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Uphill Transport of Ce(III) by Supported Liquid Membranes Containing Octyl(Phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine Oxide in 2-Nitrophenyl Octyl Ether

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ABSTRACT

Experiments on the facilitated transport of Ce(III) from mixed aqueous $HNO_3/NaNO_3$ solutions to water through supported liquid membranes (SLM) were performed using a stirred permeation cell. The SLMs consisted of organic solutions of octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in 2-nitrophenyl octyl ether (2-NPOE) absorbed into microporous polypropylene membranes. The effects of the temperature and the carrier concentration on the permeation rate of Ce(III) were investigated. It was shown that the uphill transport of

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Ce(III) could be achieved without adding masking agents of Ce(III) in the strip solution. A mathematical model for analyzing the facilitated transport of Ce(III) was proposed. The permeation rate of Ce(III) could be simulated by using various physical and chemical parameters that were independently determined or estimated.

Key Words: Facilitated transport; Supported liquid membranes; Microporous polypropylene membranes; Ce(III); Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphatine oxide.

INTRODUCTION

Facilitated transport of metal ions through supported liquid membranes (SLM) has been attracting attention because only a small amount of extractant is needed, selectivity is very high, and the process is very simple.[1,2] Several studies on the application of SLMs to the treatment of radioactive wastewater have been reported.[3–8] Danesi et al.[3] demonstrated that the organic solution of octyl(phenyl)-*N*,*N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO), absorbed on a thin microporous polypropylene membrane, can be used as a supported liquid membrane to permeate trivalent actinide cations. Furthermore, Danesi et al.[4] and Chiarizia and Danesi[5] performed experiments on the separation of actinides and lanthanides from acidic liquid nuclear waste using SLMs consisting of 0.25 M CMPO and 0.75 M tributyl phosphate (TBP) dissolved in decalin. The reason for adding TBP to CMPO is to improve the solubility of CMPO in the diluent, reduce the possibility of the third phase formation, and increase the loading capacity of the organic phase.

In our previous works,[6,7] aqueous Ce(III) solutions containing nitric and/or sodium nitrate were used as a simulated low level radioactive wastewater, since the extraction behavior of Ce(III) is similar to that of Am(III).[9] We performed experiments on the transport of Ce(III) through SLMs using CMPO/TBP in dodecane as carriers, and the effects of experimental conditions, such as temperature and the composition of feed and strip solutions on the permeation characteristics were studied in detail.[6] A simple method for stabilizing a plate- and frame-type SLM module was also proposed.[7]

In these types of membrane systems, metal ions can be transported against its concentration gradient by maintaining HNO_3 concentration in the feed side higher than that in the strip side. Two factors affect the permeability of metal ions. First, since both CMPO and TBP transport HNO_3 across the membrane to the strip solution, the transport rate of metal ions through SLM tends to decrease gradually during the permeation experiment. To avoid this decrease, the concentration of HNO_3 in the strip solution must be kept low. Danesi et al.[4] proposed a "double liquid membrane system" where in addition to the

CMPO/TBP membrane, another membrane, a primary amine membrane, was used to remove nitric acid continuously from the strip solution of the CMPO/TBP membrane to a second strip solution of the primary amine membrane. In our previous work, a high permeation rate of Ce(III) was obtained by adjusting the composition of the feed solution condition as 0.05 M HNO_3 and 2.95 M $NaNO_3$, since only a small amount of HNO_3 permeated the membrane and a higher distribution ratio of Ce(III) was obtained.[6] This result is similar to that of Muscatello et al.,[8] who reported the best condition for americium transfer was 0.1 M HNO_3 plus 6.9 M $NaNO_3$. Second, the concentration of free metal ions in the strip solution increases gradually during the permeation process, which leads to the back-diffusion of metal ions from the strip to the feed side. Sodium citrate (Na_3CA) was added to the strip solution as a masking agent of metal ions to reduce the free metal concentration in the strip solution.[6,9] However, the addition of the masking agent is not desirable, because it will cause storage problems.

The objective of this work, was to explore the permeation possibilities without additions of TBP and masking agent. Furthermore, a mathematical model for analyzing the facilitated transport of Ce(III) is proposed. 2-Nitrophenyloctylether (2-NPOE) was used as the diluent for CMPO, since the stability of SLMs can be improved because of its low volatility and low solubility in water. Another advantage of using NPOE is that the third phase formation can be prevented without an addition of TBP to the liquid membrane. Therefore, the HNO_3 concentration in the strip solution is expected to remain very low during the permeation experiment, since nitric acid is mainly transported by TBP through the membrane. Therefore, uphill transport of Ce(III) can be achieved without adding masking agents to the strip solution. Furthermore, for the system without TBP addition, it is easier to perform a mechanistic study than for the mixed CMPO–TBP system.

EXPERIMENTAL

Materials

The CMPO was purchased from Hokko Chemical Industry, Ltd., Japan, and used as received. The NPOE was obtained from Wako Pure Chemicals, Ltd., Japan. The liquid membrane solutions were prepared by dissolving CMPO in NPOE. The formula of CMPO is shown in Fig. 1. A microporous polypropylene membrane (Akzo Nobel Faser AG, Membrana, thickness: 150 μm, pore size: 0.2 μm, porosity: 0.75) was used as a support for the liquid membrane. The supported liquid membranes were prepared by impregnating the supports with the liquid membrane solutions. Feed solutions were prepared by

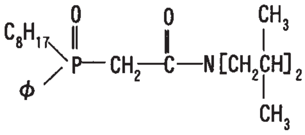

Figure 1. Structure of CMPO.

dissolving nitrate salts of Ce(III), Fe(III), Cr(III), and Ca(II) in aqueous 0.05-M $HNO_3/2.95$-M $NaNO_3$ solutions. Deionized water was used as a strip solution.

Extraction Equilibrium

Extraction of Nitric Acid

In the extraction experiment of nitric acid, the distribution ratio of HNO_3 between an organic CMPO–NPOE solution and an aqueous mixed HNO_3/$NaNO_3$ solution was measured at 308 K. After the aqueous and the organic phases had been shaken in a shaker for about 24 hr, the two phases were separated. The nitric acid concentration of the aqueous solution was measured by titrimetric analysis using a standardized sodium hydroxide solution.

Extraction of Ce(III)

Aqueous solutions were prepared by dissolving $Ce(NO_3)_3$ in aqueous 0.05 M $HNO_3/2.95$ M $NaNO_3$ solutions. Organic solutions were prepared by dissolving CMPO in NPOE. The initial CMPO concentration was varied from 0.2 to 0.5 M. The distribution ratios of Ce(III) between liquid membrane solutions and aqueous solutions were measured at 308, 318, and 328 K by the same procedure described elsewhere.[6] The Ce(III) concentration in the aqueous solution was analyzed by inductively coupled plasma spectroscopy (ICP, Shimadzu, ICPS-1000III). The concentration of Ce(III) in the organic phase was calculated from a mass balance.

Permeation Experiments

The transport of Ce(III) was carried out using a stirred permeation cell described in our previous study.[6] The volumes of both the aqueous feed and strip solutions were 21 mL. The membrane area was 7.07 cm^2. The stirring speed of each solution was kept constant at 600 rpm. Samples were withdrawn from the aqueous strip solutions and the final samples were withdrawn from both the strip and feed solutions. The concentration of Ce(III) was determined by ICP. At the end of each experiment, the nitrate ion concentration in the strip solution was determined using an ion chromatography (Shimadzu, Lc-6A; column, Shim-pac ICA3S; electric conductivity detector, CDD-6A, mobile phase, *p*-hydroxybenzoic acid).

RESULTS AND DISCUSSION

Extraction Equilibrium

Extraction of Nitric Acid

Since the extraction of HNO_3 by CMPO also takes place in this system, the formation of the HNO_3–CMPO complex must be considered. The chemical reaction describing the extraction of HNO_3 from aqueous nitrate solutions into the CMPO solutions is expressed as follows:

$$\mathrm{HNO_3} + n'\overline{\mathrm{CMPO}} \Longleftrightarrow \overline{\mathrm{HNO_3(CMPO)}_{n'}} \quad (1)$$

where the bar indicates species in the organic phase. The following equation holds for the distribution ratio of HNO_3

$$D_{\mathrm{H}} = \frac{\overline{[\mathrm{HNO_3(CMPO)}_{n'}]}_{\mathrm{eq}}}{[\mathrm{HNO_3}]_{\mathrm{eq}}} = K_{\mathrm{H}}\overline{[\mathrm{CMPO}]}_{\mathrm{eq}}^{\;n'} \quad (2)$$

which can be expressed in logarithmic form as

$$\ln D_{\mathrm{H}} = \ln K_{\mathrm{H}} + n' \ln \overline{[\mathrm{CMPO}]}_{\mathrm{eq}} \quad (3)$$

where K_H is the apparent extraction constant of HNO_3 taking into account all thermodynamic activity coefficients. The slope-analysis method[10] was used to determine the coordination number n' and K_H from experimental data in which the organic-phase extractant concentration was varied with other variables held constant.

Extraction experiments of nitric acid were performed at the organic-phase CMPO concentrations of 0.1, 0.2, 0.3, 0.382, and 0.5 M at 318 K. If we assume that the extraction of nitric acid with CMPO is predominated by the 1 : 1

complex formation,[10] the equilibrium concentrations of HNO_3 and CMPO in the organic phase are expressed as follows:

$$\overline{[HNO_3]}_{o,eq} = [HNO_3]_{W,0} - [HNO_3]_{w,eq} \tag{4}$$

$$\overline{[CMPO]}_{o,eq} = \overline{[CMPO]}_{o,0} - ([HNO_3]_{w,0} - [HNO_3]_{w,eq}) \tag{5}$$

where the subscript 0 refers to the initial concentration, w the aqueous solution, and o the organic solution. The plot of D_H vs. $[CMPO]_{o,eq}$ on log–log coordinates based on Eq. (3) is shown in Fig. 2. From these data, n' and K_H were determined as 1 and 4.51 M^{-1}, respectively.

Extraction Constants of Ce(III)

Prior to the evaluation of the extraction constant of Ce(III), the effect of the initial nitric acid concentration in the aqueous solution on the distribution ratio of Ce(III), D_{Ce}, was studied and the result is shown in Fig. 3. The ionic strength and nitrate ion concentration were kept constant at $[HNO_3] + [NaNO_3] = 3\,M$, and the initial CMPO concentration in the organic solution was 0.382 M. It is clearly seen that the distribution ratio D_{Ce} decreases with increasing nitric acid concentration. According to Boerrigter et al.,[11] CMPO ligands have basic amide and phosphoryl moieties and these groups are sensitive to protonation. The fraction of protonated ligand increases with increasing the HNO_3 concentration and this competitive reaction leads to the

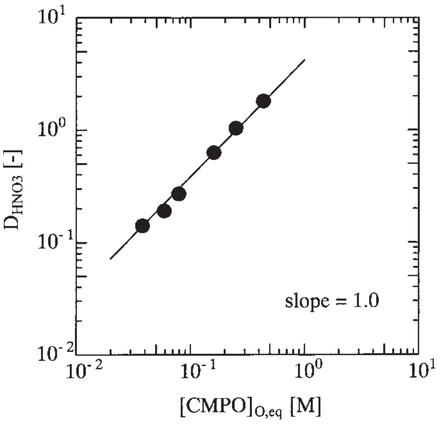

Figure 2. Effect of CMPO concentration on distribution ratio of HNO_3. Aqueous phase: 0.1 M HNO_3 + 2.9 M $NaNO_3$; organic phase: 0.382 M CMPO; $V_o/V_w = 1$; 308 K.

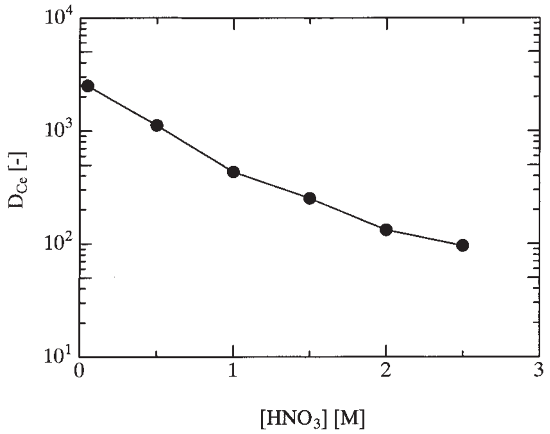

Figure 3. Effect of HNO$_3$ concentration on distribution ratio of Ce. Aqueous phase: $[HNO_3] + [NaNO_3] = 3\,M$; organic phase: $[CMPO]_{o,0} = 0.382\,M$; $V_o/V_w = 0.25$; $[Ce]_{w,0} = 4.33\,mM$; 308 K.

low distribution ratio. Figure 4 shows the effect of temperature on D_{Ce}. The value of D_{Ce} decreased with increasing temperature. D_{Ce} at 328 K, however, is still as high as about 1000.

Although the extraction of trivalent ions with CMPO is mainly predominated by 1 : 3 complex formation,[3] the chemical reaction describing the extraction of Ce(III) from aqueous nitrate solution into organic solution is generally expressed as follows:[4]

$$Ce^{3+} + 3NO_3^- + n\overline{CMPO} \Longleftrightarrow \overline{Ce(NO_3)_3(CMPO)_n} \tag{6}$$

Since the CMPO behaves as a neutral extractant and does not ionize when extracting trivalent metal ions, Ce(III) must be extracted with three anions to maintain electroneutrality.[11] The distribution ratio of Ce(III) is expressed as follows:

$$\begin{aligned} D_{Ce} &= \frac{\overline{[Ce(NO_3)_3(CMPO)_n]}_{eq}}{[Ce^{3+}]_{eq}} \\ &= K_{ex}[NO_3^-]_{eq}{}^3\,\overline{[CMPO]}_{eq}{}^n = K'_{ex}\overline{[CMPO]}_{eq}{}^n \end{aligned} \tag{7}$$

$$K'_{ex} = K_{ex}[NO_3^-]^3 \tag{8}$$

Here, K_{ex} is the extraction constant taking into account all thermodynamic activity coefficients. The nitrate ion concentration in the aqueous feed solution at equilibrium is considered to be almost the same as the initial nitrate

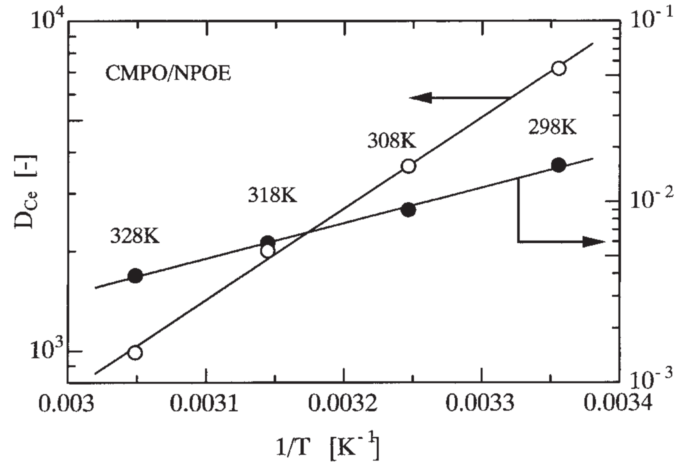

Figure 4. Effect of temperature on D_{Ce} and viscosity of membrane solution. $[CMPO]_{o,0} = 0.382$ M in NPOE; $V_o/V_w = 0.25$; $[HNO_3]_{w,0} = 0.05$ M; $[NaNO_3]_{w,0} = 2.95$ M; $[Ce]_{w,0} = 3.97$ mM; 308 K.

concentration ($[NO_3^-]_0 = 3$ M). K'_{ex} is defined as the apparent extraction constant of Ce(III). The values of n and K'_{ex} can be determined from the slope and intercept of the plot of ln D_{Ce} vs. ln $\overline{[CMPO]}_{o,eq}$.

Because HNO_3 is also extracted by CMPO simultaneously, the effect of the extraction of HNO_3 on free CMPO concentration was considered here. The free CMPO concentration was calculated by subtracting the concentrations of the HNO_3–CMPO complex [1 : 1 complex in the organic phase, refer to Eq. (11)] and the Ce(III)–CMPO complex (1 : 3 complex in the organic phase) from the initial CMPO concentration. The equilibrium concentrations of Ce and CMPO were calculated as follows:

$$\overline{[Ce]}_{o,eq} = \frac{V_w}{V_o}([Ce]_{w,0} - [Ce]_{w,eq}) \tag{9}$$

$$\overline{[CMPO]}_{o,eq} = \overline{[CMPO]}_{o,0} - 3\overline{[Ce]}_{o,eq} - \overline{[HNO_3 \cdot CMPO]}_{o,eq} \tag{10}$$

$$\overline{[HNO_3 \cdot CMPO]}_{o,eq} = \frac{V_w}{V_o}([HNO_3]_{w,0} - [HNO_3]_{w,eq}) \tag{11}$$

The effect of CMPO concentrations on D_{Ce} is shown in Fig. 5. D_{Ce} increases with increasing the CMPO concentration. K'_{ex} and n calculated from the plots are summarized in Table 1. The slope decreases as temperature decreases. At 308 and 318 K, the slopes are less than 3. If the extraction of nitric acid was not considered, third-power dependencies were obtained at all

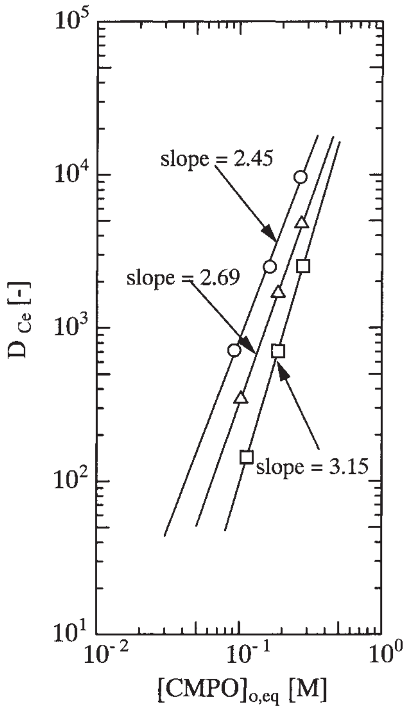

Figure 5. Effect of CMPO concentration on distribution ratio of Ce. $[CMPO]_{o,0} = 0.382$ M in NPOE; $V_o/V_w = 0.25$; $[HNO_3]_{w,0} = 0.05$ M; $[NaNO_3]_{w,0} = 2.95$ M; $[Ce]_{w,0} = 10.6$ mM; ○, 308 K; △, 318 K; □, 328 K.

three temperatures, although not shown here. This result is similar to that of Horwitz et al.,[12] who did not consider the HNO_3 extraction in evaluating the equilibrium CMPO concentration. Since the extraction behavior in this system is very complicated, further research is necessary to clarify the extraction behavior.

Permeation Rate of Ce(III)

The effect of temperature on the permeation rate of Ce(III) is shown in Fig. 6. The y axis is the Ce(III) concentrations in the feed solution and in the strip solution. The concentrations in the feed solution decreased with time, while those in the strip solution increased. After the concentration in the feed solution became equal to that in the strip solution, uphill transport of Ce(III) was achieved. The permeation rate increased with increasing temperature

Table 1. Extraction constant and coordination number.

	Temperature (K)	Extraction constant $(M)^{-n\,a}$	Coordination number
HNO_3	308	4.52	1.0
Ce(III)	308	2.33×10^5	2.45
Ce(III)	318	1.59×10^5	2.69
Ce(III)	328	1.49×10^5	3.15

[a] Refer to the coordination number.

from 308 to 328 K. As shown in Fig. 4, D_{Ce} decreased with increasing temperature, which gives unfavorable effect on the permeation rate. However, the diffusivities of the carrier and complex increased, since the viscosity of the liquid membrane decreased, as shown in Fig. 4, and this favorable temperature effect is the reason for higher permeation rate at higher temperature. Figure 7 shows the effect of the CMPO concentration on the permeation rate of Ce(III). The permeation rate increased with increasing the CMPO concentration. Since the viscosity of the membrane solution is much higher at 0.5 M CMPO (1.46×10^{-2} Pa sec) than that at 0.2 M CMPO (0.99×10^{-2} Pa sec), the permeation rate leveled off at this condition.

In the early stage of permeation, the Ce(III) concentration is high, and saturation of the carrier occurs, which means that almost all the carrier at the

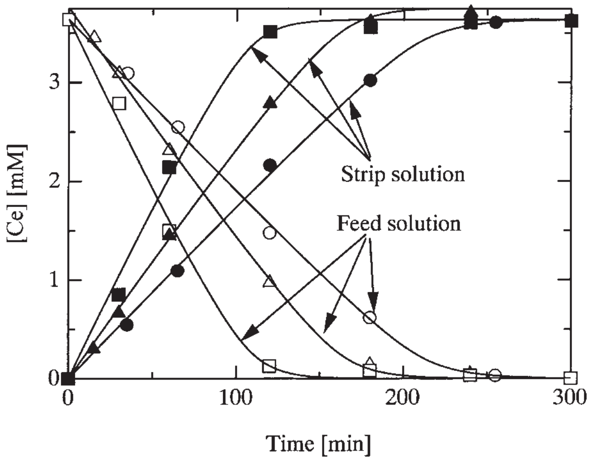

Figure 6. Effect of temperature on permeation rate of Ce. $[CMPO]_{o,0} = 0.382$ M; feed solution, $[HNO_3]_{w,0} = 0.05$ M; $[NaNO_3]_{w,0} = 2.95$ M; strip solution, water; ●, 308 K; △, 318 K; ○, 328 K. The curves are simulation results.

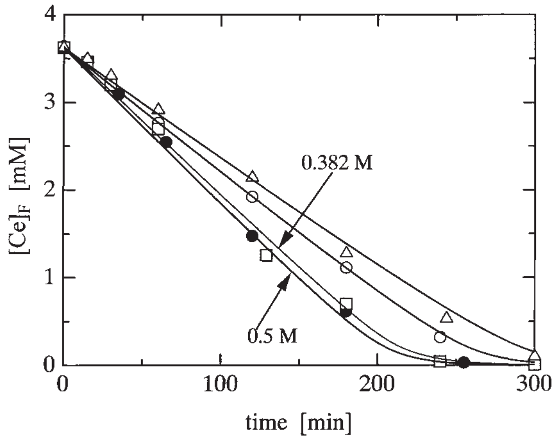

Figure 7. Effect of carrier concentration on permeation rate of Ce. $[\mathrm{CMPO}]_{o,0}$, △, 0.2 M; ○, 0.3 M; ●, 0.382 M; □, 0.5 M; feed solution, $[\mathrm{HNO_3}]_{w,0} = 0.05$ M; $[\mathrm{NaNO_3}]_{w,0} = 2.95$ M; strip solution, water; 308 K. The curves are simulation results.

feed–SLM interface is converted to the complex. Therefore, the flux is constant at this stage, and the Ce(III) concentration decreases with time linearly. On the other hand, in the final stage of permeation, the Ce(III) concentration in the feed solution is low and Ce(III) flux decreases with time, since the complex concentration at the feed side of membrane decrease gradually. This behavior will be discussed later.

In this liquid membrane system, Ce(III) can be transported against its concentration gradient due to the much lower nitrate ion concentration in the strip solution than in the feed solution. At the end of the permeation experiment, the nitrate ion concentration in the strip solution was in the range from 0.013 to 0.019 M. Only the liquid membrane without addition of TBP could result in such a low NO_3^- concentration in the strip solution. It was found that the quantity of transferred NO_3^- was one order of magnitude lower than that in our previous study, which used CMPO/TBP in dodecane.[6] Except for the experiment with 0.2 M CMPO, more than 99% of Ce(III) could be transported to the strip solution.

Comparison of the Stability of CMPO/NPOE Membrane and CMPO/TBP/Dodecane Membrane

The permeation experiments of Ce(III) through the SLM of 0.382 M = CMPO/NPOE were performed at 308 K, and compared with that of an SLM containing 0.382 M CMPO/0.868 M TBP/dodecane. In the

CMPO/TBP/dodecane membrane test, an aqueous trisodium citrate solution (0.3 M) was used as the strip solution instead of water. Figure 8 shows the results of the time course of the Ce(III) concentrations of the feed and strip solutions. Although the permeation rate of Ce(III) through the TBP/dodecane membrane was faster than that through the NPOE membrane in the early stage, and more than 99% of Ce(III) were transported to the strip solution after 5 hr for both membranes. After that, the Ce(III) in the strip solution was found to be back-transported from the strip solution to the feed solution in TBP/dodecane membrane, which means that the membrane is unstable. In contrast, the NPOE membrane was stable during the permeation of 48 hr.

Simulation of Permeation Rate of Ce(III) by Permeation Model

Permeation Model

The transport mechanism of Ce(III) is schematically shown in Fig. 9. Facilitated transport of Ce(III) from the feed solution through the SLM into the strip solution consists of the following consecutive steps:

- *Step 1.* Diffusion of Ce(III) from the bulk of the feed solution through the boundary layer adjacent to the membrane phase to the feed–SLM interface;

$$J_{\mathrm{A}} = k_{\mathrm{AF}}(C_{\mathrm{A,F}} - C_{\mathrm{A,Fi}}) \tag{12}$$

- *Step 2.* Extraction of Ce(III) with three anions (ion-pair formation) by carrier to form complex at the feed–SLM interface of the membrane. Since the chemical reaction between Ce(III) and CMPO occurs very rapidly, local equilibrium always holds at the aqueous-membrane interface[3]

$$K'_{\mathrm{ex}} = \frac{\bar{C}_{\mathrm{C,Fi}}}{C_{\mathrm{A,Fi}}\bar{C}_{\mathrm{B,Fi}}} \tag{13}$$

- *Step 3.* Diffusion of the Ce–CMPO complex from the feed side to the strip side of the SLM

$$J_{\mathrm{C}} = k_{\mathrm{MC}}(\bar{C}_{\mathrm{C,Fi}} - \bar{C}_{\mathrm{C,Fi}}) \tag{14}$$

- *Step 4.* Decomplexation of Ce(III) at the strip side of the SLM.

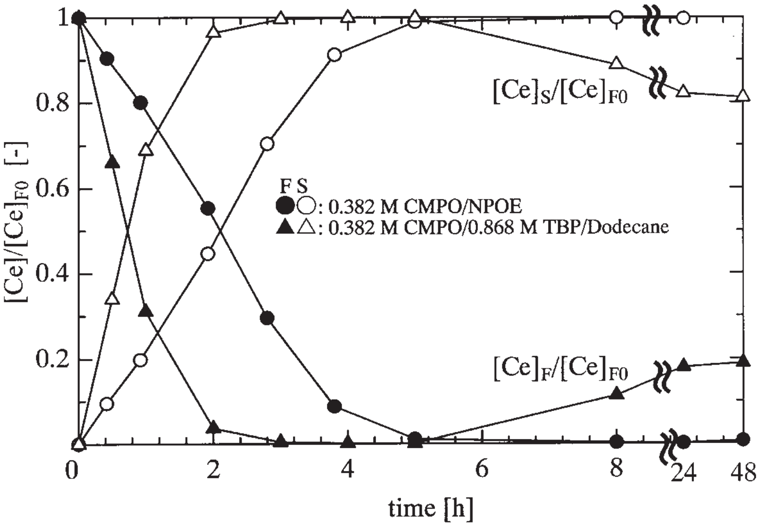

Figure 8. Comparison of stability of CMPO/TBP/dodecane and CMPO/NPOE membranes. Feed solution: $[Ce]_{F,0} = 3.6\,mM$; $[HNO_3] = 0.05\,M + [NaNO_3] = 2.95\,M$; strip solution: $[CANa_3] = 0.3\,M$ for TBP/dodecan; water for NPOE, 308 K.

- *Step 5.* Diffusion of CMPO from the strip side interface to the feed side interface of SLM

$$J_B = k_{MB}(\bar{C}_{B,Si} - \bar{C}_{B,Fi}) \tag{15}$$

- *Step 6.* Diffusion of Ce(III) from the strip–SLM interface to the bulk of the strip solution through the boundary layer adjacent to the membrane.

In addition, the transport of HNO_3 from the feed solution through the membrane to the strip solution is considered. Since the distribution ratio of HNO_3 in the feed–membrane interface is very low, mass transfer resistance in the feed phase can be neglected compared to the membrane resistance. Therefore, the HNO_3 concentration at the feed side interface of the SLM is assumed to be the HNO_3 concentration at the bulk solution. Then, the extraction equilibrium at the feed side interface of SLM is expressed as follows:

$$K_H = \frac{\bar{C}_{HC,Fi}}{C_{H,F}\bar{C}_{B,Fi}} \tag{16}$$

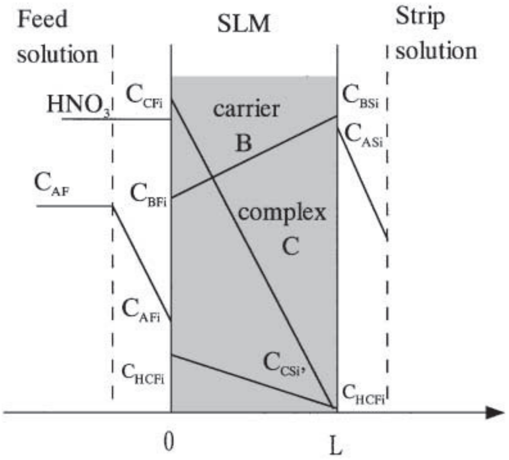

Figure 9. Mechanism of Ce facilitated transport through an SLM.

The flux of HNO_3 through the membrane is expressed as follows:

$$J_H = k_H(C_{H,F} - C_{H,S}) = k_H(\bar{C}_{HC,Fi} - \bar{C}_{HC,Si}) \tag{17}$$

The conservation of CMPO in the liquid membrane is expressed as follows:

$$C_{B0} = \frac{1}{2}(\bar{C}_{B,Fi} + \bar{C}_{B,Si}) + \frac{3}{2}(\bar{C}_{C,Fi} + \bar{C}_{C,Fi}) + \frac{1}{2}(\bar{C}_{HC,Fi} + \bar{C}_{HC,Si}) \tag{18}$$

Here, J_i is the flux of species i, k_i is the mass-transfer coefficient of species i. C_A, C_B, C_C, and C_{HC} are concentrations of Ce, CMPO, Ce–CMPO complex, and HNO_3–CMPO complex, respectively. The subscripts F, Fi, and Si refer to the feed side, and the feed–SLM and strip–SLM interfaces, respectively.

At steady-state, the relation $J_A = J_C$ holds. If the extraction of Ce with CMPO is 1 : 3 complex, J_B can be expressed as follows:

$$J_B = 3J_C + J_H \tag{19}$$

Since the interfacial reaction is considered to be very fast, steps 2 and 4 are not rate determining. Furthermore, the distribution ratio of Ce(III) at the strip side interface of the SLM is very low due to low HNO_3 concentration. Therefore, we can assume that $C_{C,Si}$ is 0. As described before, the HNO_3 concentration at the strip solution is much lower than that at the feed solution, $C_{H,Si}$ can be taken as 0. Then, the five concentrations at the interface, $C_{A,Fi}$, $C_{B,Fi}$, $C_{C,Fi}$, $C_{B,Si}$, and $C_{H,Fi}$ can be determined by five independent equations, Eqs. (12), (13), (16), (18), and (19), by the trial and error procedure for each experimental condition. Fluxes of Ce(III) and HNO_3 are related to the concentration changes with time as follows:

$$\frac{dC_{\mathrm{AF}}(t)}{dt} = -\frac{A}{V} J_{\mathrm{A}}(t) \tag{20}$$

$$\frac{dC_{\mathrm{H}}(t)}{dt} = -\frac{A}{V} J_{\mathrm{H}}(t) \tag{21}$$

where V is the volume of the feed solution, and A is the membrane area. The changes of Ce(III) and HNO_3 concentrations with time were calculated from Eqs. (20) and (21) by means of Runge–Kutta–Gill method.

Estimation of Parameters

According to the Wilke–Chang equation, the diffusivity is inversely proportional to (molar volume)$^{0.6}$ and liquid viscosity:

$$D_{\mathrm{AB}} \propto \frac{T}{\mu V_{\mathrm{A}}{}^{0.6}} \tag{22}$$

where μ is the viscosity of the solution and V_{A} is the molar volume of solute. If the molar volume ratio of CMPO to the complex is 1 : 3, the following relation between k_{MB} and k_{MC} holds:

$$\frac{k_{\mathrm{MB}}}{k_{\mathrm{MC}}} = 3^{0.6} \tag{23}$$

To make the calculated results agree with the experimental results, the value of k_{MB} was determined and listed in Table 2. Parameters, K_{H}, K'_{ex}, n, and n' were determined by the extraction equilibrium experiments as described,

Table 2. Parameters used to simulate the profile of Ce(III) concentration.

Temperature (K)	$[\mathrm{CMPO}]_0$ (M)	$k_{\mathrm{FA}} \times 10^3$ (cm/sec)	$k_{\mathrm{MB}} \times 10^5$ (cm/sec)
308	0.382	2.34	1.10
318	0.382	2.87	1.54
328	0.382	3.59	2.55
308	0.200	2.34	1.64
308	0.300	2.34	1.20
308	0.500	2.34	0.90

previously. The values of K_H and n' obtained from the extraction equilibrium experiment of HNO_3 under the condition of 308 K and 0.382 M CMPO were used to other conditions in the mathematical model. The values of k_H was determined from the HNO_3 permeation experiment under the condition of 0.382 M CMPO and 308 K so that the calculated result might agree with the experimental result of the HNO_3 permeation test ($k_H = 6.11 \times 10^{-7}$ m/sec). The value was applied to all conditions in the mathematical model. The k_{FA} was determined from experiments using feed solutions of low Ce(III) concentration (about 0.12 mM) at 308, 318, and 328 K. When $[Ce]_F$ is sufficiently low compared with the carrier concentration, D_{Ce} is so high that the permeation rate is limited by the diffusion rate of Ce through the boundary layer of the feed solution.[13] In this case, since almost all the Ce(III) at the feed–SLM interface is consumed by the complex formation, the $[Ce]_{Fi}$ is assumed to be 0, as will be shown later. Substitution of Eq. (12) into Eq. (20) gives the following equation:

$$\frac{d[Ce]_F}{dt} = -\frac{A}{V} k_{FA} [Ce]_F \tag{24}$$

which is integrated to give

$$\ln \frac{[Ce]_t}{[Ce]_0} = -\frac{A}{V} k_{FA} t \tag{25}$$

where $[Ce]_0$ is the initial Ce(III) concentration in the feed solution. Figure 10 shows the experimental results. The values of k_{AF} were evaluated from the slopes of the plots and are summarized in Table 2.

Simulation Results

The solid lines in Figs. 6 and 7 show the calculated results, which are in agreement with the experimental results.

Next, the effects of the temperature and the viscosity on the estimated values of k_{MB} are discussed. As shown in Figs. 11 and 12, the slopes are 0.95 and 1.08, respectively, which indicates that the estimated membrane mass-transfer coefficients are consistent with the Wilke–Chang equation.

Figure 13(a) shows the calculated time-courses of $C_{A,F}/C_{A,0}$, $C_{C,Fi}/C_{B,0}$, $C_{B,Fi}/C_{B,0}$, and $C_{A,Fi}/C_{A,F}$ at $C_{B,0} = 0.382$ M and $T = 308$ K. The change of D_{Ce}, which is calculated from Eq. (7), is also shown. Figure 13(b) shows how the calculated flux (J_A) and permeability (P_A) change with $C_{A,F}$. Here, permeability P_A is defined by the following equation:

$$P_A = \frac{J_A}{C_{A,F}} \tag{26}$$

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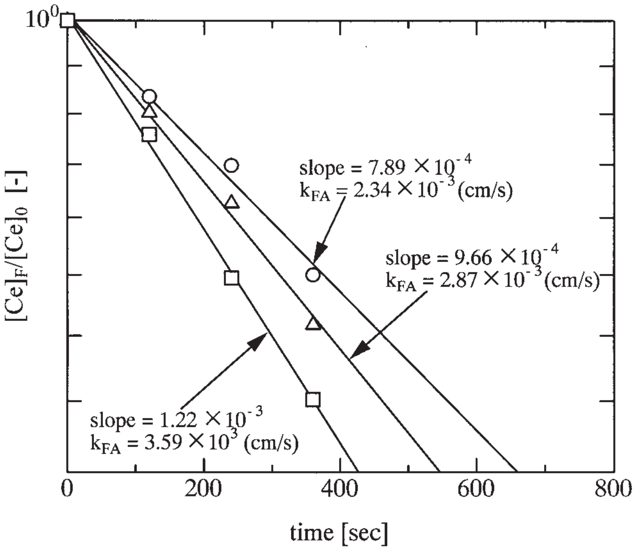

Figure 10. Plot of log([Ce]/[Ce]$_0$) vs. time for determination of k_{FA}. [CMPO]$_{o,0}$ = 0.382 M; [Ce]$_{w,0}$ = 0.12 mM; [HNO$_3$]$_{w,0}$ = 0.05 M; [NaNO$_3$]$_{w,0}$ = 2.95 M; ○, 308 K; △, 318 K; □, 328 K.

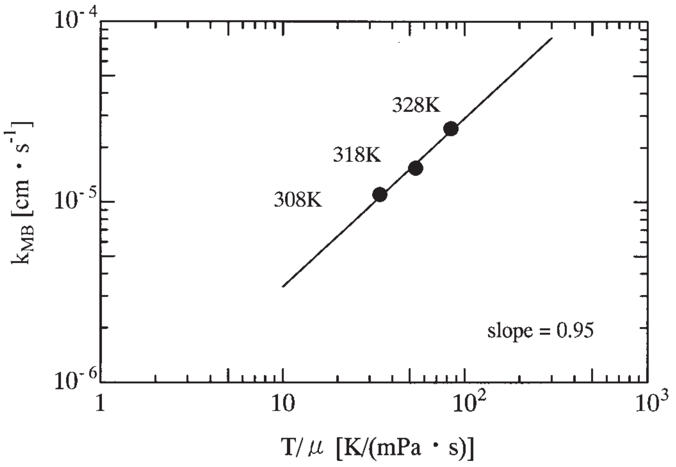

Figure 11. Effect of temperature on k_{MB}. The values of k_{MB} were determined by the simulation of the data shown in Fig. 6.

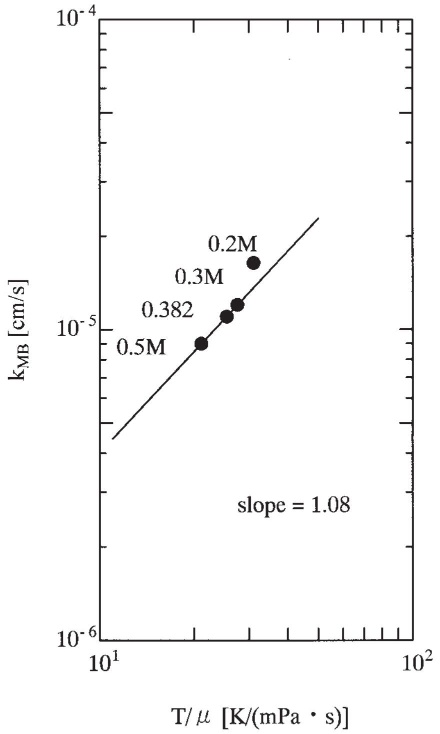

Figure 12. Effect of carrier concentration on k_{MB}. The values of k_{MB} were determined by the simulation of the data shown in Fig. 7.

As shown in Fig. 13(a), in the early stage of permeation experiment where $C_{A,F}$ is high, most of the carrier at the feed–SLM interface is converted to the complex and $C_{C,Fi}$ is constant. Therefore, as shown in Fig. 13(b), J_A is constant and P_A is inversely proportional to $C_{A,F}$. In the later stage of permeation where $C_{A,F}$ is low, D_{Ce} increases remarkably with time [see Fig. 13(a)], and the mass-transfer resistance in the feed solution limits Ce(III) transport. Therefore, $C_{A,Fi}/C_{A,F}$ becomes very low and J_A is approximately expressed by $J_A = k_F C_{A,F}$, i.e., J_A is proportional to $C_{A,F}$ and P_A is constant, as shown in Fig. 13(b). These results are consistent with the present experimental results and predictions just described.

CONCLUSION

Facilitated transport of Ce(III) from mixed aqueous HNO_3–$NaNO_3$ solutions to water through supported liquid membranes were performed. The

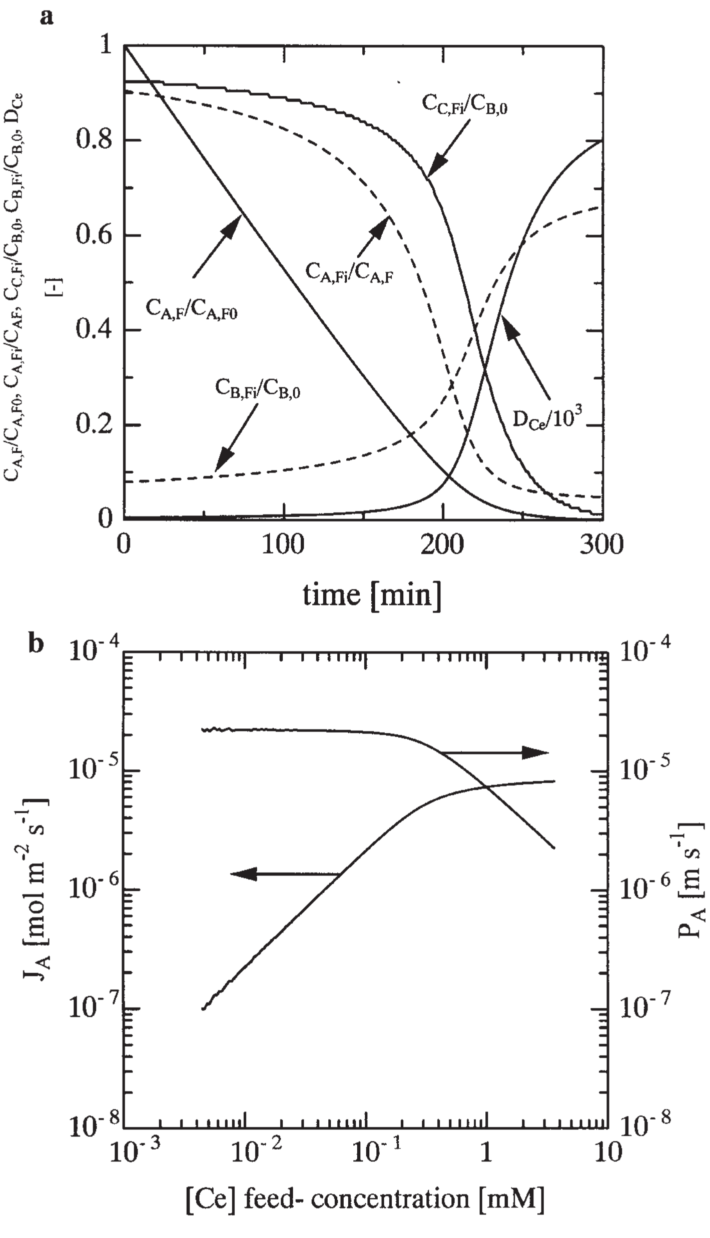

Figure 13. Calculated results. (a) Variations of concentration and distribution ratio with time at the feed side interface. (b) Effect of initial Ce concentration on the permeation flux and permeability of Ce. $[\mathrm{CMPO}]_{o,0} = 0.382\,\mathrm{M}$, 308 K.

effects of the temperature and the concentration of the carrier on the permeation rate of Ce(III) were investigated. Since the transport of HNO_3 to the strip solution could be effectively prevented, uphill transport of Ce(III) could be achieved without adding any masking agent of Ce(III) to the strip solution. A mathematical model for analyzing the facilitated transport of Ce(III) was developed. The permeation rate of Ce(III) could be simulated by using various physical and chemical parameters that were independently determined or estimated.

NOMENCLATURE

A = membrane area (m^2)
C_A = concentration of Ce ($mol\,m^{-3}$)
C_B = concentration of carrier ($mol\,m^{-3}$)
C_C = concentration of Ce–CMPO complex ($mol\,m^{-3}$)
C_H = concentration of HNO_3 ($mol\,m^{-3}$)
C_{HC} = concentration of HNO_3–CMPO complex ($mol\,m^{-3}$)
D_{Ce} = distribution ratio of Ce
D_H = distribution ratio of HNO_3
J_A = permeation flux of Ce ($mol\,m^{-2}\,sec^{-1}$)
J_B = permeation flux of carrier ($mol\,m^{-2}\,sec^{-1}$)
J_C = permeation flux of complex ($mol\,m^{-2}\,sec^{-1}$)
J_H = permeation flux of HNO_3 ($mol\,m^{-2}\,sec^{-1}$)
k_{FA} = mass-transfer coefficient of Ce ($m\,sec^{-1}$)
k_{MC} = mass-transfer coefficient of complex ($m\,sec^{-1}$)
k_{MB} = mass-transfer coefficient of CMPO ($m\,sec^{-1}$)
k_H = mass-transfer coefficient of HNO_3 defined by $J_H = k_H(C_{H,F} - C_{H,S})$ ($m\,sec^{-1}$)
K_{ex} = extraction constant of Ce(III)
K_H = extraction constant of HNO_3
K'_{ex} = apparent extraction constant of Ce(III)
n = coordination number of Ce
n' = coordination number of HNO_3
P_A = permeability of Ce(III) ($m\,sec^{-1}$)
t = time (sec)
V_o = organic phase volume in solvent extraction experiment (m^3)
V_w = aqueous phase volume in solvent extraction experiment (m^3)
V = volume of feed solution (m^3)

Greek Letters

μ = viscosity (Pa sec)

Subscripts

A = Ce(III)
B = CMPO
C = complex
eq = equilibrium value
F = feed solution
H = HNO_3
i = interface
o = organic phase
S = strip solution
w = aqueous phase
0 = initial value

REFERENCES

1. Danesi, P.R. Separation of metal species by supported liquid membrane. Sep. Sci. Technol. **1984–85**, *19* (11&12), 857.
2. Ramanujam, A.; Dhami, P.S.; Gopalakrishnan, V.; Dudwadkar, N.L.; Chitnis, R.R.; Mathur, J.N. Partitioning of actinides from high level waste of PUREX origin using octylphenyl-N, N′-diisobutylcarbamoylmethyl phosphine oxide (CMPO)-based supported liquid membrane. Sep. Sci. Technol. **1999**, *34*, 1717.
3. Danesi, P.R.; Horwitz, E.P.; Rickert, P.G. Rate and mechanism of facilitated americium(III) transport through a supported liquid membrane containing a bifunctional organophosphorus mobile carrier. J. Phy. Chem. **1983**, *87*, 4708.
4. Danesi, P.R.; Chiarizia, R.; Rickert, P.; Horwitz, E.P. Separation of actinides and lanthanides from acidic nuclear wastes by supported liquid membranes. Solvent Extr. Ion Exch. **1985**, *3*, 111.
5. Chiarizia, R.; Danesi, P.R. A double liquid membrane system for the removal of actinides and lanthanides from acidic nuclear wastes. Sep. Sci. Technol. **1987**, *22*, 641.
6. Teramoto, M.; Fu, S.S.; Takatani, K.; Ohnishi, N.; Maki, T.; Fukui, T.; Arai, K. Treatment of simulated low level radioactive wastewater by supported liquid membranes: uphill transport of Ce(III) using CMPO as carrier. Sep. Purif. Technol. **2000**, *18*, 57.
7. Teramoto, M.; Sakaida, Y.; Fu, S.S.; Ohnishi, N.; Matsuyama, H.; Maki, T.; Fukui, T.; Arai, K. An attempt for the stabilization of supported liquid membrane. Sep. Purif. Technol. **2000**, *21*, 137.

8. Muscatello, A.C.; Navratil, J.D.; Killion, M.E.; Price, M.Y. Supported extractant membranes for americum and plutonium recovery. Sep. Sci. Technol. **1987**, *22*, 843.
9. Horwitz, E.P.; Kalina, D.G.; Diamond, H.; Vandegrift, G.F. The TRUEX process-a process for the extraction of the transuranic elements from nitric acid wastes utilizing modified PUREX solvent. Solvent Extr. Ion Exch. **1985**, *3*, 75.
10. Spencer, B.B.; Counce, R.M.; Egan, B.Z. Extraction of nitric acid from aqueous media with OϕD(iB)CMPO-*n*-dodecane. AIChE J. **1997**, *43*, 555.
11. Boerrigter, H.; Verboom, W.; Jong, F.; Reinhoudt, N. Europoim(III) extraction with new resorcinarene cavitand CMP(O) ligands: slovent extraction and mechanistic study. Radiochim. Acta **1998**, *81*, 39.
12. Horwitz, E.P.; Kalina, D.G.; Kaplan, L.; Mason, G.W.; Diamond, H. Selected alkyl(phenyl)-N,N-dialkylcarbamoylmethylphosphine oxides as extractants for Am(III) from nitric acid media. Sep. Sci. Technol. **1982**, *17*, 1261.
13. Danesi, P.R.; Cianetti, C. Permeation of metal ions through a series of two complementary supported liquid membranes. J. Membrane Sci. **1984**, *20*, 201.

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