concentrations of HBTA: (●) 50 m*M*, (◇) 100 m*M*, (□) 150 m*M*, (△) 200 m*M*, (○) 250 m*M*. The membrane solvent used was the ONPOE-TBEP 3:1 mixture.

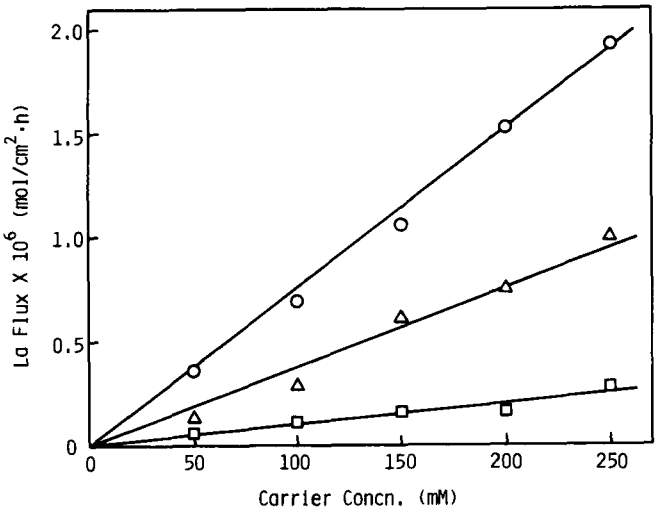

FIG. 7. Plots of lanthanum flux against carrier concentration for the membranes using β-diketones as carriers: (○) HBTA, (△) HTTA, (□) HFTA. The membrane solvent used was the ONPOE-TBEP 3:1 mixture. The flux is expressed as a mean value in the range of 0.5 to 2 h after the start of the lanthanum transport.

This relation can apply at both interfaces:

$$K = [MA_3]_0[H^+]_I^3/[M^{3+}]_I[HA]_0^3 = [MA_3]_L[H^+]_{II}^3/[M^{3+}]_{II}[HA]_L^3 \quad (4)$$

where the subscripts 0 and L refer to the membrane surfaces on the sides of Compartments I and II, respectively, and the subscripts I and II refer to the aqueous phases in Compartments I and II, respectively. Provided that the rare earth ion is transported only by the carrier in the membrane, the flux of the ion, J_M, across the membrane is given by

$$J_M = D_{MA_3}([MA_3]_0 - [MA_3]_L)/L \quad (5)$$

where D_{MA_3} is the diffusion coefficient of the rare earth-β-diketone complex in the membrane, and L is the membrane thickness. Assuming that the reactions at both interfaces, represented by Eq. (2), are fast relative to diffusion, and that the pH difference between both the aqueous phases is great, the value of $[MA_3]_L$ in Eq. (5) can be neglected. Hence, Eq. (5) becomes

$$J_M = D_{MA_3}[MA_3]_0/L \tag{6}$$

The total concentration of carrier added to the membrane, $\bar{C}$, is given by

$$\bar{C} = [HA] + 3[MA_3] \tag{7}$$

At the membrane surface on the side of Compartment I, Eq. (7) becomes

$$\bar{C} = [HA]_0 + 3[MA_3]_0 \tag{8}$$

Provided that the value of $[MA_3]_0$ is considerably smaller than that of $\bar{C}$, from Eqs. (4), (6), and (8) we obtain (*2*)

$$J_M = D_{MA_3}K[M^{3+}]_I\bar{C}^3/L([H^+]_I^3 + 9K[M^{3+}]_I\bar{C}^2) \tag{9}$$

In the case of $[H^+]_I^3 \ll 9K[M^{3+}]_I\bar{C}^2$, Eq. (9) becomes

$$J_M = D_{MA_3}\bar{C}/9L \tag{10}$$

When the β-diketones were added to the solvent (ONPOE–TBEP 3:1 mixture), a slight decrease in viscosity was observed for some of the mixtures: the viscosity decreased 4 and 6% for HBTA, and 3 and 4% for HFTA at concentrations of 200 and 250 m*M*, respectively. In the other cases it remained unaltered. Even if the decrease in viscosity by the addition of the β-diketones is taken into consideration, the results shown in Fig. 7 satisfy Eq. (10).

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