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Solvent Extraction of Europium with Diisostearylphosphoric Acid and Its Application to an Emulsion Liquid Membrane Technique

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ABSTRACT

The extraction equilibrium of europium (Eu) with diisostearylphosphoric acid (DISPA, HR) was measured in various solvents at 303 K. The stoichiometry of the complex extracted and the extraction equilibrium constants were determined. The extraction rate of Eu with DISPA was measured using a stirred transfer cell. The extraction rate was found to be limited by the diffusion process. The permeation of Eu through an emulsion liquid membrane containing DISPA as a carrier and Span 80 as a surfactant was carried out. Under the experimental conditions, the reaction resistance contributed to the overall permeation process. An interfacial reaction model was proposed to explain the experimental results.

INTRODUCTION

In a previous paper (1) the extraction of samarium with diisostearylphosphoric acid (DISPA) and its permeation through a supported liquid membrane were carried out. We concluded that the extraction and permeation processes were limited by the diffusion processes in the aqueous feed solution and the organic one. In such a case, the separation factor is determined by the extraction equilibrium constant and the mass transfer coefficient. The separation factor among rare earth metals, however, cannot be enhanced because the extraction and the mass transfer behaviors

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of adjacent elements are very similar. Recently, the addition of a water (2–7) or an oil (8–10) soluble chelating reagent to the extraction system of the rare earth metals was examined as a means to enhance the separation factor by using the difference in the stability constants between the chelating reagent and lanthanides. However, the extraction rates were significantly decreased by the addition of these compounds because of a decrease in the free metal ion concentrations. Some investigators (11–13) studied the extraction of europium by emulsion liquid membranes containing 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester as a carrier and reported the contribution of the reaction to the permeation process. An improvement of the separation factor under the condition of reaction control is easier than that under diffusion control. In the present work we carried out the extraction of europium through emulsion liquid membranes (ELM) and examined the permeation mechanism through ELM, along with the extraction equilibrium and the extraction mechanism between two phases.

EXPERIMENTAL

Extraction Equilibrium

The extractant, diisostearylphosphoric acid (DISPA), was kindly supplied by Daihachi Chemical Co., Japan. The purity of DISPA was determined by nonaqueous titration with ethanolic potassium hydroxide. Other organic and inorganic chemicals used were of guaranteed reagent grade. The extraction equilibrium of europium with DISPA was measured at 303 K. The organic phase was prepared by dissolving the extractant in *n*-heptane. The aqueous solution was prepared by dissolving europium chloride in 100 mol/m^3 of a 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 europium and the pH of the aqueous solution were measured. The concentration of europium was determined by inductively coupled plasma-atomic emission spectrophotometer (Shimadzu ICPS-8000).

Extraction Rate

The rate of europium extraction by DISPA was measured using a stirred transfer cell which was described in a previous paper (1). The concentration change of europium in the aqueous solution with time was measured under various experimental conditions. The organic solvent used was toluene.

Permeation through Emulsion Liquid Membrane

W/O emulsions were prepared by mixing 50 cm^3 of the oil phase and 50 cm^3 of the internal water phase in a homogenizer (Nichion Ikarikakikai NS-50) at 50 s^{-1} for 5 minutes. The oil phase was composed of DISPA as a carrier, Span 80 as an emulsifier, and *n*-heptane as a solvent. An aqueous hydrochloric acid solution with a concentration of 100 mol/m^3 was used as the internal water phase for stripping. ELM operation was performed at 303 K by pouring 100 cm^3 of the W/O emulsion into 300 cm^3 of europium solution by agitating the content at 5 s^{-1}. Samples were taken at proper time intervals.

RESULTS AND DISCUSSION

Extraction Equilibrium

In the samarium extraction with DISPA in various diluents, the stoichiometry of the complex extracted was found to be SmR_3 (1).

In the present case, therefore, the following equation is assumed:

$$Eu^{3+} + 3HR \rightleftharpoons EuR_3 + 3H^+ \qquad (1)$$

The distribution ratio, D, is written as follows:

$$\log D = \log(C_{\mathrm{HR}}^3 C_{\mathrm{H}}^{-3}) + \log K_{\mathrm{ex}} \qquad (2)$$

All the experimental results according to Eq. (2) are plotted in Fig. 1, from which straight lines with slopes of 1 were obtained. The values of K_{ex} obtained from the intercepts are listed in Table 1. Aliphatic solvents gave high values of K_{ex} compared with those of aromatic solvents, which is the same as seen in other systems (1, 14).

Extraction Rate

From the curves for the concentration change of europium with time, the initial extraction rate of Eu, R_0, for each run was obtained. Figure 2 shows the relation between the logarithm of R_0 and pH. In the range of low pH, the slope of this relation is 2.0, but in the high pH range the slope approaches zero. Figure 3 shows the relation between R_0 and the initial concentration of europium, C_{Eu0}, on a log scale. R_0 is proportional to C_{Eu0}. Figure 4 shows the relation between R_0 and the initial concentration of HR, C_{HR0}. In the range of low C_{HR0} the slope of this relation is 1, but in the high C_{HR0} range the slope approaches zero. Each solid curves in Figs. 2 to 4 were calculated by a method described later.

In our previous work (1) on the extraction of samarium with DISPA, the extraction rate was found to be limited by a diffusion process. The

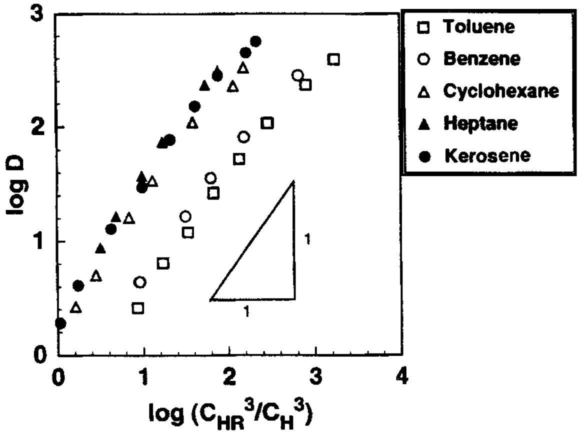

FIG. 1 Equilibrium plot of DISPA–Eu extraction system for various organic solvents.

following diffusion equations of europium and the complex, therefore, are considered in the initial period of the extraction.

$$R_0 = k_{\mathrm{Eu}}(C_{\mathrm{Eu0}} - C_{\mathrm{Eui}}) \qquad (3)$$

$$= k_c C_{ci} \qquad (4)$$

where k_j is the mass transfer coefficient of the species j and subscript i represents the zone adjacent to the interface. Diffusion equations for DISPA and hydrogen ion were not taken into account because the extractant was present in a large excess compared with europium and the buffer solution that was used.

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

$$K_{ex} = C_{ci}C_{\mathrm{H0}}^3/C_{\mathrm{Eui}}C_{\mathrm{HR0}}^3 \qquad (5)$$

TABLE 1
Extraction Equilibrium Constant

Solvent	K_{ex}
Benzene	0.51
Toluene	0.32
Cyclohexane	2.2
n-Heptane	3.7
Kerosene	2.9

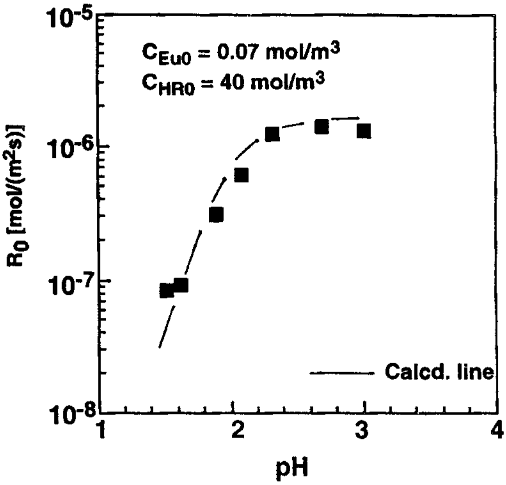

FIG. 2 Effect of pH on initial extraction rate.

From Eqs. (4) and (5), Eq. (6) is derived.

$$R_0 = k_c K_{ex} C_{Eui} (C_{HR0}/C_{H0})^3 \tag{6}$$

The europium concentration in the interfacial zone, C_{Eui}, in Eq. (6) was calculated as follows. The mass transfer coefficient of europium, k_{Eu}, was

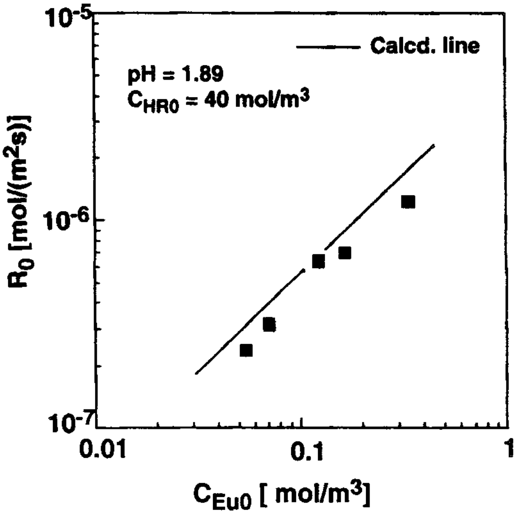

FIG. 3 Effect of C_{Eu0} on R_0.

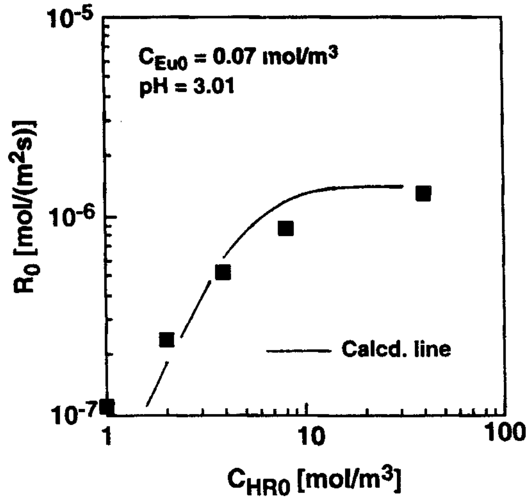

FIG. 4 Effect of C_{HR0} on R_0.

evaluated from the high pH range in Fig. 2 as 2.2 × 10^{-5} m/s. So C_{Eui} was calculated by the observed extraction rate and the k_{Eu} value using Eq. (3). Figure 5 shows the plot based on Eq. (6). As expected, a linear relationship between R_0 and $C_{Eui}(C_{HR0}/C_{H0})^3$ was obtained. The value of

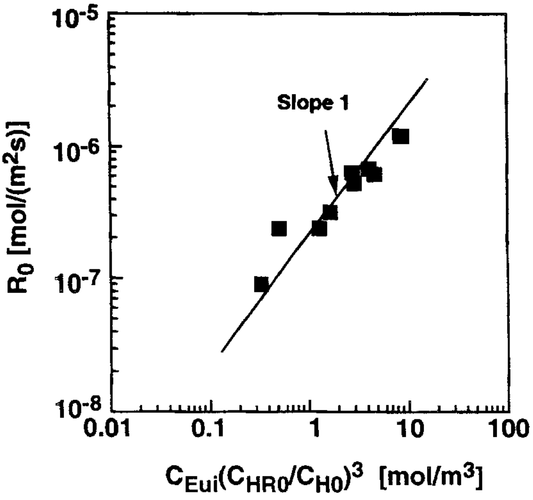

FIG. 5 Relationship between R_0 and C_{Eui} $(C_{HR0}/C_{H0})^3$.

k_c was calculated to be 8.5×10^{-7} m/s from the slope of this plot. The solid curves shown in Figs. 2 to 4 were calculated by using the above values. In the present study, the extraction rate of Eu with DISPA is limited by the diffusion process in the same manner as in Sm extraction with DISPA (1).

Permeation of Europium through ELM

The permeation coefficient, P, of europium through the ELM is defined as

$$-dC_{\mathrm{Eu}}/dt = PC_{\mathrm{Eu}} \tag{7}$$

Figure 6 shows the semilog plot of $C_{\mathrm{Eu}}/C_{\mathrm{Eu0}}$ under various experimental conditions for pH and time according to Eq. (7). A straight line was obtained for each experiment, and the value of P was calculated from the slope. Figure 7 shows the relation between P and $C_{\mathrm{HR0}}/C_{\mathrm{H0}}$. In the low pH range the slope of this relation is 1, but in the high pH range the slope approaches zero.

The permeation process of europium through the ELM is assumed to be controlled by the diffusion process to or from the interface between the external aqueous solution and the membrane solution because the interfacial area between the internal aqueous solution and the membrane solution is much larger than that between the external aqueous solution

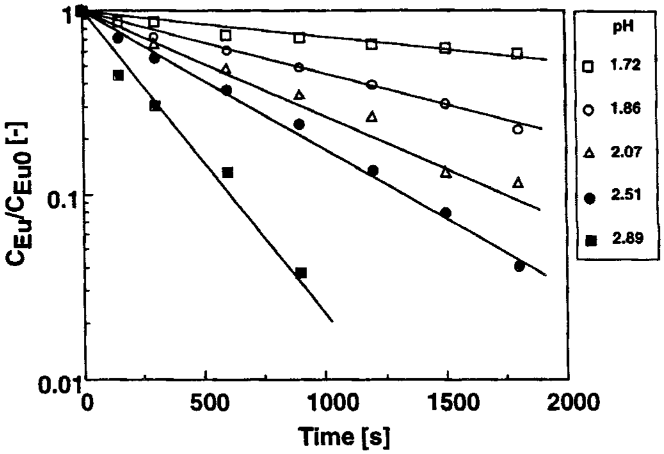

FIG. 6 Effect of pH on extraction of europium with ELM.

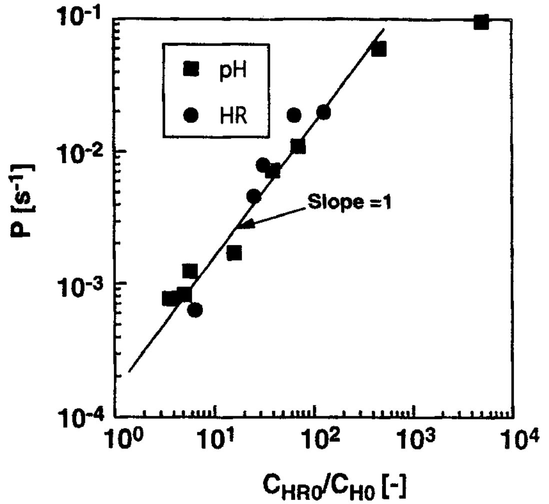

FIG. 7 Relationship between P and $C_{\mathrm{HR0}}/C_{\mathrm{H0}}$.

and membrane solution. The permeation flux, J_{M}, was expressed by

$$J_{\mathrm{M}} = k'_{\mathrm{Eu}}(C_{\mathrm{Eu0}} - C_{\mathrm{Eui}}) \tag{8}$$

$$= k'_{\mathrm{c}}C_{\mathrm{ci}} \tag{9}$$

From Eqs. (7) to (9), Eq. (10) is derived.

$$\frac{1}{P} = \frac{1}{ak'_{\mathrm{Eu}}} + \frac{1}{ak'_{\mathrm{c}}K_{\mathrm{ex}}}\frac{C^3_{\mathrm{H0}}}{C^3_{\mathrm{HR0}}} \tag{10}$$

Equation (10) indicates that P is proportional to $(C_{\mathrm{HR0}}/C_{\mathrm{H0}})^3$ under the condition of diffusion control of the complex, that is, in a low pH or a low C_{HR0} range. The diffusion control model, however, does not give a satisfactory explanation of the experimental results, and this suggests the contribution of the reaction resistance to the permeation process by the decrease in the extraction rate is due to addition of the surfactant.

Matsuyama et al. (15, 16) studied the extraction kinetics of metals with acidic organophosphorus compounds in detail. They concluded that the extraction of metal obeys an eigenmechanism. When the rate constant of the complex formation is large, as it is for most metal ions, the extraction rate is limited by the diffusion process (15), and in the case of a small rate constant, as for Fe^{3+}, the rate is limited by the interfacial reaction (16). According to the their model, the following reaction scheme can be written.

$$HR_{ad} \rightleftharpoons H^+ + R_{ad}^- \qquad (K_a') \tag{11}$$

$$Eu_i^{3+} + R_{ad}^- \rightleftharpoons EuR_{ad}^{2+} \qquad (k/k') \tag{12}$$

$$EuR_{ad}^{2+} + 2R_{ad}^- \rightleftharpoons EuR_{3i} \tag{13}$$

The rate-controlling step is the interfacial reaction between the dissociated form of the extractant and europium in the interfacial zone, Eq. (12). The permeation rate, therefore, is expressed as

$$J_M = kK_a'C_{Eui}C_{HRo}/C_{Ho} \tag{14}$$

From the experimental results, the external film diffusion, Eq. (8), should be taken into account. By using Eqs. (8) and (14), the permeation coefficient, P, is derived as

$$\frac{1}{P} = \frac{1}{ak_{Eu}'} + \frac{1}{akK_a'}\frac{C_{Ho}}{C_{HRo}} \tag{15}$$

Figure 8 shows the plot according to Eq. (15); linear relationship was obtained. From the slope and the intercept, the values of the volumetric mass transfer coefficient, ak_{Eu}' and the apparent reaction rate constants, akK_a', were determined as 0.20 s^{-1} and 2.0×10^{-4} s^{-1}, respectively.

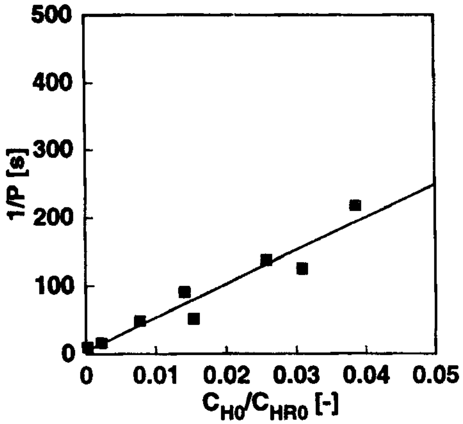

FIG. 8 Reciprocal plot between P and C_{HRo}/C_{Ho}.

CONCLUSION

The extraction equilibrium of europium (Eu) with diisostearylphosphoric acid (DISPA, HR) was examined. It was found that the complex, EuR_3, was formed. The extraction rate of Eu with DISPA was measured using a stirred transfer cell. Extraction rates were limited by the diffusion process. Permeation of europium through the emulsion liquid membrane containing DISPA as a carrier was carried out. Under the experimental conditions, the reaction resistance contributed to the permeation process because of the reduction in the extraction rate by the addition of surfactant. The interfacial reaction model we proposed agreed well with the experimental results. The values of the volumetric mass transfer coefficient and the apparent reaction rate constants were determined.

ACKNOWLEDGMENTS

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NOTATIONS

a	specific area of emulsion droplets (m^{-1})
C_j	concentration of species j (j = Eu, HR, H) (mol/m^3)
D	distribution ratio of europium (—)
J_M	permeation rate of europium through emulsion liquid membrane [$mol/(m^2 \cdot s)$]
K'_a	acid dissociation constant at interface (m^3/mol)
K_{ex}	extraction equilibrium constant (—)
k	forward reaction rate constant of Eq. (12) [$mol/(m^2 \cdot s)$]
k'	backward reaction rate constant of Eq. (12) [$mol^2/(m^5 \cdot s)$]
k_c	mass transfer coefficient of complex for organic film (m/s)
k_{Eu}	mass transfer coefficient of europium for aqueous film (m/s)
k'_c	apparent mass transfer coefficient of complex for membrane (m/s)
k'_{Eu}	mass transfer coefficient of europium for external solution (m/s)
P	permeation coefficient of europium through emulsion liquid membrane (s^{-1})
R	extraction rate [$mol/(m^2 \cdot s)$]
t	time (s)

Subscript

i	zone adjacent to the interface
0	initial state

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