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Effect of Quaternary Ammonium Salts on Carrier-Mediated Transport of Lanthanide Ions through Cellulose Triacetate Membranes

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ABSTRACT

Fluxes of all lanthanides, except promethium, across cellulose triacetate membranes were determined by using mixtures of *o*-nitrophenyl *n*-octyl ether and quaternary ammonium salts as plasticizers, and 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (BMPP) and 4-trifluoroacetyl-3-methyl-1-phenyl-5-pyrazolone (TMPP) as carriers. The quaternary ammonium salts used were didodecyldimethyl-, distearyldimethyl-, tetrahexyl-, tetraoctyl-, and tetradecylammonium bromides [referred to as $(C_{12})_2NBr$, $(C_{18})_2NBr$, $(C_6)_4NBr$, $(C_8)_4NBr$, and $(C_{10})_4NBr$, respectively]. The effect of these ammonium bromides on the flux was demonstrated. For membranes containing 0.1 M $(C_{12})_2NBr$ and $(C_{18})_2NBr$, BMPP exhibited considerably high fluxes. The fluxes of lanthanum and cerium using BMPP for $(C_{12})_2NBr$ were higher than those of the other lanthanides. For the membranes containing 0.5 M $(C_{12})_2NBr$ and 0.1 M $(C_{18})_2NBr$, however, no difference in flux among the lanthanides was observed. The fluxes using TMPP for $(C_{12})_2NBr$ and $(C_{18})_2NBr$ were very small, with the exception of some lanthanides. Appreciably high fluxes were observed for membranes containing 0.1 M $(C_6)_4NBr$ using BMPP. For $(C_8)_4NBr$ and $(C_{10})_4NBr$, BMPP exhibited low fluxes. For these membranes using TMPP, the lanthanides were scarcely transported.

INTRODUCTION

In previous work (1) the author studied the effect of polyoxyethylene *n*-alkyl ethers (POE ethers) on the transport of trivalent lanthanide ions through cellulose triacetate (CTA) membranes containing hinokitiol (β-isopropyltropolone; HIPT) as carrier. POE ethers with different alkyl and polyoxyethylene chain lengths were incorporated in the CTA membrane as plasticizers, together with *o*-nitrophenyl *n*-octyl ether (ONPOE). The lanthanide flux was markedly affected by these chain lengths. The highest flux was observed for the incorporation of trioxyethylene *n*-dodecyl ether [$C_{12}H_{25}(OCH_2CH_2)_3OH$, referred to as $C_{12}E_3$]. However, the order of the lanthanides in the flux was not altered by the type of POE ether.

For the present work, the effect of quaternary ammonium salts having two or four long alkyl chains on the transport of trivalent lanthanide ions through the CTA membranes was demonstrated by using two pyrazolone derivatives, 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (BMPP) and 4-trifluoroacetyl-3-methyl-1-phenyl-5-pyrazolone (TMPP), as carriers. It has been known that quaternary ammonium salts having two long alkyl chains form stable bilayer membranes similar to phospholipids (2, 3). In addition, they have been used as stabilizers for emulsion-type liquid membranes (4).

In the present work the fluxes of 14 kinds of lanthanides are first determined by using a mixture of $C_{12}E_3$ and ONPOE as the plasticizer. From this result, the lanthanide-binding and transport functions of the pyrazolone carriers are compared with those of the HIPT carrier used in previous work (1). Subsequently, the lanthanide fluxes are determined by using mixtures of di-*n*-alkyldimethyl- or tetra-*n*-alkylammonium bromides and ONPOE as the plasticizers. From the experimental results, the effect of these ammonium bromides on the transport of the lanthanides is discussed.

EXPERIMENTAL

Preparation of CTA Membranes

Five milliliters of a dichloromethane solution containing 12.5 g/L CTA, 0.2 mL of a ONPOE solution containing 0.1 or 0.5 M of the quaternary ammonium salt, or 0.5 M $C_{12}E_3$, and 0.2 mL of a dichloromethane solution containing 100 mM of BMPP or TMPP were mixed in a glass culture dish (flat bottom, 6 cm diameter). The mixed solution was slowly air-dried at room temperature, as described previously (5, 6). The thickness of the resulting membrane was about 0.06 mm. The concentrations of the plasticizer and carrier in the membrane were the same as those for the membranes used in previous work (1). In the present paper the concentrations of the quaternary ammonium salts and $C_{12}E_3$ in the membrane are expressed as their concentrations in the plasticizer. The CTA was obtained from Eastman Kodak Co., ONPOE from Dojindo Lab., and $C_{12}E_3$ from Sigma Chemical Co. The quaternary ammonium salts used were didodecyldimethyl-, distearyldimethyl-, tetrahexyl-, tetraoctyl-, and tetradecylammonium bromides. For brevity, these will be referred to as $(C_{12})_2NBr$, $(C_{18})_2NBr$, $(C_6)_4NBr$, $(C_8)_4NBr$, and $(C_{10})_4NBr$, respectively. $(C_{12})_2NBr$, $(C_{18})_2NBr$, and $(C_{10})_4NBr$ were obtained from Tokyo Kasei Kogyo Co., $(C_6)_4NBr$ from Eastman Kodak Co., and $(C_8)_4NBr$ from Lancaster Synthesis Ltd. The carriers, BMPP and TMPP, were obtained from Tokyo Kasei Kogyo Co.

Permeability Measurements

The apparatus was the same as that used in previous work (1): the half volume of the permeability cell was 32 mL, and the effective membrane area was 7.07 cm^2. The CTA membrane was fixed between two compartments of the cell. Two aqueous solutions were added to the compartments: one (source phase; Compartment I) initially contained 1.0 mM lanthanide nitrate and 0.1 M sodium acetate buffer of pH 6.1, and the other (receiving phase; Compartment II) contained 1.0 mM lanthanide nitrate and 0.05 M sulfuric acid. The permeation experiments were performed at 25°C. The lanthanide concentrations in the two compartments after a definite time were determined by the xylenol orange method (6, 7).

Membrane Potential Measurements

The membrane potentials were measured by using a Keithley Model 610C electrometer as described elsewhere (8, 9).

Viscosity Measurements

The relative viscosities of the plasticizers used were measured at 25°C by the method described in a previous paper (1).

RESULTS AND DISCUSSION

Lanthanide Fluxes for $C_{12}E_3$

The shapes of the curves of lanthanide concentrations in the two compartments against time obtained from the permeation experiments were similar to those shown in previous papers (1, 7); some of these curves will be shown later. The lanthanide fluxes across the CTA membranes in the presence and absence of $C_{12}E_3$ are shown in Fig. 1. In the present paper the flux obtained from the permeation experiment is expressed as the mean value in the transport process for 6.5 hours. Further, it is plotted against an ionic radius (10) of the trivalent lanthanide in six-coordination for the reason given in a previous paper (7).

The pyrazolone derivatives, BMPP and TMPP, behaved as carriers of the lanthanides in the present membrane systems. The fluxes using BMPP were higher than those using TMPP. In addition, these values for BMPP were higher than those obtained for HIPT under the same experimental condition in a previous work (1). However, no difference in the flux among the lanthanides was observed. On the other hand, the flux using TMPP increased rapidly with an increase in the ionic radius in the range of neodymium to lanthanum. For the membranes containing no $C_{12}E_3$, BMPP exhibited relatively low fluxes, while the fluxes using TMPP were very

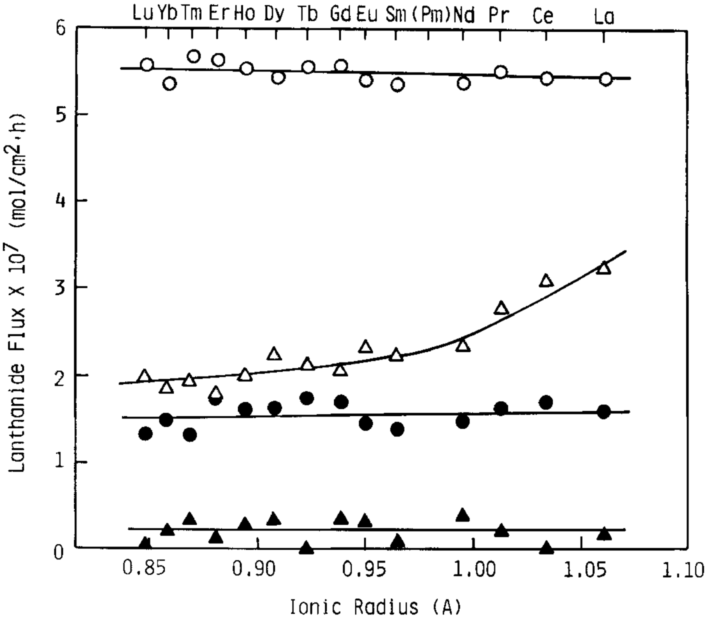

FIG. 1 Lanthanide fluxes using BMPP and TMPP for the membranes containing 0.5 M $C_{12}E_3$: (○) BMPP, (△) TMPP. $C_{12}E_3$ absent: (●) BMPP, (▲) TMPP.

small. In these cases no difference in the flux among the lanthanides was observed. For the extractions of uranium and beryllium by BMPP and TMPP in chloroform, it has been known that the values of $\beta_N p_N$ (β_N: stability constant, p_N: partition coefficient) for the BMPP–metal complexes are higher than those for the TMPP–metal complexes (11, 12); i.e., the quantities of the metals extracted by BMPP are larger than those extracted by TMPP. Therefore, the higher fluxes of the lanthanides using BMPP are likely due to the extraction of larger quantities of the lanthanides in the membrane phase.

Effect of Quaternary Ammonium Salts

Plots of lanthanum concentrations in the two compartments and membrane potential against time for the membranes containing $(C_{12})_2NBr$, $(C_{18})_2NBr$, $(C_6)_4NBr$, and $(C_{10})_4NBr$ are shown in Figs. 2 and 3. The tendencies of the curves of membrane potential against time for the other lanthanides are similar to those shown in Figs. 2 and 3. The lanthanide fluxes using BMPP and TMPP for the membranes containing $(C_{12})_2NBr$ and $(C_{18})_2NBr$ are shown in Fig. 4. Those using BMPP for $(C_6)_4NBr$, $(C_8)_4NBr$, and $(C_{10})_4NBr$ are shown in Fig. 5. The fluxes of lanthanum,

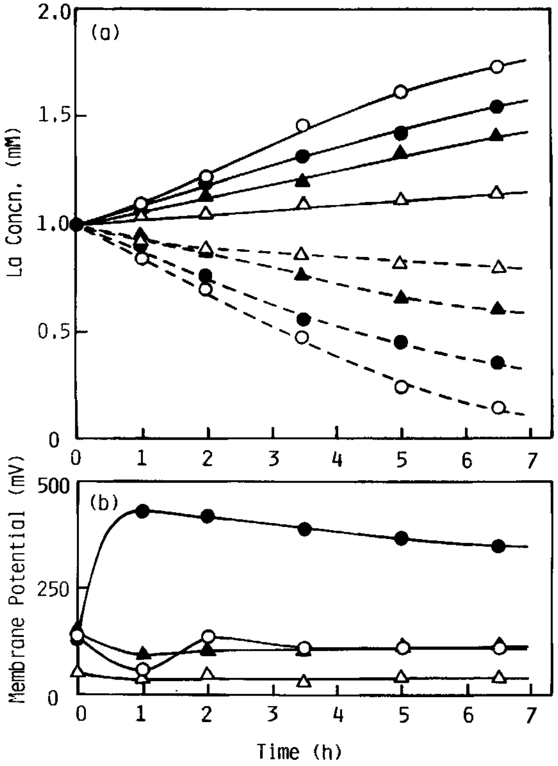

FIG. 2 Plots of lanthanum concentrations in the two compartments (a) and membrane potential (b) against time for the membranes containing 0.1 M $(C_{12})_2NBr$ and $(C_{18})_2NBr$ using BMPP and TMPP: (○) $(C_{12})_2NBr$-BMPP, (△) $(C_{12})_2NBr$-TMPP, (●) $(C_{18})_2NBr$-BMPP, (▲) $(C_{18})_2NBr$-TMPP. The dashed and solid lines (a) represent the concentration against time curves in Compartments I and II, respectively. The polarity of the membrane potential (b) was positive in Compartment I with respect to Compartment II.

praseodymium, samarium, terbium, erbium, and lutetium using TMPP for the membranes containing 0.5 M $(C_{12})_2NBr$ and 0.1 M $(C_6)_4NBr$, $(C_8)_4NBr$, and $(C_{10})_4NBr$ are listed in Table 1.

In the presence of the quaternary ammonium salts, the lanthanides were transported more effectively by BMPP than by TMPP. The fluxes using TMPP were very small, with the exception of lanthanum, cerium, praseodymium, and neodymium for the membranes containing 0.1 M $(C_{12})_2NBr$ and $(C_{18})_2NBr$.

As described in a previous paper (7), the flux of a metal ion, J_M, across a membrane depends on the concentration of the carrier–metal complex

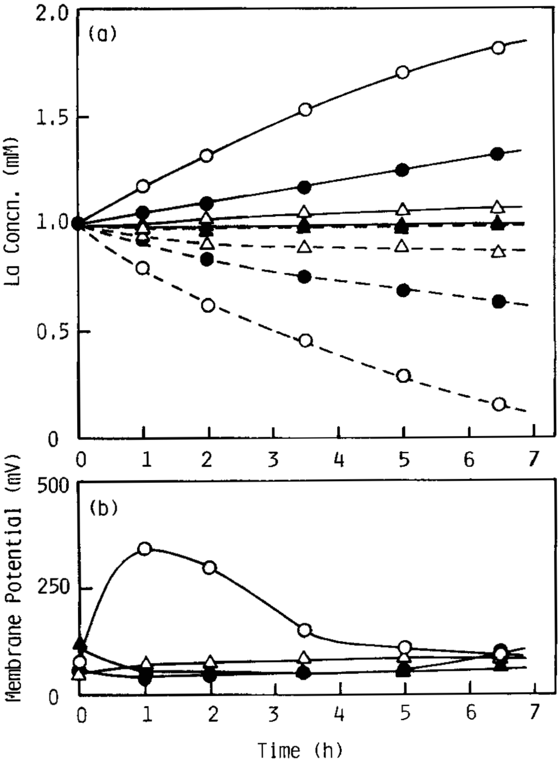

FIG. 3 Plots of lanthanum concentrations in the two compartments (a) and membrane potential (b) against time for the membranes containing 0.1 M $(C_6)_4NBr$ and $(C_{10})_4NBr$ using BMPP and TMPP: (○) $(C_6)_4NBr$-BMPP, (△) $(C_6)_4NBr$-TMPP, (●) $(C_{10})_4NBr$-BMPP, (▲) $(C_{10})_4NBr$-TMPP. The curves have the same meanings as in Fig. 2.

at the membrane surface on the side of the source phase (Compartment I), $[MA]_0$, and the viscosity of the membrane phase, η, as follows:

$$J_M \cong D_{MA}[MA]_0/L \tag{1}$$

$$D_{MA} = kT/6\pi r\eta \tag{2}$$

where D_{MA} is the diffusion coefficient of the complex in the membrane, L is the membrane thickness, k is the Boltzmann constant, T is the absolute temperature, and r is the molecular radius of the complex. The value of $[MA]_0$ also depends on the stability constant of the complex and on its partition coefficient between the membrane and aqueous phases (12).

The addition of the quaternary ammonium salts to the plasticizer in the membrane brings about the changes in both the viscosity of the membrane

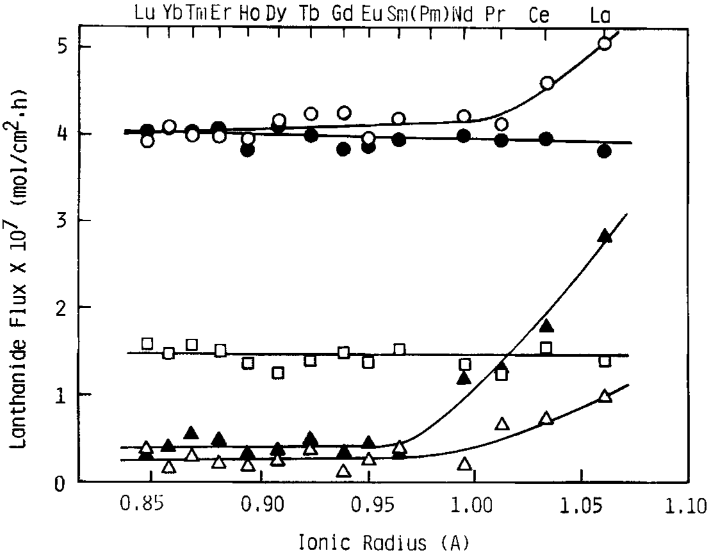

FIG. 4 Lanthanide fluxes using BMPP and TMPP for the membranes containing $(C_{12})_2NBr$ and $(C_{18})_2NBr$: (○) 0.1 M $(C_{12})_2NBr$-BMPP, (△) 0.1 M $(C_{12})_2NBr$-TMPP, (□) 0.5 M $(C_{12})_2NBr$-BMPP, (●) 0.1 M $(C_{18})_2NBr$-BMPP, (▲) 0.1 M $(C_{18})_2NBr$-TMPP.

phase and the partition coefficient of the complex at the interface. Consequently, these changes affect the lanthanide flux. In fact, for membranes containing $(C_{18})_2NBr$ using BMPP, the highest flux of samarium was observed at a concentration of 0.1 M $(C_{18})_2NBr$. In addition, as seen in Fig. 4, the fluxes using BMPP decreased as the concentration of $(C_{12})_2NBr$ varied from 0.1 to 0.5 M.

The relative viscosity values of the plasticizers used are listed in Table 2. The viscosities of the plasticizers containing 0.5 M $(C_{12})_2NBr$ and 0.1 M $(C_{18})_2NBr$ and $(C_{10})_4NBr$ could not be measured. In these ONPOE solutions, $(C_{12})_2NBr$ and $(C_{18})_2NBr$ formed suspended aggregates or gels, and a part of $(C_{10})_4NBr$ precipitated.

The fluxes using BMPP and TMPP increased by the addition of $C_{12}E_3$ to the plasticizer (Fig. 1). These results are likely due to increases in the partition coefficients of BMPP- and TMPP-lanthanide complexes. As described in a previous paper (1), the increase in the partition coefficient may be attributed to the slight decrease in lipophilicity of the membrane phase. In the case of the quaternary ammonium salts, they combine extreme lipo- and hydrophilicities in the same molecule. Hence, some of their molecules are apt to be oriented at the membrane surface, and the others

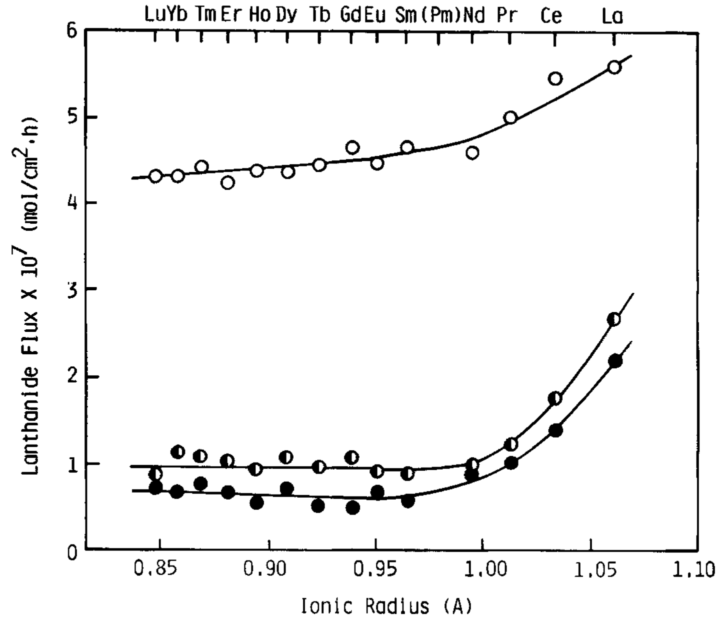

FIG. 5 Lanthanide fluxes using BMPP for the membranes containing 0.1 M $(C_6)_4NBr$, $(C_8)_4NBr$, and $(C_{10})_4NBr$: (○) $(C_6)_4NBr$, (◐) $(C_8)_4NBr$, (●) $(C_{10})_4NBr$.

form micelles or aggregates in the inner phase of the membrane; the lipophilicity of the membrane surface decreases and that of the inner phase varies with the form of the aggregated molecules.

On the other hand, it has been known that the lanthanide nitrates can be extracted by trioctylmethylammonium salt in kerosene, and its extract-

TABLE 1
Lanthanide Fluxes Using TMPP for the Membranes Containing $(C_{12})_2NBr$, $(C_6)_4NBr$, $(C_8)_4NBr$, and $(C_{10})_4NBr$

Ammonium salt	Concentration[a] (M)	Flux × 10^7 (mol/cm^2·h)					
		La	Pr	Sm	Tb	Er	Lu
$(C_{12})_2NBr$	0.5	0.3	0.2	0.2	0	0.2	0
$(C_6)_4NBr$	0.1	0.4	0	0	0.3	0.2	0
$(C_8)_4NBr$	0.1	0	0	0	0	0	0.2
$(C_{10})_4NBr$	0.1	0	0.1	0	0	0	0

[a] Concentration of the quaternary ammonium salt added to the plasticizer incorporated in the membrane.

TABLE 2
Relative Viscosities of Plasticizers Incorporated in the Membranes

Plasticizer	Relative viscosity[a]
ONPOE	1.00
ONPOE + 0.5 M $C_{12}E_3$	1.05[b]
ONPOE + 0.1 M $(C_{12})_2NBr$	1.28
ONPOE + 0.1 M $(C_6)_4NBr$	1.20
ONPOE + 0.1 M $(C_8)_4NBr$	1.30

[a] Viscosity ratio of plasticizer to ONPOE.
[b] Value obtained in the previous work (1).

ability is excellent for lanthanides having large ionic radii, particularly lanthanum (13). In fact, a low flux of lanthanum was observed in cotransport of lanthanum and thiocyanate or perchlorate ions using the membrane containing 0.1 M trioctylmethylammonium chloride as carrier. In the similar cotransport of lanthanum and thiocyanate ions using the membranes containing 0.1 M $(C_{12})_2NBr$, $(C_{18})_2NBr$, and $(C_6)_4NBr$, no transport of lanthanum occurred. However, in the countertransport systems used in the present work, a decrease in the lanthanum concentration in Compartment I was observed for the membranes containing 0.1 M $(C_{12})_2NBr$, $(C_{18})_2NBr$, $(C_6)_4NBr$, and $(C_{10})_4NBr$ in the absence of BMPP or TMPP. The order of the decrease in the lanthanum concentration was $(C_{12})_2NBr > (C_{18})_2NBr \gg (C_6)_4NBr > (C_{10})_4NBr$. These facts show the existence of an interaction between the quaternary ammonium salt and lanthanide. The interaction may contribute to the transport of the lanthanides, particularly those having a large ionic radius.

As seen in Fig. 4, BMPP exhibited considerably high fluxes for membranes containing 0.1 M $(C_{12})_2NBr$ and $(C_{18})_2NBr$. However, as the concentration of $(C_{12})_2NBr$ increased, the fluxes decreased. The fluxes of lanthanum and cerium using BMPP for the membranes containing 0.1 M $(C_{12})_2NBr$ were higher than those of the other lanthanides. The higher fluxes may be attributed to the interaction between $(C_{12})_2NBr$ and lanthanum or cerium. For membranes containing 0.5 M $(C_{12})_2NBr$ and 0.1 M $(C_{18})_2NBr$, no difference in the flux among the lanthanides was observed. In these cases the effect of the interaction between the quaternary ammonium salt and lanthanide disappeared. This result is likely due to the formation of micelles or aggregates of the quaternary ammonium salt in the membrane; the oriented alkyl chains of the quaternary ammonium salt affect the transport of the BMPP–lanthanide complex in the membrane more strongly. It is thought that remarkably high membrane potentials for the membranes containing 0.1 M $(C_{18})_2NBr$ are developed when large quantities of the complexes are transported through the lipophilic region between the micelles or aggregates.

On the other hand, TMPP exhibited very low fluxes for membranes containing $(C_{12})_2NBr$ and $(C_{18})_2NBr$, with the exception of some lanthanides (Fig. 4 and Table 1). These low fluxes are the result of high hydrophilicity of the membrane surface, which brings about a decrease in the partition coefficient of the TMPP–lanthanide complex at the interface. The relatively high fluxes of the lanthanides from lanthanum to neodymium (Fig. 4) may be attributed to a strong interaction between the TMPP and lanthanide, as in the case of $C_{12}E_3$. For these membrane systems the effect of the interaction between the quaternary ammonium salt and lanthanide is not clear.

Appreciably high fluxes were observed for membranes containing 0.1 M $(C_6)_4NBr$ using BMPP. For the membrane containing 0.1 M $(C_8)_4NBr$ and $(C_{10})_4NBr$, BMPP exhibited low fluxes (Fig. 5). In these cases the flux increased in the range of the lanthanides from neodymium to lanthanum. These higher fluxes are likely due to the interaction between the quaternary ammonium salt and lanthanide. The orientation of the quaternary ammonium salts having four long alkyl chains is lower than that of the double-chain ammonium salts. Therefore, the effect of these alkyl chains on the transport of the complex must be small. The low fluxes for $(C_8)_4NBr$ and $(C_{10})_4NBr$ may be caused by an increase in lipophilicity of the inner phase of the membrane with increasing alkyl chain length.

For membranes containing $(C_6)_4NBr$, $(C_8)_4NBr$, and $(C_{10})_4NBr$ using TMPP, little or no transport of the lanthanides occurred. These results are mainly due to the high hydrophilicity of the membrane surface. In these cases, however, the effects of the interaction between the quaternary ammonium salt and lanthanide, and the lipophilicity of the membrane phase on the transport, are not clear.

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