Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Sugiura, Masaaki(1990) 'Transport of Lanthanide Ions through Cellulose Triacetate Membranes Containing Hinokitiol and Flavonol as Carriers', Separation Science and Technology, 25: 11, 1189 — 1199
To link to this Article: DOI: 10.1080/01496399008051847
URL: http://dx.doi.org/10.1080/01496399008051847

SEPARATION SCIENCE AND TECHNOLOGY, 25(11 & 12), pp. 1189–1199, 1990

Transport of Lanthanide Ions through Cellulose Triacetate Membranes Containing Hinokitiol and Flavonol as Carriers

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Abstract

Fluxes of trivalent lanthanide ions across cellulose triacetate membranes were determined by using hinokitiol (HIPT) and flavonol (HFL) as carriers. The transport of the lanthanides was coupled to a flow of hydrogen ions. The effects of added anion and the pH in the source phase, and the plasticizer incorporated in the membrane on the lanthanide flux, were examined. In the case of HIPT, the fluxes for the lanthanides from samarium to lutetium were much higher than those for lanthanum to neodymium. In the transport using HFL, the flux increased with decreasing ionic radius of the lanthanide species. The addition of perchlorate or thiocyanate ions to the source phase resulted in a rise in the lanthanide flux. With decreasing pH difference between the aqueous phases, the fluxes using HIPT decreased gradually while those using HFL decreased rapidly. The flux was affected by the type of plasticizer added to the membrane.

INTRODUCTION

In a previous work (*1*) the fluxes of trivalent rare earth ions across cellulose triacetate (CTA) membranes containing a plasticizer were determined by using several β-diketone carriers. In these transport processes the flows of the rare earth and hydrogen ions were coupled. When benzoyl- and thenoyltrifluoroacetones were used as the carriers, appreciably high fluxes of the rare earths were observed. However, no significant difference in flux among the rare earths was recognized, with the exception of scandium. A similar relation was obtained in systems of supported liquid membranes using the above-mentioned carriers (*2*).

It has been shown (*3*) that the free energy of formation of a complex between a metal ion and ligand is directly and inversely proportional to the charge and the crystal radius of the metal ion, respectively. Actually,

in the solvent extraction of lanthanides whose crystal radii resemble each other, the differences in value of the extraction constant and of the pH at which extraction occurs among the lanthanides are small (*4*). In the carrier-mediated transport of a metal ion through a membrane, its flux depends mainly on the concentration of the metal–carrier complex extracted at the membrane surface on the side of the source phase and on the diffusion coefficient of the complex in the membrane, as will be described below. In the membrane transport of lanthanides, therefore, the difference in flux among the lanthanides may be small if the structures of the complexes formed resemble each other.

For the present work the fluxes of all lanthanides, except promethium, across CTA membranes were determined by using hinokitiol (β-isopropyltropolone; HIPT) and flavonol (3-hydroxyflavone; HFL) as carriers. These carriers exhibited a significant difference in flux among the lanthanides. In addition, this paper describes the effects of anion and pH in the source phase and of the plasticizer incorporated in the membrane on the lanthanide flux.

EXPERIMENTAL

Preparation of Cellulose Triacetate Membrane

In 200 mL dichloromethane, 2.5 g CTA obtained from Eastman Kodak Co. was dissolved. Five milliliters of the CTA solution, 1.5 mL of a dichloromethane solution containing 10 vol% *o*-nitrophenyl *n*-octyl ether (ONPOE), 0.5 mL of a dichloromethane solution containing 10 vol% tris(2-*n*-butoxyethyl) phosphate (TBEP), and 2 mL of a dichloromethane solution containing 10 m*M* HIPT or HFL were mixed in a glass culture dish (flat bottom, 6 cm diameter). The ONPOE and TBEP were used as plasticizers of the CTA. In experiments testing the effect of plasticizer on the lanthanide flux, tri-*n*-amyl phosphate (TAP), sorbitan trioleate (Span 85), polyoxyethylene monooleyl ether (POEOE, average number of oxyethylene units; $n = 2$), and polyoxyethylene mono-*p*-nonylphenyl ether (POENE, $n = 2$) were used in place of TBEP. After the mixed solution in the culture dish was slowly air-dried at room temperature, the resulting membrane was peeled from its bottom, as described previously (*1*, *5*). The thickness of the membrane was about 0.06 mm. The plasticizer ONPOE was obtained from Dojindo Lab.; TBEP form Aldrich Chemical Co.; Span 85 from Wako Pure Chemical Ind.; and POEOE and POENE from Tokyo Kasei Kogyo Co., Ltd. The carrier HIPT was obtained from Kanto Chemical Co. and HFL from Eastman Kodak Co.

Apparatus

The apparatus used for the permeation experiments was similar to that previously used (*1*, *5*): the permeability cell consisted of two cylindrical glass compartments. The half-cell volume was 32 mL and the effective membrane area was 7.07 cm^2.

Procedure

The CTA membrane was fixed between two compartments of the cell. To each compartment was added 32 mL of an aqueous solution: one (source phase; Compartment I) initially contained 1.0 m*M* lanthanide nitrate and 0.1 *M* sodium acetate buffer of pH 6.1, and the other (receiving phase; Compartment II) contained 1.0 m*M* lanthanide nitrate and 0.05 *M* sulfuric acid. In the permeation experiments using these aqueous phases and the CTA membranes containing ONPOE and TBEP, all lanthanides, except promethium, were used. In experiments testing the effect of anion on the lanthanide flux, Compartment I additionally contained 0.1 *M* sodium perchlorate, thiocyanate, nitrate, or chloride. In experiments testing the effect of pH on the flux, Compartment I contained 0.1 *M* sodium acetate buffer of pH 4.0, 4.5, 5.1, or 5.5 in place of that of pH 6.1. The lanthanides used in these two types of experiments and in experiments testing the effect of plasticizer on the flux were lanthanum, praseodymium, samarium, terbium, erbium, and lutetium. All 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 (*1*, *2*, *6*): after a small volume of the aqueous solution had been pipetted off (0.05 mL La, Ce, Pr, Nd, Sm, and Eu; 0.03 mL Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), 5 mL of 0.1 *M* sodium acetate buffer solution of pH 6.1 and 0.5 mL of 10^{-3} *M* xylenol orange solution were added to the solution. Its absorbance was then measured at 578 nm.

RESULTS AND DISCUSSION

Some of the curves of lanthanide concentrations in the two compartments against time obtained from the permeation experiments are shown in Fig. 1. The tendencies of the changes of the lanthanide concentrations with time for the other membrane systems were similar to those shown in Fig. 1. From these experimental data, the lanthanide fluxes across the membranes were calculated. In the present paper the flux is expressed as the mean value in the transport process for 6.5 h. Further, since the crystal radius of a metal ion is involved in the formation of a complex between the metal ion and ligand as described above, the flux is plotted against an ionic radius (*7*) of the trivalent lanthanide in six-coordination.

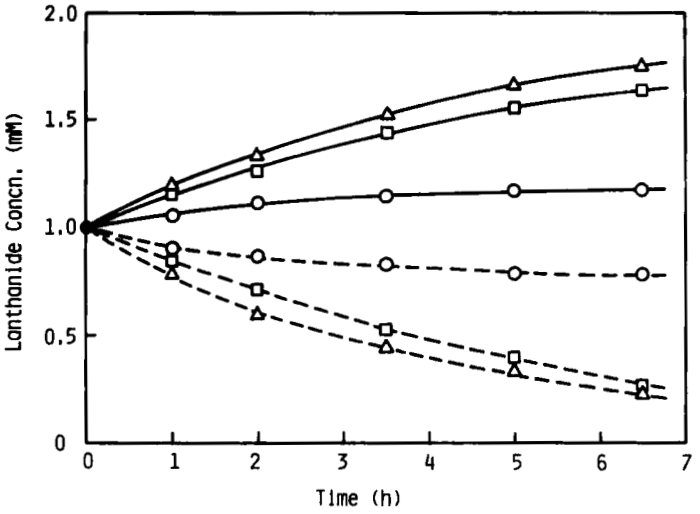

FIG. 1. Plots of lanthanide concentrations in the two compartments against time for some membrane systems: (○) La(permeant)–HIPT(carrier), (△) Er–HIPT ($NaClO_4$ was further added to Compartment I), (□) Lu–HFL. The dashed and solid lines represent the concentration against time curves in Compartments I and II, respectively. Plasticizer: ONPOE–TBEP. Compartment I: pH 6.1 acetate buffer.

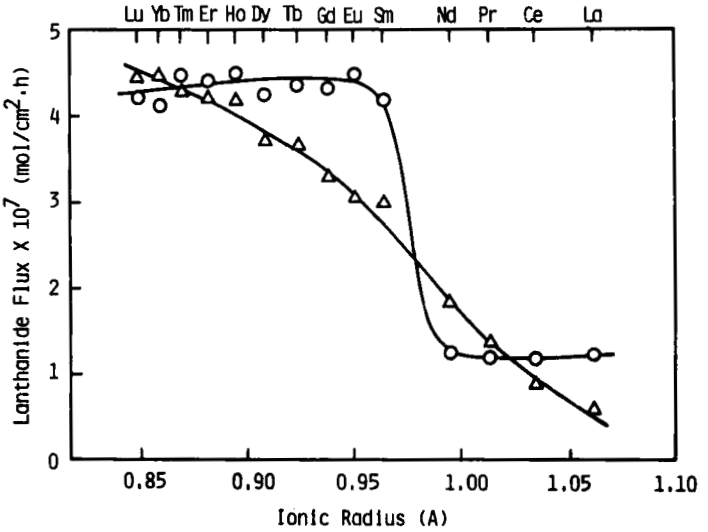

FIG. 2. Plots of flux against ionic radius for various kinds of lanthanides. Carrier: (○) HIPT, (△) HFL. Plasticizer: ONPOE–TBEP. Compartment I: pH 6.1 acetate buffer.

The fluxes of 14 kinds of lanthanides obtained by using HIPT and HFL are given in Fig. 2. In the case of HIPT, the fluxes for samarium to lutetium are much higher than those for lanthanum to neodymium. In the transport using HFL, the flux increased with decreasing ionic radius of the lanthanide species.

In general, at the interface between the source phase and the membrane, a metal ion M^{N+} reacts with a carrier HA, giving an uncharged complex MA_N as follows:

$$M^{N+} + NHA = MA_N + NH^+ \quad (1)$$

If the pH of the source phase is considerably higher than that of the receiving phase, the complex MA_N moves to the opposite side of the membrane, and the metal ion M^{N+} is then liberated into the receiving phase.

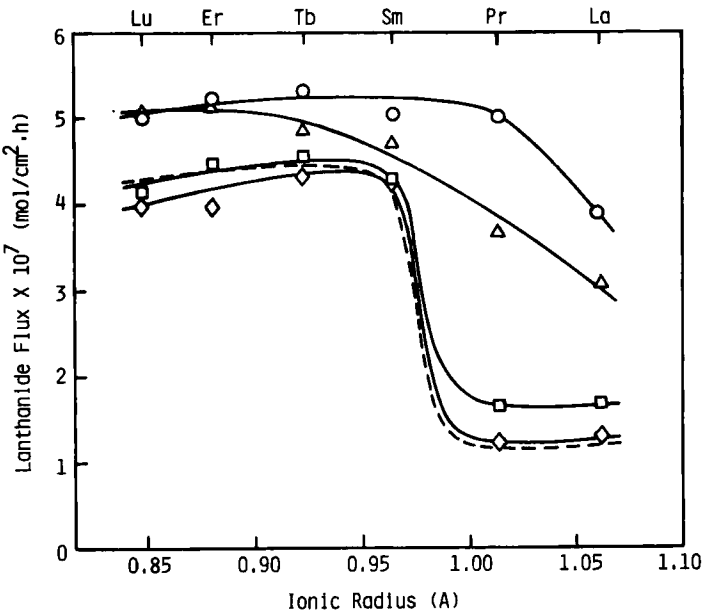

FIG. 3. Effect of anion added to Compartment I on the lanthanide flux for the membrane containing a ONPOE–TBEP mixture and HIPT: (○) $NaClO_4$, (△) NaSCN, (□) $NaNO_3$, (◇) NaCl. The dashed line represents the flux against ionic radius curve for the membrane system containing no additional anion (the data are shown in Fig. 2). Compartment I: pH 6.1 acetate buffer.

The flux of the metal ion, J_M, across the membrane is given by

$$J_M = D_{MA_N}([MA_N]_0 - [MA_N]_L)/L \quad (2)$$

where D_{MA_N} is the diffusion coefficient of the complex in the membrane, $[MA_N]_0$ and $[MA_N]_L$ are the concentrations of the compex at the membrane surfaces on the sides of the source and receiving phases, respectively, and L is the membrane thickness. Assuming that the reactions at both interfaces are fast relative to diffusion and that the pH difference between the aqueous phases is large, the value of $[MA_N]_L$ can be neglected in comparison with that of $[MA_N]_0$. Hence, Eq. (2) becomes

$$J_M = D_{MA_N}[MA_N]_0/L \quad (3)$$

If the structures of the lanthanide complexes formed at the interface differ from each other, the difference in flux among the lanthanides becomes great, since the diffusion coefficient of the complex is affected by

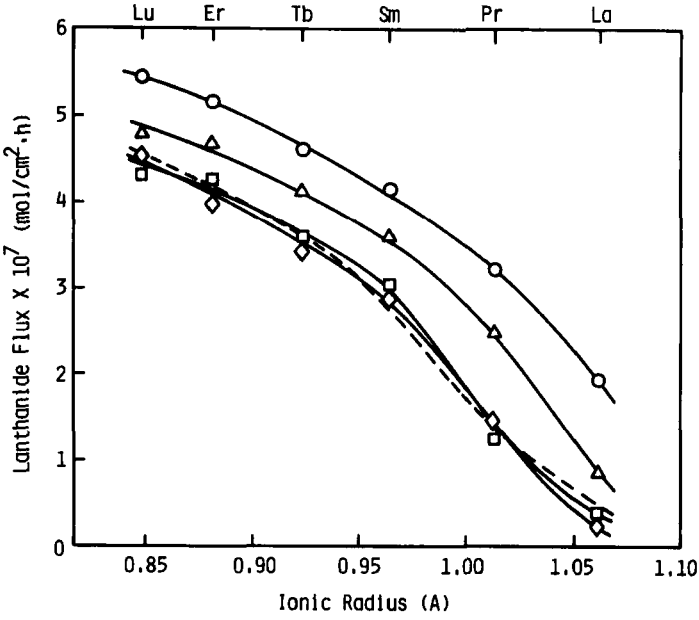

FIG. 4. Effect of anion added to Compartment I on the lanthanide flux for the membrane containing a ONPOE–TBEP mixture and HFL. The notation is the same as in Fig. 3. Compartment I: pH 6.1 acetate buffer.

its structure. It has been shown (*8*) for the extraction of lanthanides by HIPT in chloroform that praseodymium is extracted as a complex of the type MA_N, and that europium, holmium, ytterbium, and lutetium are extracted as MA_NHA. In the present permeation experiments using HIPT, the types of complexes for lanthanum to neodymium may appreciably differ from those for samarium to lutetium. On the other hand, the structure of the lanthanide complex formed by HFL may vary somewhat with the lanthanide species.

The effect of anion added to Compartment I on the lanthanide flux for the membranes using HIPT and HFL is shown in Figs. 3 and 4, respectively. The flux versus ionic radius curve for the membrane system containing no additional anion is represented by a dashed line in each figure (the data are shown in Fig. 2). In both cases a rise in flux was observed on the addition of perchlorate or thiocyanate ions, whereas the addition of nitrate or chloride ions scarcely affected the flux.

In a co-transport process (*9*), the plasticizer TBEP behaved as the carrier of scandium in the presence of thiocyanate ions. In the present experiments, however, no transport of erbium occurred in the presence of perchlorate

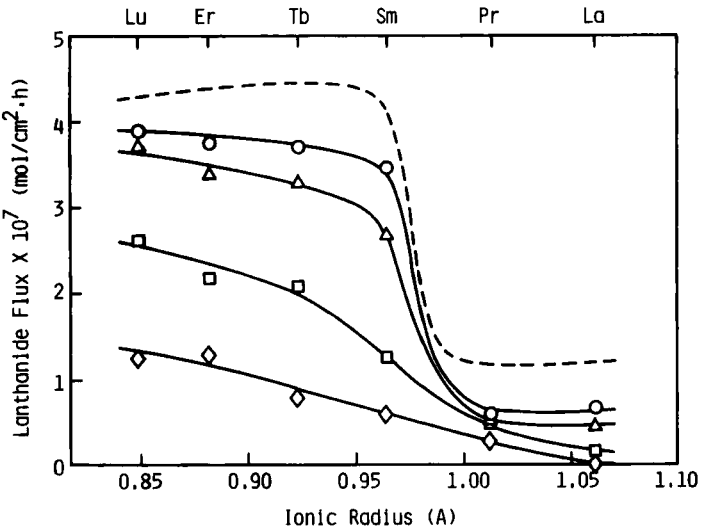

FIG. 5. Effect of pH in Compartment I on the lanthanide flux for the membrane containing a ONPOE–TBEP mixture and HIPT: (○) pH 5.5, (△) pH 5.1, (□) pH 4.5, (◇) pH 4.0. The dashed line represents the flux against ionic radius curve for pH 6.1 (the data are shown in Fig. 2).

or thiocyanate ions for the membrane containing no HIPT or HFL. It is thought that TBEP has no function as the carrier of the lanthanides.

The anions added to Compartment I are apt to participate in the formation of the lanthanide complex (*7*), although the structures of the complexes formed are not clear. It is presumed that the additions of perchlorate and thiocyanate ions, which are lipophilic anions, result in an increase in concentration of the complex at the membrane surface on the side of Compartment I, and consequently the flux rises.

The effect of pH in Compartment I on the flux for the membranes using HIPT and HFL is shown in Figs. 5 and 6, respectively. The curve for pH 6.1 is represented by a dashed line in each figure (the data are shown in Fig. 2). In the case of HIPT, as the pH decreased the fluxes decreased gradually as a whole and the curve became smooth. On the other hand, the fluxes using HFL decreased rapidly with decreasing pH, and no transport of lanthanum and praseodymium occurred below pH 5.5.

In the extractions of lanthanum and lutetium by 0.1 *M* HIPT in chloroform, the pH values at which 50% of them are extracted are 4.44 and 2.76, respectively (*8*). The pH values for the other lanthanides are distributed in this pH range. In the present membrane systems, similarly, the pH range in which the extraction or transport of the lanthanides begins to

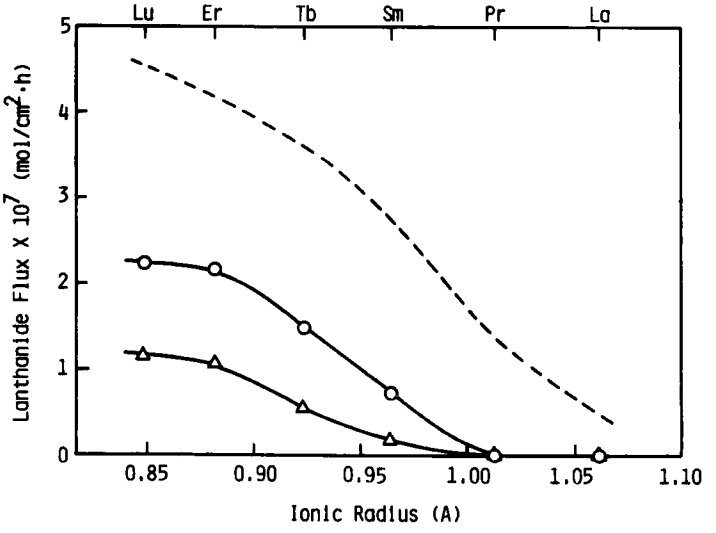

FIG. 6. Effect of pH in Compartment I on the lanthanide flux for the membrane containing a ONPOE–TBEP mixture and HFL. The notation is the same as in Fig. 5.

occur must be small. Therefore, it is difficult to separate the lanthanides from each other by utilizing the pH difference in the source phase. The lowering of pH in Compartment I brings about a decrease in concentration of the complex at the membrane surface on the side of Compartment I. Consequently, the flux decreases.

The effect of plasticizer on the flux for the membranes using HIPT and HFL is shown in Figs. 7 and 8, respectively. The curve for the membrane containing ONPOE and TBEP is represented by a dashed line in each figure (the data are shown in Fig. 2). In the case of HIPT, the addition of TAP in the place of TBEP increased the fluxes of lanthanum and praseodymium. In the experiments using the membrane containing Span 85, the highest flux was observed for terbium. For the membrane containing POEOE or POENE, the flux increased gently with decreasing ionic radius of the lanthanide species. The fluxes for POEOE were higher than those for POENE. In the transport using HFL, the flux increased gradually with decreasing ionic radius in all cases. The order of plasticizers in the lanthanide flux is TAP > TBEP > Span 85 > POEOE > POENE. In the experiments using the membranes containing these plasticizers, no transport of erbium occurred in the absence of HIPT or HFL.

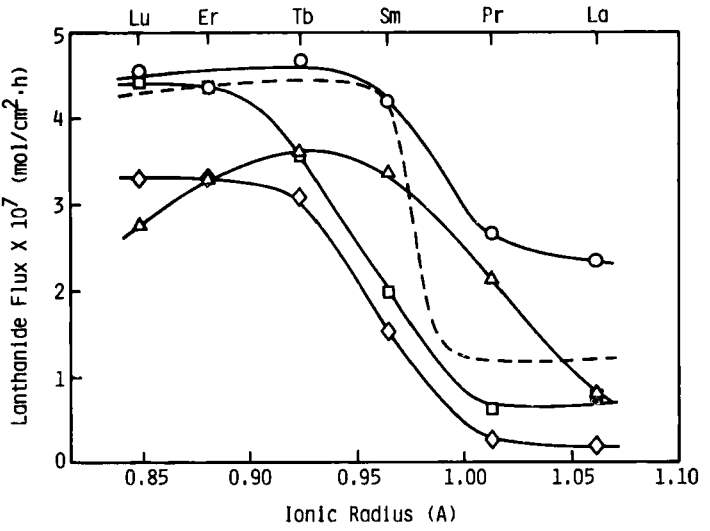

FIG. 7. Effect of plasticizer on the lanthanide flux for the membranes using HIPT: (○) ONPOE–TAP, (△) ONPOE–Span 85, (□) ONPOE–POEOE, (◇) ONPOE–POENE. The dashed line represents the flux against ionic radius curve for ONPOE–TBEP (the data are shown in Fig. 2). Compartment I: pH 6.1 acetate buffer.

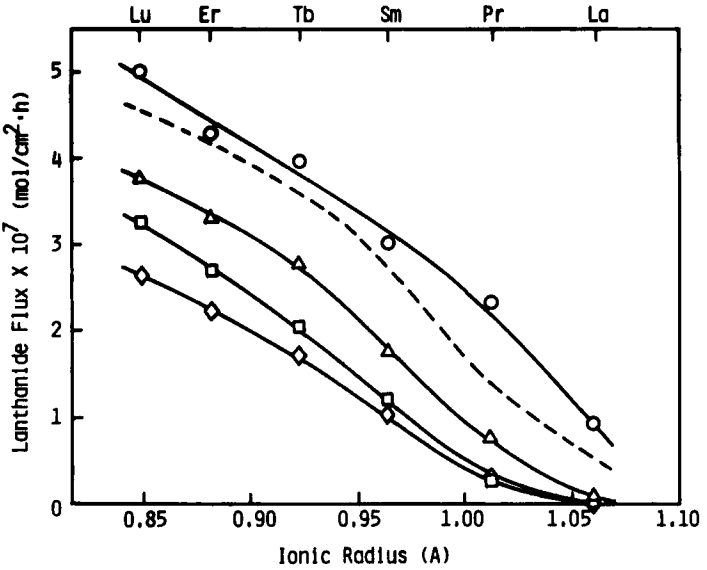

FIG. 8. Effect of plasticizer on the lanthanide flux for the membranes using HFL. The notation is the same as in Fig. 7. Compartment I: pH 6.1 acetate buffer.

The diffusion coefficient of the complex in the membrane is inversely proportional to the viscosity of the membrane phase, η, if it follows the Stokes-Einstein equation:

$$D = kT/6\pi r\eta \tag{4}$$

where k is the Boltzmann constant, T is the absolute temperature, and r is the molecular radius of the complex. The values of relative viscosity of

TABLE 1
Relative Viscosities of Plasticizers Used

Plasticizer[a]	Relative viscosity[b]
ONPOE–TBEP	0.94
ONPOE–TAP	0.79
ONPOE–Span 85	1.63
ONPOE–POEOE	1.19
ONPOE–POENE	1.53

[a]3:1 mixture.
[b]Viscosity ratio of plasticizer to ONPOE.

the plasticizers used are given in Table 1. These viscosities were measured at 25°C by the method described previously (*2*). As seen in Table 1, the order of plasticizers in the reciprocal of the viscosity agrees with that in the lanthanide flux, with the exception of Span 85. This fact shows that the diffusion of the complex in the membrane is mainly governed by the viscosity of the plasticizer, except in the case of Span 85. At this stage, the behavior of Span 85 in the membrane is not clear.

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Received by editor September 26, 1989