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(1992) 'Effect of Polyoxyethylene *n*-Alkyl Ethers on Carrier-Mediated Transport of Lanthanide Ions through Cellulose Triacetate Membranes', Separation Science and Technology, 27: 2, 269 — 276
To link to this Article: DOI: 10.1080/01496399208018878
URL: http://dx.doi.org/10.1080/01496399208018878

SEPARATION SCIENCE AND TECHNOLOGY, 27(2), pp. 269–276, 1992

Effect of Polyoxyethylene *n*-Alkyl Ethers on Carrier-Mediated Transport of Lanthanide Ions through Cellulose Triacetate Membranes

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Abstract

Fluxes of 14 kinds of lanthanides across cellulose triacetate membranes were determined by using mixtures of *o*-nitrophenyl *n*-octyl ether and a series of polyoxyethylene *n*-alkyl ethers (POE ethers) as plasticizers, and hinokitiol as carrier. Effects of alkyl and polyoxyethylene (POE) chains of the POE ether on the flux were demonstrated. The transport of the lanthanides was coupled to a flow of hydrogen ions. The POE ethers used [$C_nH_{2n+1}(OCH_2CH_2)_xOH$, referred to as C_nE_x] were $C_{10}E_3$, $C_{12}E_3$, $C_{14}E_3$, $C_{16}E_3$, $C_{12}E_2$, $C_{12}E_4$, $C_{12}E_6$ and $C_{12}E_8$. In all cases, high fluxes were observed for the lanthanides from samarium to lutetium. On the contrary, the fluxes for lanthanum to neodymium were extremely low. In experiments testing the effect of the alkyl chain, the order of the POE ethers in the lanthanide flux for samarium to lutetium was $C_{12}E_3 > C_{10}E_3 > C_{14}E_3 > C_{16}E_3$. In experiments testing the effect of the POE chain, the flux decreased with an increase in the chain length.

INTRODUCTION

In previous work (*1*) the fluxes of trivalent lanthanide ions across cellulose triacetate (CTA) membranes were determined by using hinokitiol (β-isopropyltropolone; HIPT) and flavonol as carriers. The effects of added anion and pH in the source phase and of the plasticizer incorporated in the membrane on the lanthanide flux were examined. For membrane systems using HIPT, the flux was remarkably affected by the type of plasticizer. In this case mixtures of *o*-nitrophenyl *n*-octyl ether (ONPOE) and some nonionic surfactants, or tri-*n*-amyl or tris(2-*n*-butoxyethyl) phosphate were used as the plasticizers.

For the present work, to further elucidate the effect of the plasticizer, the fluxes of all lanthanides, except promethium, across CTA membranes containing the HIPT carrier were determined by using mixtures of ONPOE and a series of polyoxyethylene *n*-alkyl ethers (POE ethers) as the plasticizers. This paper mainly describes the effects of alkyl and polyoxyethylene (POE) chains of the POE ether on the lanthanide flux.

EXPERIMENTAL

Preparation of CTA Membranes

Five milliliters of a dichloromethane solution containing 12.5 g/L CTA and 4.0 m*M* HIPT, and 0.2 mL of a ONPOE solution containing a given concentration of the POE ether 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 (*2*, *3*). The thickness of the resulting membrane was about 0.06 mm. The concentrations of the plasticizer and carrier in the membrane were 3.2 mL/g·CTA and 0.32 mmol/g·CTA, respectively. These values are the same as those for the membranes used in the previous work (*1*).

The CTA was obtained from Eastman Kodak Co., and ONPOE from Dojindo Lab. The POE ethers used have the general formula, $C_nH_{2n+1}(OCH_2CH_2)_xOH$. For brevity, these will be referred to as C_nE_x. Samples with an E_3 chain, namely $C_{10}E_3$, $C_{12}E_3$, $C_{14}E_3$, and $C_{16}E_3$, were obtained from Sigma Chemical Co., and those with a C_{12} chain, namely $C_{12}E_2$, $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$, from Tokyo Kasei Kogyo Co., Ltd. The carrier HIPT was obtained from Kanto Chemical Co.

Apparatus

The apparatus used for the permeation experiments was similar to that previously used (*1*, *2*): 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.

Permeability Measurements

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. 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, as described previously (*1*, *3*).

Viscosity Measurements

Viscosities and specific gravities of the plasticizers used were measured at 25°C by using an Ostwald viscometer and a Wadon pycnometer, respectively. From these experimental data, relative viscosities of the plasticizers were calculated.

RESULTS AND DISCUSSION

Lanthanide Concentration versus Time Curve

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 lanthanide concentrations versus time for the other membrane systems were similar to those shown in Fig. 1.

In the present paper the lanthanide flux obtained from the permeation experiment is expressed as the mean value in the transport process for 6.5 h.

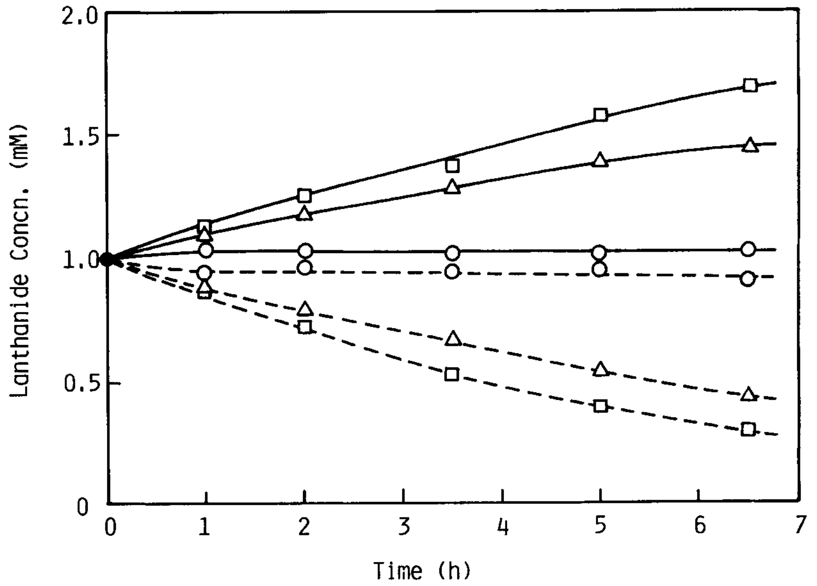

FIG. 1. Plots of lanthanide concentrations in the two compartments against time for some membrane systems: (○) La(permeant)-$C_{12}E_2$ (POE ether in plasticizer), (△) Eu-$C_{16}E_3$, (□) Dy-$C_{12}E_3$. The dashed and solid lines represent the concentration against time curves in Compartments I and II, respectively. The concentration of the POE ethers in the plasticizer was 0.5 *M*.

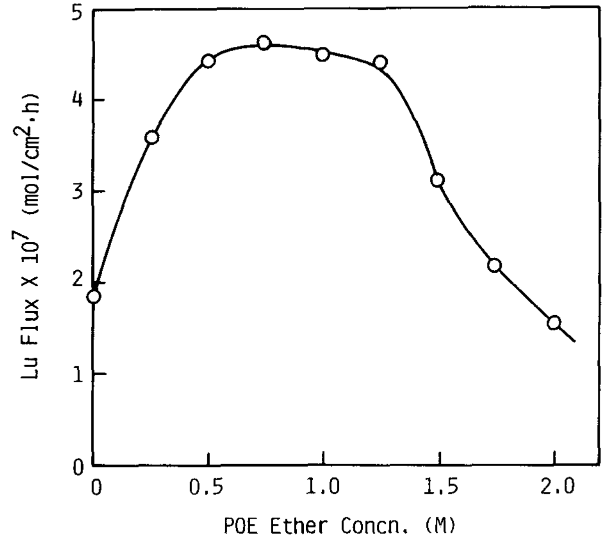

FIG. 2. Effect of concentration of POE ether ($C_{12}E_2$) in the plasticizer on the lutetium flux.

Effect of Concentration of POE Ether

The curve of lutetium flux against concentration of $C_{12}E_2$ in the plasticizer is shown in Fig. 2. In this case high fluxes were observed in the concentration range of 0.5 to 1.25 *M*. In the subsequent experiments testing the effects of alkyl and POE chains of the POE ether on the lanthanide flux, considering the high molecular weight of the POE ethers used, their concentration of 0.5 *M* was employed.

Effect of Alkyl Chain of POE Ether

The fluxes of 14 kinds of lanthanides obtained by using $C_{10}E_3$, $C_{12}E_3$, $C_{14}E_3$, and $C_{16}E_3$ are given in Fig. 3. For the reason given in the previous paper (*1*), the flux is plotted against an ionic radius (*4*) of the trivalent lanthanide in six-coordination. The curve for the membrane containing no POE ether is shown in Fig. 3.

In all cases the fluxes for the lanthanides from samarium to lutetium were much higher than those for lanthanum to neodymium. In addition, the fluxes for lanthanum to neodymium were lower than those obtained for the membranes containing the mixture of ONPOE and tri-*n*-amyl or tris(2-*n*-butoxyethyl) phosphate in the previous work (*1*). The order of the POE ethers in the lanthanide flux for samarium to lutetium was $C_{12}E_3 >$

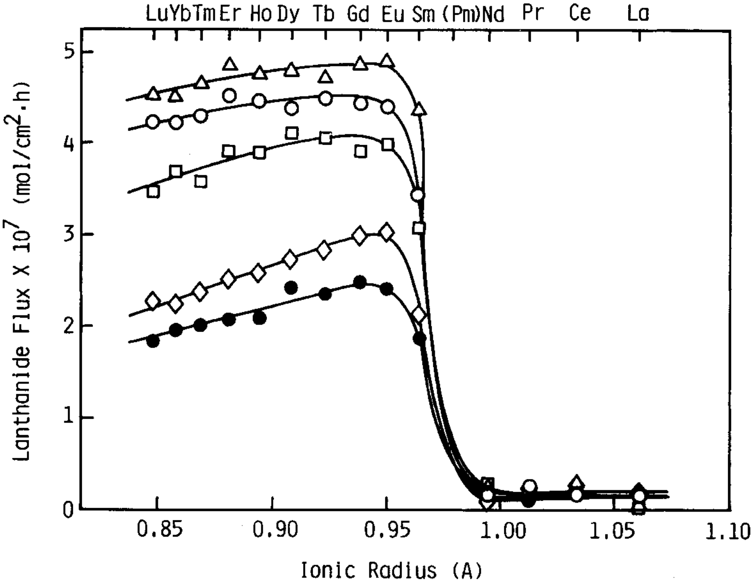

FIG. 3. Effect of alkyl chain of POE ether on the lanthanide flux: (○) $C_{10}E_3$, (△) $C_{12}E_3$, (□) $C_{14}E_3$, (◇) $C_{16}E_3$, (●) POE ether absent. The concentration of the POE ethers in the plasticizer was 0.5 *M*.

$C_{10}E_3 > C_{14}E_3 > C_{16}E_3$. In the range of dysprosium to lutetium, the flux decreased slightly with a decrease in ionic radius of the lanthanide.

As described in the previous paper (*1*), the flux of a metal ion, J_M, across a membrane is given by

$$J_M \cong D_{MA}[MA]_0/L \qquad (1)$$

where D_{MA} is the diffusion coefficient of a complex of the metal and carrier in the membrane, $[MA]_0$ is the concentration of the complex at the membrane surface on the side of the source phase, and L is the membrane thickness. The value of D_{MA} is inversely proportional to the viscosity of the membrane phase, η, if it follows the Stokes–Einstein equation:

$$D_{MA} = kT/6\pi r\eta \qquad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, and r is the molecular radius of the complex. The relative viscosities of the plasticizers containing 0.5 *M* POE ethers are given in Table 1. The viscosity

TABLE 1
Relative Viscosities of Plasticizers Containing 0.5 *M* POE Ethers

POE ether	Relative viscosity[a]
$C_{10}E_3$	1.02
$C_{12}E_3$	1.05
$C_{14}E_3$	1.13
$C_{16}E_3$	1.20
$C_{12}E_2$	0.97
$C_{12}E_4$	1.19
$C_{12}E_6$	1.27
$C_{12}E_8$	1.49

[a] Viscosity ratio of plasticizer to ON-POE.

increased with an increase in alkyl chain length of the POE ether. Hence, the increase of its length results in a decrease in value of D_{MA}. On the other hand, the value of $[MA]_0$ depends on the partition coefficient of the complex between the membrane and aqueous phases. In the range of samarium to lutetium, the highest flux was observed for $C_{12}E_3$. This fact shows that the partition coefficient for $C_{12}E_3$ is higher than that for $C_{10}E_3$.

Effect of POE Chain of POE Ether

The lanthanide fluxes obtained by using $C_{12}E_2$, $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$ are given in Fig. 4. The flux versus ionic radius curve for $C_{12}E_3$ is represented by a dashed line in this figure. Its data are shown in Fig. 3.

The fluxes for $C_{12}E_2$ nearly agreed with those for $C_{12}E_3$. For the other POE ethers, the flux decreased with an increase in POE chain length in the range of samarium to lutetium. In the case of $C_{12}E_8$, the fluxes were lower than those for the membrane containing no POE ether.

The presence of a small number of oxyethylene units in the membrane results in an increase in the partition coefficient of the complex between the membrane and aqueous phases. However, a further increase in oxyethylene unit brings about increases both in hydrophilicity and in viscosity (see Table 1) of the membrane phase; that is, decreases in the partition coefficient and in the diffusion coefficient. Consequently, the flux decreases.

Effect of Distribution of Oxyethylene Units

To examine the effect of distribution of the oxyethylene units in the membrane on the lanthanide flux, the permeation experiments were per-

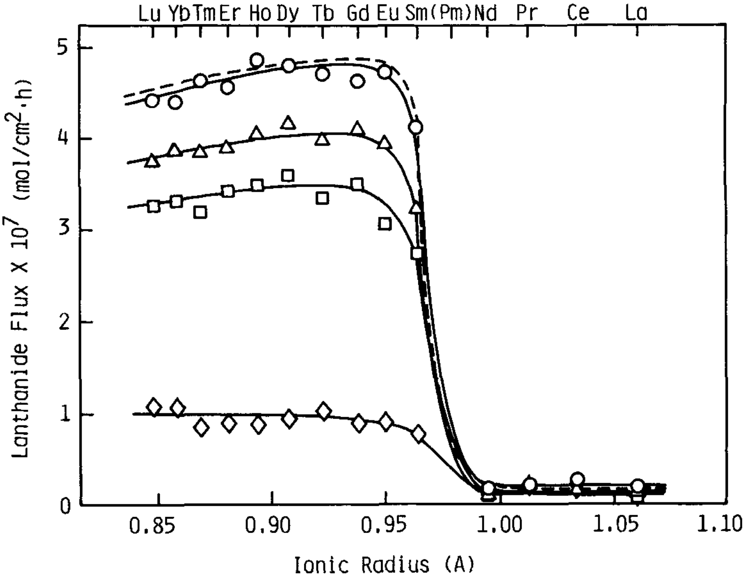

FIG. 4. Effect of POE chain of POE ether on the lanthanide flux: (○) $C_{12}E_2$, (△) $C_{12}E_4$, (□) $C_{12}E_6$, (◇) $C_{12}E_8$. The dashed line represents the flux against the ionic radius curve for $C_{12}E_3$ (the data are shown in Fig. 3). The concentration of the POE ethers in the plasticizer was 0.5 *M*.

formed for the membranes containing a definite number of oxyethylene units of $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$: the concentrations of $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$ in the plasticizer were 0.25, 0.167, and 0.125 *M*, respectively. The number of oxyethylene units in these membranes is the same as that in the membrane containing 0.5 *M* $C_{12}E_2$. The lanthanides used in these measurements were lanthanum, praseodymium, neodymium, samarium, terbium, erbium, and lutetium. These results are shown in Fig. 5. The curve for $C_{12}E_2$ is represented by a dashed line in this figure. Its data are shown in Fig. 4.

In the range of samarium to lutetium, the fluxes for $C_{12}E_4$ and $C_{12}E_6$ were lower than those for the membranes containing 0.5 *M* of their POE ethers. On the other hand, the fluxes for $C_{12}E_8$ were higher than those for the membrane containing 0.5 *M* of its POE ether.

The POE ethers used are known as nonionic surfactants, and their POE chains are apt to be oriented at the membrane surface. An increase in POE chain length results in an increase in hydrophilicity of the membrane surface around the POE chains. The high hydrophilicity lowers the flux, as described above. With a decrease in the number of molecules of the

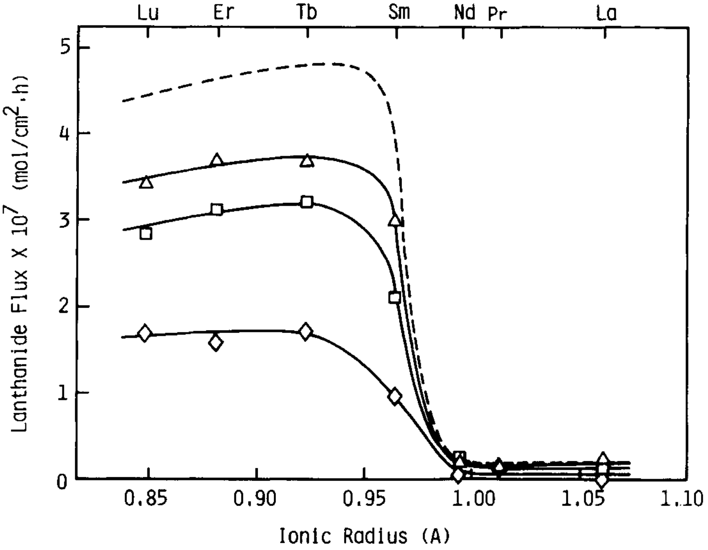

FIG. 5. Effect of distribution of oxyethylene units in the membrane on the lanthanide flux: (△) $C_{12}E_4$, (□) $C_{12}E_6$, (◇) $C_{12}E_8$. The dashed line represents the flux against the ionic radius curve for $C_{12}E_2$ (the data are shown in Fig. 4). The concentrations of $C_{12}E_4$, $C_{12}E_6$, and $C_{12}E_8$ in the plasticizer were 0.25, 0.167, and 0.125 *M*, respectively. The number of oxyethylene units in these membranes is the same as that in the membrane containing 0.5 *M* $C_{12}E_2$.

POE ether in the membrane, the value of the flux approaches that for the membrane containing no POE ether.

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Received by editor January 15, 1991