

EXTRACTION OF CERIU (III) BY SOLID EXTRACTANT IMPREGNATED WITH DIHEXYL-N,N-DIETHYLCARBAMOYLMETHYLPHOSPHONATE

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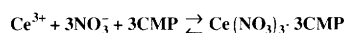
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A solid extractant, a porous styrene-divinylbenzene copolymer (SDB) impregnated with dihexyl-N, N-diethylcarbamoylmethylphosphonate (CMP), was developed for the extraction of rare-earth elements. Solid extractants supported by SDB particles with different crosslinking and pore volume were prepared and the extraction of Ce (III) from aqueous phase containing nitrate ion was examined.

SEM observation suggested that the impregnated CMP was dissolved in the SDB polymer network. The CMP content increased by use of SDB particles with lower crosslinking and higher pore volume. The stoichiometric relation for the extraction reaction was represented by



which was the same as that for the liquid-liquid extraction.

The extraction rate increased with decrease of particle size. The rate-controlling step was the intraparticle diffusion of Ce (III) for solid extractant of diameter greater than 0.2 mm. For smaller particles, it changed to the reaction between CMP and Ce (III).

Introduction

Extraction chromatography using a solid extractant, porous particles impregnated with organic extraction solvent, can be used for the production of microgram to kilogram amounts of metals¹⁾. This technique has the advantages that the extraction behavior can be changed by the selection of various organic solvents, a multi-stage effect is obtained by use of a chromatography column and the extracted metal can be easily recovered by solvent washing of the column¹⁾. Some studies of the separation of transition metals and actinide metals have been carried out²⁻⁴⁾. It has been clarified that this method is suitable for the recovery of trace metals in an aqueous solution, for example the recovery of plutonium from nuclear waste solution or the recovery of gallium from the Bayer solution^{3, 4)}. Extraction chromatography seems to be applicable as a substitute for conventional ion exchange chromatography¹⁾. However, very few fundamental studies have been reported on the extraction equilibrium and the extraction rate.

Bidentate organophosphorus compounds containing both phosphoryl and carbamoyl group have high activity for extracting trivalent rare-earth elements^{1, 3)}. We are investigating the extraction of rare-earth ele-

ments by a solid extractant, a porous styrene-divinylbenzene copolymer (SDB) impregnated with a bidentate organophosphorus compound, DHDECMP (dihexyl-N, N-diethylcarbamoylmethylphosphonate, abbreviated as CMP). **Figure 1** shows the chemical structure of CMP. We carried out some preliminary experiments by using a chromatography column and found that the breakthrough curves for the extraction of trivalent cerium ion, Ce (III), was affected by the degree of crosslinking and the polymerization of the SDB particles⁵⁾.

In this work, solid extractants using SDB particles with different crosslinking and pore volume were prepared. The effects of the crosslinking and pore volume on the impregnation of CMP into the SDB particles were examined. The equilibrium and rate of extraction of Ce (III) from aqueous nitrate solution with the solid extractants were measured batchwise. The rate-controlling step for the solid-liquid extraction was evaluated from the relation between the extraction rate and the particle diameter.

1. Experimental Procedure

1.1 Preparation of solid extractant

Porous SDB particles were produced by means of the capsule polymerization technique⁶⁾. A mixture of sty-

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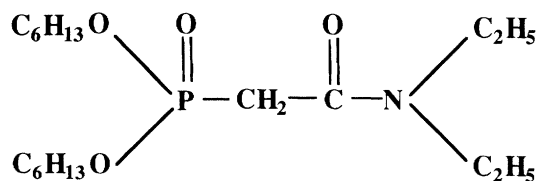


Fig. 1 Chemical structure of DHDECMP

Table 1. Effect of degree of crosslinking, specific surface area and pore volume on CMP content

Particle No.	Properties of SDB particles			CMP content [kg-CMP/kg-SDB]
	crosslinking degree [wt%-DVB]	surface area [m ² /kg]	pore volume [m ³ /kg]	
1	5	5.41×10^4	1.50×10^{-3}	1.72
2	5	2.67×10^4	2.09×10^{-3}	1.91
3	5	1.86×10^4	2.94×10^{-3}	2.45
4	10	1.28×10^5	1.60×10^{-3}	1.81
5	20	1.40×10^5	1.75×10^{-3}	1.20
6	45	1.40×10^5	1.75×10^{-3}	0.35

rene, divinylbenzene (DVB) and n-heptane was used as a monomer solution. The degree of crosslinking and pore volume of the SDB particles can be controlled by changing the content of DVB and that of n-heptane in the monomer solution, respectively⁷⁾. The specific surface area and pore volume of the prepared particles were measured by means of the BET method and by using a mercury porosimeter, respectively.

The impregnation of CMP was carried out by suspending of SDB particles in CMP/dichloromethane solution at 25°C for 10 h. Subsequently, the particles were washed with distilled water several times and dried in vacuo at 50°C. The CMP content (S_{CMP}), defined as

$$S_{CMP} = \frac{\text{[weight of impregnated CMP]}}{\text{[weight of SDB support]}} \quad (1)$$

was calculated from the difference of particle weight before and after CMP impregnation. The interior of the SDB particles before and after CMP impregnation was observed by a scanning electron microscope (SEM).

1.2 Measurement of distribution ratio of Ce (III)

The extraction equilibrium of Ce (III) was measured by contacting the solid extractant with a test solution in a 20 cm³ stoppered glass flask. SDB particles with 5 % crosslinking and 1.5×10^{-3} m³/kg pore volume were used as a support and impregnated with CMP of 0.32 to 1.72 kg-CMP/kg-SDB. Test solutions contained 1.71 mol/m³ Ce (NO₃)₃ and 0.33 to 1.33 kmol/m³ Al (NO₃)₃. (1 + S_{CMP}) grams of solid extractant was added in 10 cm³ of test solution. The SDB/liquid ratio was kept constant at 0.1 kg-SDB/dm³-aq. for all experiments. The glass flask was shaken in a thermostated bath at 25°C for 1 d to attain equilibrium. The concentration of Ce (III) in the test solution was measured by an inductivity coupled plasma spectrometer

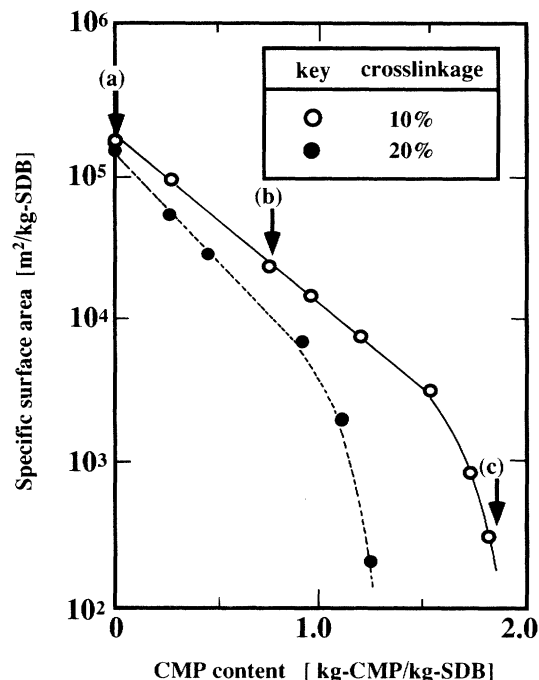


Fig. 2 Relation between specific surface area and CMP content. The surface area was measured by BET method. Signs (a) to (c) represent the point of SEM observation shown in Fig. 3.

(ICP). The co-extraction of Al (III) was ignored because the extraction amount of Al (III) is less than one hundredth of that of Ce (III) under these experimental conditions¹¹⁾. The concentration of phosphorus in the aqueous solution was measured by ICP and the solubility of CMP was evaluated.

The mass balance of Ce (III) in the flask is described as follows:

$$q_{eq} f = C_0 - C_{eq} \quad (2)$$

where f denotes the ratio of the volume of the test solution to the weight of the SDB support. C_0 and C_{eq} denote the initial and equilibrium concentrations of Ce (III) in the test solution, respectively. The distribution ratio (D) is defined by

$$D = \frac{\text{[moles of Ce (III) extracted in 1 kg SDB support]}}{\text{[moles of Ce (III) remaining in 1 m³ test solution]}} \quad (3)$$

and calculated by

$$D = \frac{q_{eq}}{C_{eq}} = \frac{1}{f} \left(\frac{C_0}{C_{eq}} - 1 \right) \quad (4)$$

1.3 Measurement of extraction rate of Ce (III)

The extraction rate was measured in a 200-cm³ stirred cell. The composition of the test solution and the temperature of the cell were the same as those in the preceding section. 1 gram of solid extractant was added in 100 cm³ of test solution. The crosslinking and pore volume of the SDB support were 5 % and 1.5×10^{-3} m³/kg, respectively. The CMP content was 1.72 kg-CMP/kg-SDB for all extractants. The SDB/liquid ratio

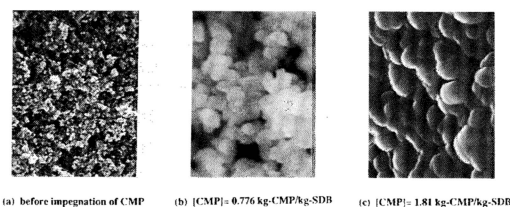


Fig. 3 SEM images of the interior of solid extractants

was 0.0036 kg-SDB/dm³-aq. The agitation speed was 10 s⁻¹. The time variation of the concentration of Ce (III) in the test solution was measured.

In preliminary experiments, it was confirmed that the extraction rate was not changed at agitation speeds faster than 6.7 s⁻¹. This result means that the diffusion rate of Ce (III) through the boundary layer around the particles is fast enough and can be neglected in evaluation of the extraction rate.

2. Results and Discussion

2.1 Impregnation of CMP into porous SDB

Table 1 shows a comparison of the CMP content in SDB particles with different crosslinking and pore volume. These values were obtained by suspending the SDB particles in pure CMP. The CMP content was increased by decreasing the degree of crosslinking and increasing the pore volume.

Figure 2 shows the relation between the specific surface area of solid extractant and the CMP content. The surface area decreased with CMP content*. Figures 3 (a) to (c) show SEM images of the interior of the solid extractants, the CMP content of which corresponds respectively to those designated by signs (a) to (c) in Fig. 2. In Fig. 3 (a), the white part represents SDB polymer, which consists of agglomerated microspheres of SDB polymer¹²⁾. The spaces between the microspheres represent pores. Comparison of these photographs shows the appearance of round spheres at higher CMP content. The round spheres would be the gel of SDB polymer swollen by the impregnation of CMP. The decrease of surface area with CMP content, as shown in Fig. 2, may be due to the disappearance of pores by the swelling of the SDB microspheres.

It is known that the degree of swelling of polymer is increased by lowering the crosslinking between polymer chains⁸⁾. The increase of CMP content for the low-crosslinked SDB particles, shown in Table 1, seems attributable to a higher degree of swelling of SDB microspheres.

2.2 Extraction equilibrium of Ce (III)

Figure 4 shows the effects of CMP content and the concentration of NO₃⁻ in the test solution on the distribution ratio of Ce (III). The distribution ratios were proportional to the third power of the CMP content and the

* After the impregnated CMP was frozen at 77 K, the specific surface area was measured by the BET method.

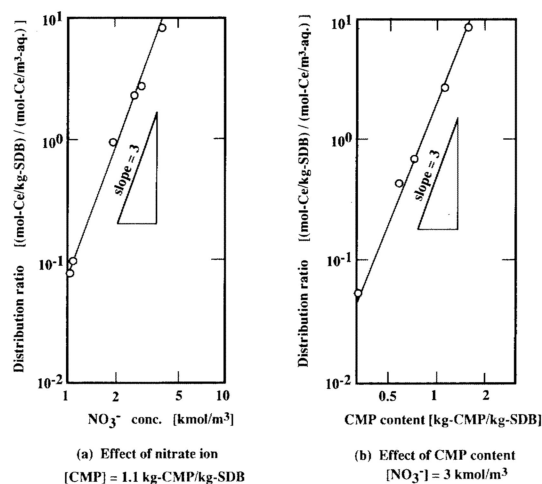
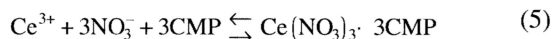


Fig. 4 Effects of NO₃⁻ concentration and CMP content on the distribution ratio of Ce (III)

NO₃⁻ concentration. The stoichiometric relation for the extraction reaction is described as follows:



which is the same as that for the liquid-liquid extraction¹¹⁾.

The extraction constant is represented by

$$K = \frac{q}{C \cdot (C_{\text{NO}_3^-} - 3qf)^3 \cdot \left(\frac{S_{\text{CMP}}}{M_w} - 3q \right)^3} \quad (6)$$

where $(C_{\text{NO}_3^-} - 3qf)^3$ is the concentration of free nitrate ion in the aqueous phase and $(S_{\text{CMP}}/M_w - 3q)$ is the concentration of free CMP in the solid extractant. The extraction constant was evaluated as $4.3 \times 10^{-12} \text{ (m}^3/\text{mol)}^4 \text{ (kg/mol)}^2$ at 25°C.

The solubility of impregnated CMP to the aqueous solution was about 10⁻² kg-CMP/m³-aq. for all experiments described in Fig. 4. If the batch experiments are repeated 100 times for the solid extractant with a CMP content of 1.0 kg-CMP/kg-SDB, the loss of impregnated CMP can be estimated as about 1 % of the total amount.

2.3 Extraction rate of Ce (III)

Figure 5 shows the time variation of the amount of extracted Ce (III). Solid extractants of diameter 0.1, 0.2, 1.0, 1.4 mm were used. The extraction rate increased with decrease in particle diameter.

The overall capacity coefficient, $K_f a_v$, was evaluated from the extraction experiments. The extraction rate is represented by

$$-\frac{dC}{dt} = K_f a_v \left(C - \frac{q}{f} \right) \quad (7)$$

Equation (7) was represented as a function of the Ce (III) concentration in aqueous phase by use of the material balance of Ce (III), $C = C_0 - qf$, and the equilibrium relation of Eq. (6) and was solved by the Runge-Kutta method under the boundary condition $C = C_0$ at $t = 0$. Solid lines shown in Fig. 5 represent the calculated results by Eq. (7). The value of $K_f a_v$ was evaluated by

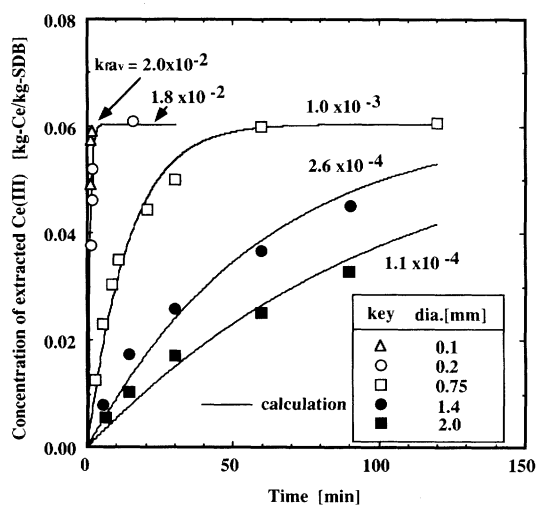


Fig. 5 Time variation in amount of extracted Ce (III). The diameter of solid extractants varied in the range from 0.1 to 2.0 mm. Solid lines represent the calculated results.

the least-squares fitting between the calculated results and the experimental data.

Figure 6 shows the relation between the obtained $K_f a_v$ and the diameter of the solid extractant. For solid extractants of diameter greater than 0.2 mm, $K_f a_v$ is in inverse proportion to the second power of d_p .

If the reaction rate between Ce (III) and CMP is so fast that the resistance by the chemical reaction can be ignored⁹⁾, $K_f a_v$ is represented by

$$\frac{1}{K_f a_v} = \frac{1}{k_f a_v} + \frac{1}{Dk_s a_v} \quad (8)$$

As $k_f \gg Dk_s$ is held at an agitation speed greater than 6.7 s^{-1} , $K_f a_v$ is represented as

$$K_f a_v \approx Dk_s a_v = D(60 D_p / d_p^2) f \quad (9)$$

The third term of Eq. (9) is an expression for $Dk_s a_v$ recommended by Vermeulen *et al.*¹⁰⁾ The result shown in Fig. 6 can be explained in terms of Eq. (9). These results indicate that the rate-controlling factor is the intraparticle diffusion of Ce (III). The diffusion coefficient in the solid extractant, D_p , is evaluated as about $1.0 \times 10^{-12} \text{ m}^2/\text{s}$ from Eq. (9).

For the solid extractant of diameter smaller than 0.2 mm, $K_f a_v$ was almost independent of size. This suggests that the rate-controlling step is changed from intraparticle diffusion to the reaction between the impregnated CMP and Ce (III).

Conclusions

(1) The SDB microspheres were swelled by the impregnation of CMP. The CMP content increased with the degree of swelling of the SDB polymer. The use of SDB particles with lower crosslinking and higher pore volume was effective in increasing the CMP content.

(2) The stoichiometric relation for the extraction

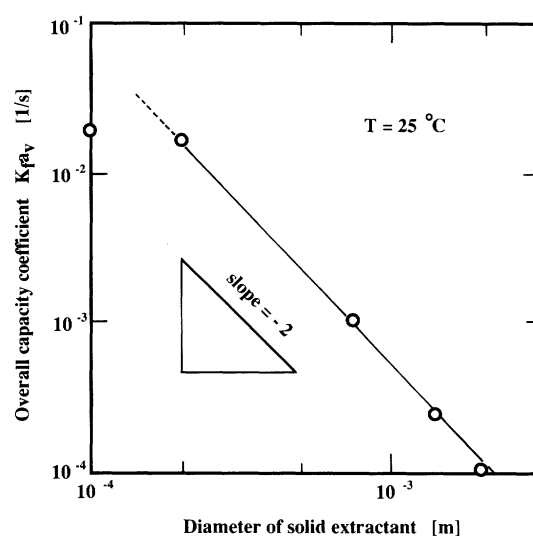
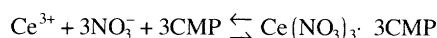


Fig. 6 Relation between $K_f a_v$ and the diameter of solid extractant

reaction between Ce (III) and the impregnated CMP was represented by



which is the same as that for liquid-liquid extraction.

(3) The extraction rate was controlled by the interparticle diffusion of Ce (III) for the solid extractants of diameter greater than 0.2 mm. For smaller particles, the rate-controlling step changed from intraparticle diffusion to the reaction between CMP and Ce (III).

Nomenclature

a_v	= surface area of solid extractant in the volume of the cell	$[\text{m}^2/\text{m}^3]$
C	= concentration of Ce (III) in aqueous phase	$[\text{mol}/\text{m}^3]$
$C_{\text{NO}_3^-}$	= concentration of NO_3^- in aqueous phase	$[\text{mol}/\text{m}^3]$
D	= distribution ratio of Ce (III)	$[(\text{mol}/\text{kg-SDB})/(\text{mol}/\text{m}^3\text{-aq.})]$
D_p	= diffusion coefficient in solid extractant	$[\text{m}^2/\text{s}]$
d_p	= diameter of solid extractant	$[\text{m}]$
f	= ratio of solid to liquid	$[\text{kg-SDB}/\text{m}^3\text{-aq.}]$
K	= extraction constant	$[(\text{m}^3/\text{mol})^4(\text{kg}/\text{mol})^2]$
K_f	= overall mass transfer coefficient	$[\text{m}/\text{s}]$
$K_f a_v$	= overall capacity coefficient	$[\text{1}/\text{s}]$
k_f	= mass transfer coefficient for aqueous phase	$[\text{m}/\text{s}]$
k_s	= mass transfer coefficient for solid extractant	$[\text{kg}/\text{m}^2\text{-s}]$
M_w	= molecular weight of CMP	$[\text{kg}/\text{mol}]$
q	= mean concentration of Ce (III) extracted in particle	$[\text{mol-Ce}/\text{kg-SDB}]$
S_{CMP}	= CMP content	$[\text{kg-CMP}/\text{kg-SDB}]$
t	= time	$[\text{s}]$

<Subscripts>

0	= initial
eq	= equilibrium

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