MECHANISMS OF SAMARIUM EXTRACTION WITH DIISOSTEARYLPHOSPHORIC ACID AND ITS PERMEATION THROUGH SUPPORTED LIQUID MEMBRANE

KAZUO KONDO, TETSUYA HASHIMOTO,
HISAHARU SUMI AND MICHIAKI MATSUMOTO
*Department of Chemical Engineering and Materials Science,
Doshisha University, Tanabe, Kyoto 610-03*

Key Words: Extraction, Rare Earth Metal, Supported Liquid Membrane, Organophosphorus Compounds, Kinetics

The extraction equilibrium of samarium (Sm) with diisostearylphosphoric acid (DISPA, HR) was measured at 303 K. The complex, SmR_3 , was formed, unlike in the case of dialkylphosphoric acids investigated previously. The extraction rate of Sm with DISPA was measured using a stirred transfer cell. The extraction rates were limited by the diffusion process. The permeation of samarium through a supported liquid membrane containing DISPA as a carrier was carried out based on the above results. Under the experimental conditions, the diffusion of samarium in the film of the aqueous feed or the diffusion of the complex in the membrane phase was anticipated to be the rate-determining step.

Introduction

Solvent extraction techniques have been extensively applied to the practical separation of rare earth metals⁵⁾ and have been studied on a laboratory scale by many investigators. The extractants used for the recovery and separation of lanthanide ions were mainly acidic organophosphorus compounds like di (2-ethylhexyl) phosphoric acid (D2EHPA)^{3, 4, 18-21)} and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA)^{8, 10, 11, 14, 23)}, which are commercially available. The selection of extractants among acidic organophosphorus compounds plays an important role in recovery and separation of lanthanide ions. Kolarik and Pankova⁷⁾ studied the effects of structure (linear or branching) and size ($\text{C}_4\text{-C}_8$) of alkyl group on extraction of lanthanides by dialkylphosphoric acids. They concluded that the extraction efficiency is lowered by branching of the alkyl group and for the same structure it is unaffected by an increase in the number of carbon atoms in the alkyl group. Recently, Ohto *et al.*¹⁷⁾ developed some new types of acidic organophosphorus compounds, phenylphosphate derivatives, for lanthanide extraction. They stated that enhancement of the extractability is attributable to a steric effect around the phosphorus atom. Based on the above studies, it is expected that dialkylphosphoric acids having longer alkyl chains than C_8 show excellent extractability due to the steric effect caused by bulky alkyl groups. From this view-point, we selected diisostearylphosphoric acid (DISPA), which has 18 carbon atoms and is commercially available, as the extractant.

As is well known, the recovery of lanthanide ions by solvent extraction requires a large number of stages for the

preparation of high-purity products, because the chemical and physical properties of rare earth metals are very similar to one another¹⁾. Recently, use of supported liquid membranes (SLM) for lanthanide separation has become of interest as an energy-saving method^{2, 6, 12, 15, 16)}. In addition, the recovery of samarium from scrap Sm-Co alloy using solvent extraction has recently become of technical interest⁹⁾.

In this study, we investigated the extraction of samarium with DISPA to characterize DISPA. The equilibrium and kinetics of extraction were examined and compared with those of D2EHPA and EHPNA. Furthermore, permeation of samarium through the supported liquid membrane containing DISPA as a carrier was carried out to clarify the permeation mechanism.

1. Experimental

1.1 Extraction equilibrium

The extractant, DISPA, was kindly supplied by Daihachi Chemical Co., Japan. The purity of DISPA was determined by non-aqueous titration with ethanolic potassium hydroxide. Other organic and inorganic chemicals used were G.R. grade. The extraction equilibrium of samarium with DISPA was measured at 303 K. The organic phase was prepared by dissolving the extractant in diluent. The diluents used were benzene, toluene, cyclohexane, *n*-heptane and kerosene. The aqueous solution was prepared by dissolving samarium chloride in 100 mol/m³ hydrochloric acid-sodium acetate solution whose pH was adjusted. Equal volumes of the aqueous and organic solutions were shaken in a thermostated bath for 24 hours to attain equilibrium. After phase separation, the concentration of samarium and the pH of the aqueous solution were

* Received on December 22, 1994. Correspondence concerning this article should be addressed to K. Kondo.

Fig. 1 Flat-sheet supported liquid membrane

measured. The concentration of samarium was determined by the Arsenazo III method using a spectrophotometer.

1.2 Extraction rate

The rate of samarium extraction by DISPA was measured using the stirred transfer cell, which was the same as described in the previous paper²⁴). The experimental procedure was the same as described previously²⁴). The concentration change of samarium in the aqueous solution with time was measured under various experimental conditions. The organic solvent used was toluene.

1.3 Permeation rate through supported liquid membrane

A membrane material, porous tetrafluoroethylene film (thickness, 47 μm ; density, 0.51 g/cm^3 ; porosity, 0.77) was kindly supplied by Japan Gore Tex Co. The SLM was prepared by impregnating the porous film with n-heptane solution containing DISPA whose concentration was 80 mol/m^3 . Hydrochloric acid solution was employed as a stripping solution. The experimental apparatus is shown in Fig. 1. A membrane with an effective area of $2 \times 10^{-3} \text{ m}^2$ was fixed by using two teflon flanges. The feed and stripping solutions were fed concurrently. At steady state, the concentration of samarium in the stripping solution was measured by the UV spectrophotometer.

The permeation rate of samarium, J_M , is defined as follows;

$$J_M = (C_{MS} \cdot U_S) / A \quad (1)$$

where C_{MS} is the concentration of samarium in the stripping solution at steady state, and U_S and A are the volumetric flow rate of the stripping solution and the effective area of SLM, respectively.

2. Results and Discussion

Fig. 2 Equilibrium plot of DISPA-Sm extraction system for various organic solvents

2.1 Extraction equilibrium

For D2EHPA and EHPNA systems, it is known that trivalent metal ion is extracted as a complex of composition, $\text{MR}_3 \cdot x\text{HR}$ into the organic solution with the dimer of the extractant. However, DISPA exists mainly as the monomer from the measurement of apparent molecular weight in toluene by vapor-phase osmometry. This may be because the bulky alkyl groups in DISPA hinder hydrogen bonding. In the present case, therefore, the monomer state of DISPA in all solvents investigated here is assumed.

The extraction reaction can be written by Eq.(2).

where HR represents the extractant, and x and K_{ex} are the solvation number and the extraction equilibrium constant, respectively. The distribution ratio of Sm, D , is given by Eq. (3) when samarium ion is assumed to be free in aqueous solution.

$$D = C_{\text{Sm,org}} / C_{\text{Sm,aq}} = K_{ex} C_{\text{HR}}^{(3+x)} / C_{\text{H}}^3 \quad (3)$$

Equation (3) is rewritten as follows.

$$\log(D C_{\text{H}}^3) = (3+x) \log C_{\text{HR}} + \log K_{ex} \quad (4)$$

Experimental results for the various organic solvents employed were plotted according to Eq.(4). The slopes of the straight lines were 3, that is, $x = 0$. Therefore, the equation for the extraction of samarium with DISPA is expressed as follows.

Furthermore, Eq.(4) is rewritten by the following equation.

$$\log D = \log(C_{\text{HR}}^3 C_{\text{H}}^{-3}) + \log K_{ex} \quad (6)$$

All the experimental results were plotted in Fig. 2 according to Eq. (6), from which straight lines with a slope of 1 were obtained. The values of K_{ex} obtained from the

Table 1 Extraction equilibrium constant

Solvent	K_{ex}
Benzene	0.148
Toluene	0.178
Cyclohexane	0.724
<i>n</i> -Heptane	1.48
Kerosene	1.55

Fig. 3 Effect of pH on initial extraction rate

Fig. 4 Effect of C_{Sm0} on R_0

intercepts were listed in **Table 1**. Aliphatic solvents gave high values of K_{ex} compared with those of aromatic solvents, which was the same result as seen in the other system⁸. For the extraction of samarium with D2EHPA^{7, 19} or EHPNA^{10, 11, 23}, the reported solvation number was 3. The different solvation number is attributed to the bulky alkyl chain of DISPA compared with those of D2EHPA and EHPNA.

2.2 Extraction rate

Figure 3 shows the relation between the logarithm of the initial extraction rate of Sm, R_0 , and pH. In the range of low pH, the slope of this relation is about 2, but in the

Fig. 5 Effect of C_{HR0} on R_0

high pH range, the slope approaches zero. **Figure 4** shows the relation between R_0 and the initial concentration of samarium, C_{Sm0} , on a log scale. R_0 is proportional to C_{Sm0} . **Figure 5** shows the relation between R_0 and the initial concentration of HR, C_{HR0} , on a log scale. In the range of low C_{HR0} , the slope of this relation is about 1, but in the high C_{HR0} , the slope approaches zero.

According to Miyake *et al.*¹³ who studied the extraction mechanism of metal ions with D2EHPA and EHPNA in detail, the extraction rates of metal ions except Fe(III) were limited by the diffusion process. The concentrations of the extractant in the organic film and of hydrogen ion in the aqueous film are assumed to be kept constant because the extractant concentration is in considerable excess over the samarium concentration and the buffer solution is used. Therefore, the diffusion equations of samarium and the complex are as follows.

$$R = k_{Sm}(C_{Sm} - C_{Smi}) \quad (7)$$

$$= k_c (C_{ci} - C_c) \quad (8)$$

where k_j is the mass transfer coefficient of the species j and subscript i represents the zone adjacent to the interface.

In the initial period, Eqs.(7) and (8) are converted to the following equations.

$$R_0 = k_{Sm}(C_{Sm0} - C_{Smi}) \quad (9)$$

$$= k_c C_{ci} \quad (10)$$

In the interfacial zone, the species are assumed to be in an equilibrium state.

$$K_{ex} = C_{ci} C_{H0}^3 / C_{Smi} C_{HR0}^3 \quad (11)$$

From Eqs.(10) and (11), Eq.(12) is derived.

$$R_0 = k_c K_{ex} C_{Smi} (C_{HR0} / C_{H0})^3 \quad (12)$$

C_{Smi} in Eq. (12) was calculated as follows. The mass transfer coefficient of samarium, k_{Sm} , was evaluated from the high pH range in Fig. 3 as 2.2×10^{-5} m/s. C_{Smi} was

Fig. 6 Relationship between R_0 and $C_{Smi}(C_{HRO}/C_{H0})^3$

Fig. 8 Effect of membrane thickness on J_M

Fig. 7 Effect of concentration of stripping reagent (HCl) on permeation rate

Fig. 9 Effect of feed concentration of samarium on J_M

calculated by the observed extraction rate and the value of k_{Sm} using Eq. (9). **Figure 6** shows the plot based on Eq. (12). As expected, a linear relationship between R_0 and $C_{Smi}(C_{HRO}/C_{H0})^3$ was obtained. The value of k_c was obtained as 6.2×10^{-7} m/s from the slope of this plot. This value is a little low compared with that reported in the Pr-EHPNA system¹³. The solid curves shown in Figs. 3 to 5 were calculated by using the above values. In the present study, the extraction rate of Sm with DISPA is considered to be limited by the diffusion process in the same manner as in metal extraction with D2EHPA or EHPNA¹³.

2.3 Permeation rate through supported liquid membrane

The permeation of samarium through the liquid membrane consists of the following steps.

- 1) Diffusion of samarium ion in the film of the aqueous feed.
- 2) Extraction of samarium at the interface between the feed solution and the membrane.

- 3) Diffusion of complex formed in the membrane.
- 4) Stripping of samarium at the interface between the stripping solution and the membrane.
- 5) Diffusion of samarium ion in the film of the stripping solution.

Figures 7 and 8 show the effects of concentration of the stripping reagent (HCl) and the membrane thickness on the permeation rate, J_M , respectively. J_M is independent of the concentration of stripping reagent and membrane thickness, but J_M is proportional to C_{Sm0} as shown in **Fig. 9**. Furthermore, from the results in 2.2, the extraction rate was faster than that of film diffusion in the aqueous feed. Therefore, steps (2), (4) and (5) are negligible and the permeation rate is controlled by step (1) or (3).

Therefore, the permeation rate is expressed as follows;

$$J_M = k_{Sm}' (C_{Sm} - C_{Smi}) \quad (13)$$

$$= k_c' K_{ex} C_{Smi} (C_{HRO}/C_{H0})^3 \quad (14)$$

Fig. 10 Effects of flow rates of feed and stripping solutions on J_M

Fig. 11 Relationship between J_M and $C_{Sm}(C_{HRO}/C_{HO})^3$ for SLM

where k_c' is the apparent mass transfer coefficient of the complex in the membrane phase.

To evaluate the mass transfer coefficient for the feed film, k_{Sm}' , the effect of volumetric velocity of the feed and the stripping solutions, U_f and U_s , on J_M was examined in Fig. 10. As expected, J_M is independent of U_s and dependent on U_f . Takahashi *et al.*²²⁾ studied the mass transfer coefficient in a flat-sheet supported liquid membrane and concluded that the mass transfer coefficient for the aqueous film was correlated by the following equation.

$$Sh_l = a Re_l^{1/2} Sc_l^{1/3} \quad (15)$$

The experimental data shown in Fig. 10 were fitted by Eq.(15) with $a = 1.2$ (k_{Sm}' : $3.4\text{--}5.5 \times 10^{-6}$ m/s). In Fig. 10, the solid line was calculated by Eq. (15). Figure 11 shows the relation between J_M and $C_{Sm}(C_{HRO}/C_{HO})^3$. The value of k_c' is 6.2×10^{-9} m/s from the slope of this relation.

Conclusion

The extraction equilibrium of samarium (Sm) with diisostearylphosphoric acid (DISPA, HR) was examined. It was found that the complex, SmR_3 , was formed. The extraction rate of Sm with DISPA was measured using a stirred transfer cell. The extraction rates were limited by the diffusion process. The permeation of samarium through a supported liquid membrane containing DISPA as the carrier was carried out based on the above results. Under the experimental conditions, the diffusion of the samarium in the feed film or that of the complex in the membrane phase was the rate-determining step.

The bulky alkyl chains of DISPA contributed unique characteristics, that is, DISPA existing as a monomer in the organic solvent and forming SmR_3 complex which were not reported previously.

Acknowledgment

The authors wish to express their thanks to Mr. S. Nakai and Mr. T. Yashiro for their valuable experimental assistance. We thank Daihachi Chemical Co. and Japan Gore Tex Co. for supplying samples of diisostearylphosphoric acid and tetrafluoroethylene film, respectively.

Nomenclature

A	= effective area of membrane	[m ²]
a	= proportional constant of Eq. (15)	[-]
C_j	= concentration of species j ($j = \text{Sm, HR, H}$)	[mol/m ³]
D	= distribution ratio of samarium	[-]
J_M	= permeation rate of samarium through supported liquid membrane	[mol/(m ² s)]
K_{ex}	= extraction equilibrium constant	[-]
k_c	= mass transfer coefficient of complex for organic film	[m/s]
k_{Sm}	= mass transfer coefficient of samarium for aqueous film	[m/s]
k_c'	= apparent mass transfer coefficient of complex for membrane	[m/s]
k_{Sm}'	= mass transfer coefficient of samarium for feed film	[m/s]
l	= length of straight channel	[m]
R	= extraction rate	[mol/(m ² s)]
Re_l	= Reynolds number with l as characteristic length	[-]
Sc	= Schmidt number	[-]
Sh_l	= Sherwood number	[-]
U	= volumetric flow rate	[m ³ /s]
x	= solvation number	[-]

<subscript>

f	= feed
i	= zone adjacent to interface
s	= stripping
0	= initial state

Literature Cited

- 1) Brown, C. G. and L. G. Sherrington, *J. Chem. Tech. Biotechnol.*, **29**, 193-209 (1979)
- 2) Danesi, P. R., R. Chiarizia, P. Rickert and E. P. Horwitz, *Solv. Extr. Ion Exch.*, **3**, 111-147 (1985)
- 3) Hirashima, Y., Y. Yamamoto, S. Takagi, T. Amano and J. Shiokawa, *Bull. Chem. Soc. Japan*, **51**, 2890-2893 (1978)
- 4) Imai, M. and S. Furusaki, *Kagaku Kogaku Ronbunshu*, **11**, 515-519 (1985)
- 5) Koch, D. F. A., *Materials Australasia*, May, p.12-15 (1987)

- 6) Kojima, T., C. Nakayama and S. Uemiya, *Can. J. Chem. Eng.*, **72**, 72-77 (1994)
- 7) Kolarik, Z. and H. Pankova, *J. Inorg. Nucl. Chem.*, **28**, 2325-2333 (1966)
- 8) Kondo, K. and M. Matsumoto, *Solv. Extr. Res. Dev., Japan*, **2**, 213-220 (1995)
- 9) Koshimura, H. and S. Yamamoto, Proc. Symp. Solv. Extr., 1987, p. 227-232 (1987)
- 10) Kubota, F., M. Goto and F. Nakashio, *Solv. Extr. Ion Exch.*, **11**, 437-453 (1993)
- 11) Ma, E., X. Yan, S. Wang, H. Long and C. Yuan, Proc. Int. Solv. Extr. Conf. 80, 80-147 (1980)
- 12) Matsuyama, H., K. Komori and M. Teramoto, *J. Membr. Sci.*, **47**, 217-228 (1989)
- 13) Miyake, Y., H. Matsuyama, M. Nishida, M. Nakai, N. Nagase and M. Teramoto, *Hydrometallurgy*, **23**, 19-35 (1990)
- 14) Mori, Y., H. Ohya, H. Ono and W. Eguchi, *J. Chem. Eng. Japan*, **21**, 86-91 (1988)
- 15) Nakamura, S. and K. Akiba, *Separ. Sci. Technol.*, **24**, 673-683 (1989)
- 16) Nishiki, T. and R. G. Bautista, *Metal. Trans. B*, **14B**, 25-31 (1983)
- 17) Ohto, K., K. Inoue, T. Yamamoto, M. Goto, F. Nakashio, S. Shinkai and T. Kago, *Bull. Chem. Soc. Japan*, **66**, 2528-2535 (1993)
- 18) Owens, T. C. and M. Smutz, *J. Inorg. Nucl. Chem.*, **30**, 1617-1633 (1968)
- 19) Peppard, D. F., G. W. Mason, J. L. Maier and W. J. Driscoll, *J. Inorg. Nucl. Chem.*, **4**, 334-343 (1957)
- 20) Pierce, T. B. and P. F. Peck, *Analyst*, **88**, 217-221 (1963)
- 21) Shibata, J., M. Sano, H. Ohmori and S. Nishimura, *J. Japan, Inst. Metals*, **51**, 749-754 (1987)
- 22) Takahashi, K., M. Nakano and H. Takeuchi, *Kagaku Kogaku Ronbunshu*, **13**, 256-259 (1987)
- 23) Teramoto, M., T. Sakuramoto, T. Koyama, H. Matsuyama and Y. Miyake, *Separ. Sci. Technol.*, **21**, 229-250 (1986)
- 24) Yoshizuka, K., K. Kondo and F. Nakashio, *J. Chem. Eng. Japan*, **18**, 342-348 (1985)

(Presented at 59th Annual Meeting of The Society of Chemical Engineers, Japan, at Sendai, March 1994)