

EQUILIBRIUM AND KINETICS OF SOLVENT EXTRACTION OF EUROPIUM WITH DIDODECYLMONOTHIOPHOSPHORIC ACID

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The rate of extraction of europium with didodecylmonothiophosphoric acid was measured by use of a stirred transfer cell, along with the extraction equilibrium. The equation for the extraction equilibrium was determined and the equilibrium constant was obtained. The dependency of the extraction rate of europium on the concentration of the chemical species taking part in the extraction was examined.

By analyzing the results based on the interfacial reaction model accompanied by diffusion, it was estimated that the rate-determining step is the reaction between the adsorbed 1:2 europium chelate complex and the extractant in the organic solution adjacent to the interface. The overall reaction rate constant and the mass transfer coefficients of europium, the extractant and the complex were obtained.

Introduction

Solvent extraction as an effective and selective method of separating rare-earth metals has attracted practical interest from the viewpoint of energy conservation. Recently, a separation technique using liquid surfactant membranes^{1,2)} or supported liquid membranes³⁾ has been noted as a novel method for separating and concentrating the rare-earth elements. In developing such a process employing a unique method, elucidation of the mechanism of metal extraction is very important. A number of studies of the extraction of the rare-earth metals have been carried out, but most are concerned with the equilibrium properties.^{1,9,10,11,13,15)} Studies of the extraction kinetics are few.^{2,4,5,6)}

Kandil *et al.*⁶⁾ studied the kinetics of thulium extraction by di(2-ethylhexyl) phosphoric acid (hereafter abbreviated as D2EHPA). They obtained a rate equation for the system which showed the dependence of pH and the extractant concentration. Danesi *et al.*⁴⁾ afterwards measured the rate of extraction of europium by D2EHPA in a stirred transfer cell and proposed a mass transfer model in which the mass transfer rate of europium is controlled by a series of slow reversible interfacial reactions between the metal cation and D2EHPA. They also measured the extraction rate of the metal by the extractant from an aqueous solution containing a mixture of lactic acid and a polyaminocarboxylic acid²⁾ and discussed the effect of the acids added to

the aqueous solution on the extraction mechanism. Recently, Imai *et al.*⁵⁾ studied the extraction of lanthanum by D2EHPA and presented an extraction mechanism in which the extraction rate is controlled by the formation reaction of inner-sphere complex.

In the studies of the interfacial reaction model introduced above, however, the state of the extractant at or close to the interface is not defined clearly. In this study, to clarify this point and the extraction mechanism in detail, the extraction of europium with didodecylmonothiophosphoric acid was carried out using a stirred transfer cell. The extraction equilibrium was also measured. The dependency of the extraction rate of europium on the concentration of the chemical species taking part in the extraction is examined and an interfacial reaction model for the extraction is presented to explain the experimental results.

1. Experimental

1.1 Reagents

The extractant, didodecylmonothiophosphoric acid (hereafter abbreviated as DDTPA), was synthesized as its ammonium salt as described in a previous paper⁷⁾.

The organic solution was prepared as follows. The ammonium salt of the extractant was first dissolved in 1000 mol/m³ sulfuric acid aqueous solution, which was then contacted sufficiently with toluene to distribute the extractant into the toluene solution. The concentration of DDTPA in the organic solution was determined by neutralization titration with alcoholic potash solution.

The aqueous solution was prepared by dissolving

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europium chloride hexahydrate into 100 mol/m³ hydrochloric acid aqueous solution. The pH of the aqueous solution was adjusted using 100 mol/m³ hydrochloric acid-sodium acetate buffer solution.

Other inorganic chemicals used were of GR grade.

1.2 Measurement of extraction equilibrium

Equal volumes (20 cm³) of aqueous and organic solutions of known concentrations were shaken in a flask immersed in a thermostated water bath (303K) and allowed to attain equilibrium. After about 24 hours, the two solutions were separated and each was removed by a pipette for analysis. A known volume of the organic solution was stripped by 100 mol/m³ hydrochloric acid. After dilution of the aqueous and stripping solutions with 100 mol/m³ hydrochloric acid in an appropriate ratio, the concentration of europium in the resulting solutions was determined spectrophotometrically by the Arsenazo III method using a spectrophotometer, Model UVIDEK-670 (Japan Spectroscopic Co., Ltd.). The pH of the aqueous solution after equilibration was measured with a Hitachi-Horiba F-7SS pH meter.

1.3 Measurement of extraction rate

A stirred transfer cell⁽¹⁴⁾ was used to measure the rate of extraction of europium by DDTA at 303 K. The cell consists of two compartments of equal volume (about 140 cm³) and the interfacial area between the solutions was 11.4 cm². The solutions in the cell were stirred in opposite directions by two flat-blade stirrers.

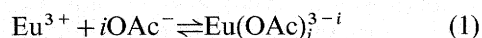
The solutions were prepared in the manner mentioned above for measuring the extraction equilibrium. The experimental procedure was the same as that described in the previous paper.⁽¹⁴⁾ Samples were taken at intervals from the organic solution. After stripping, the europium concentration was determined by the method mentioned above.

The initial rates of europium extraction were obtained from the concentration change of europium chelate complex in the organic solution with time.

2. Results and Discussion

2.1 Extraction equilibrium of europium

1) Determination of extracted species and extraction equilibrium constant It is known that europium ion, Eu³⁺, forms complexes with acetate anion, OAc⁻, in aqueous solution.



$$\beta_i = \frac{[\text{Eu}(\text{OAc})_i^{3-i}]}{[\text{Eu}^{3+}][\text{OAc}^-]^i} \quad (2)$$

The values of β_i ($\beta_1 = 1.35 \times 10^{-1} \text{ m}^3/\text{mol}$, $\beta_2 = 4.37 \times 10^{-3} \text{ m}^6/\text{mol}^2$ and $\beta_3 = 1.74 \times 10^{-5} \text{ m}^9/\text{mol}^3$) are available⁽⁸⁾. So the concentration of free europium ion can be calculated, using the following equation.

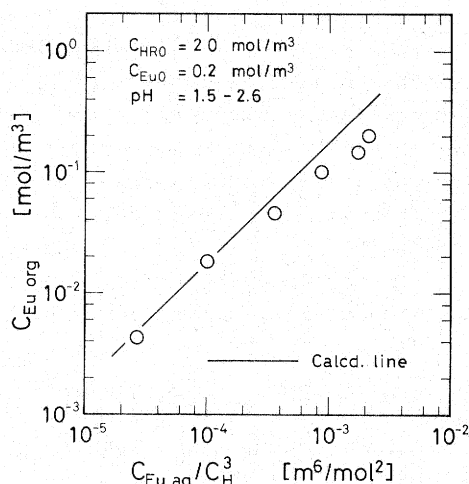
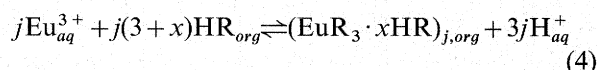


Fig. 1. Determination of j -value for extraction of europium

$$[\text{Eu}^{3+}]_{aq} = [\text{Eu}^{3+}]_t / (1 + \sum \beta_i [\text{OAc}^-]^i) \quad (3)$$

where $[\text{Eu}^{3+}]_t$ is the total concentration of europium ion.

The extractant, DDTA, is known to exist as the monomer in toluene.⁽⁷⁾ So assuming that europium ion is extracted as a j -merized complex of composition $(\text{EuR}_3 \cdot x\text{HR})_j$ into the organic solution with the monomer of DDTA, HR, from the aqueous solution, the extraction equilibrium can be expressed as follows.



The extraction equilibrium constant, K_{ex} , is written as follows.

$$K_{ex} = \frac{[(\text{EuR}_3 \cdot x\text{HR})_{j,org}][\text{H}^+]_{aq}^{3j}}{[\text{Eu}^{3+}]_{aq}^j [\text{HR}]_{org}^{j(3+x)}} \quad (5)$$

Denoting free europium concentration and hydrogen-ion concentration in the aqueous solution, and europium concentration in the organic solution by $C_{Eu,aq}$, C_H and $C_{Eu,org}$, respectively, Eq. (5) is rewritten as follows.

$$\log C_{Eu,org} = j \log (C_{Eu,aq} \cdot C_H^{-3}) + \log \{ j K_{ex} C_H^{j(3+x)} \} \quad (6)$$

The experimental results are rearranged using Eq. (6), and the results are shown in Fig. 1. A straight line with a slope of 1 was obtained. This indicates that $j = 1$. That is, europium ion is extracted as a monomer, $\text{EuR}_3 \cdot x\text{HR}$, as is clear from Eq. (6).

When $j = 1$, the distribution ratio of europium based on free europium ion in the aqueous phase, D , is given as follows.

$$D = C_{Eu,org} / C_{Eu,aq} = K_{ex} C_H^{3+x} / C_H^3 \quad (7)$$

Equation (7) is rearranged as follows.

$$\log (DC_H^3) = \log K_{ex} + (3+x)\log C_{HR} \quad (8)$$

The experimental results are plotted in Fig. 2 based on Eq. (8). As is evident from Fig. 2, a linear relation was obtained. The slope of the straight line is 3, indicating that x is equal to zero, as is obvious from Eq. (8). Therefore, the extracted species is estimated to be EuR_3 .

From the above results, the equation for the extraction equilibrium of europium is represented as follows.



The extraction equilibrium constant, K_{ex} , was obtained from Fig. 2 as follows.

$$K_{ex} = 2.3 \times 10^{-2} \quad (10)$$

The straight lines shown in Figs. 1 and 2 are the results calculated by using Eqs. (8) and (10).

2) Comparison of this study with other works In the extraction of rare-earth elements by a typical dialkylphosphoric acid, di(2-ethylhexyl) phosphoric acid (D2EHPA), extraction of a species of $\text{MR}_3(\text{HR})_3$ has been reported.^{1,9,15)} The influence of the organic solvent used on the extraction equilibrium constant is remarkable. The constant of europium extraction varies from 0.034 for chloroform solvent⁹⁾ to 1.1 for toluene solvent.¹⁾

However, MR_3 was confirmed to be the species extracted by DDTPA in this work. This type of extracted species has been reported in the extraction of neodymium by a monothio- β -diketone¹⁰⁾ and in the extraction of europium by a commercial extractant, Kelex 100.¹³⁾ Motomizu and Freiser⁹⁾ studied the extraction of lanthanides with dibutylmonothiophosphoric acid and concluded that the extracted species was MR_3 . The value of K_{ex} for the extraction of europium was 8.5×10^{-3} , which is smaller than that in this work.

2.2 Extraction rate of europium

1) Effect of stirring speed on extraction rate The effect of stirring speed on the initial extraction rate is shown in Fig. 3. It is clear that the rate depends on the stirring speed, indicating that the extraction rate is affected by the diffusion rate. Since the interface was highly disturbed at 3.33 r.p.s., the experiment thereafter was carried out at 1.67 r.p.s. (100 r.p.m.).

2) Effect of pH on extraction rate The effect of pH on the initial extraction rate is shown in Fig. 4. The rate varies inversely as the 2nd power of hydrogen-ion concentration at a pH value below about 2.5, but at a pH above 2.5 is scarcely affected by hydrogen-ion concentration. Therefore, it is anticipated that the extraction mechanism in the high pH range is different from that in the low pH range.

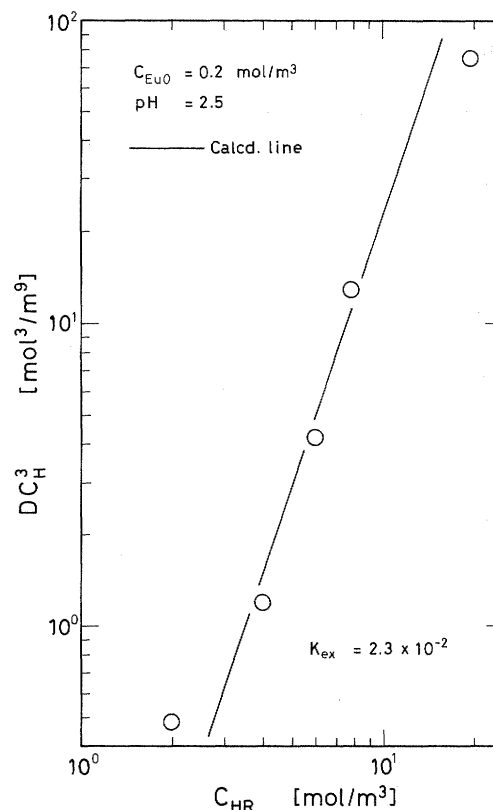


Fig. 2. Determination of x -value for extraction of europium

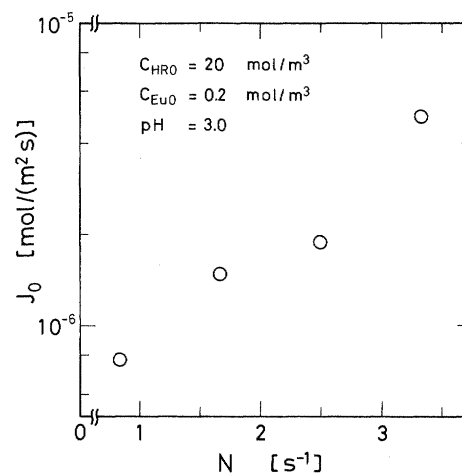


Fig. 3. Effect of stirring speed on initial extraction rate of europium

3) Effect of extractant concentration on extraction rate From the experimental results shown in Fig. 5, it is found that the initial extraction rate varies as the 3rd power of extractant concentration in the low concentration range but that the rate is scarcely affected by extractant concentration in the high concentration range.

4) Effect of europium concentration on extraction rate The effect of europium concentration on the initial extraction rate is shown in Fig. 6. It is evident that the rate is proportional to europium concentration.

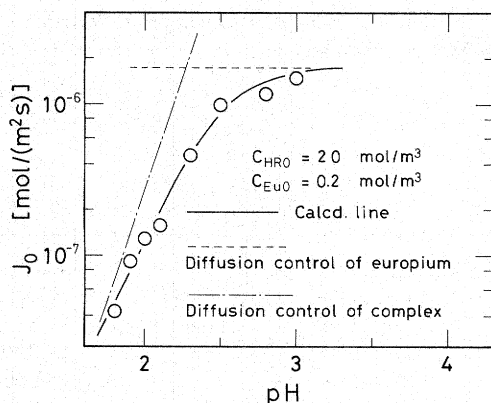


Fig. 4. Effect of pH on initial extraction rate of europium

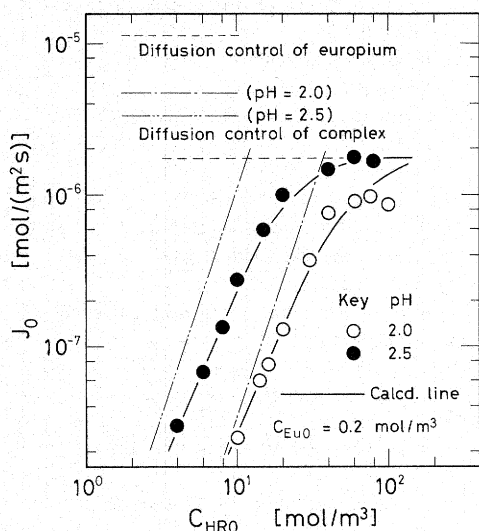


Fig. 5. Effect of extractant concentration on initial extraction rate of europium

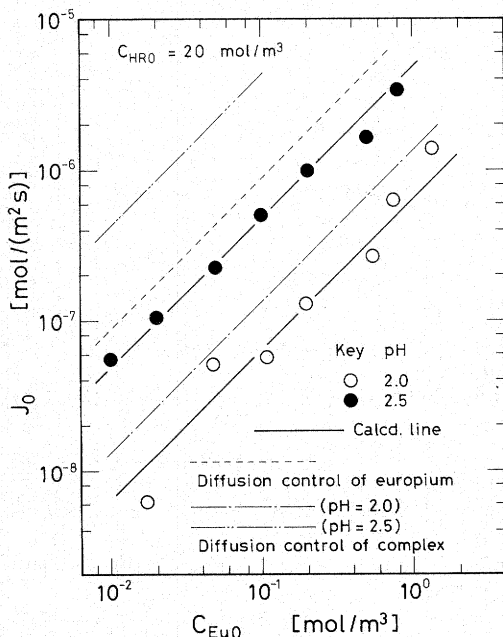
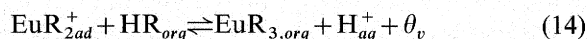
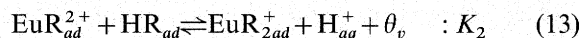
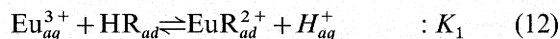


Fig. 6. Effect of europium concentration on initial extraction rate of europium

2.3 Extraction mechanism of europium

Considering that the extractant, DDTPA, exists as the monomer in toluene and has interfacial activity as shown in the previous paper,⁷⁾ the following interfacial reaction model is proposed.



where subscripts *aq*, *org* and *ad* denote aqueous phase, organic phase and adsorbed state, respectively. θ_v is the fraction of active vacant site at the interface. K_{HR} is the adsorption equilibrium constant of DDTPA. K_1 and K_2 are the equilibrium constants for the reactions of Eqs. (12) and (13), respectively. Assuming that the reaction of Eq. (14) is the rate-determining step, the reaction rate can be expressed as follows.

$$r = k_3[\text{EuR}^+_{2ad}][\text{HR}]_{org} - k_{-3}[\text{EuR}^+_{3,org}][\text{H}^+]_{aq}\theta_v \quad (15)$$

where k_3 and k_{-3} are the forward and reverse reaction rate constants for the reaction of Eq. (14). Equation (15) is rewritten as follows, using the equilibrium constants.

$$r = k_3 K_1 K_2 \left(\frac{K_{HR}}{S_{HR}} \right)^2 \frac{C_{Eu} C_{HRi}^3}{C_{Hi}^2} \theta_v - k_{-3} C_{EuR3i} C_{Hi} \theta_v \quad (16)$$

where S_{HR} is the interfacial area occupied by unit mole of the extractant and subscript *i* denotes aqueous or organic solution adjacent to the interface. At the early stage of extraction, since the fractions of active site at the interface occupied by EuR^{2+} , EuR^+_{2ad} and $\text{EuR}^+_{3,org}$ are negligibly small compared with that of HR, the following equation is reasonable.

$$\theta_v + \theta_{HR} = \theta_v + K_{HR} C_{HRi} \theta_v = 1 \quad (17)$$

Letting $k_3 K_1 K_2 (K_{HR}/S_{HR})^2$ be replaced by k_f , therefore, Eq. (16) can be rewritten as follows.

$$r_0 = k_f \frac{C_{Eu} C_{HRi}^3 / C_{Hi}^2 - C_{EuR3i} C_{Hi} / K_{ex}}{1 + K_{HR} C_{HRi}} \quad (18)$$

The concentration of the species adjacent to the interface is obtained from the following relation, in which the interfacial reaction rate equals the mass transfer rate at the steady state.

$$\begin{aligned} J_0 = r_0 &= k_{Eu}(C_{Eu0} - C_{Eu}) \\ &= (k_{HR}/3)(C_{HR0} - C_{HRi}) \\ &= k_{EuR3} C_{EuR3i} \end{aligned} \quad (19)$$

where k_{Eu} , k_{HR} and k_{EuR3} are the mass transfer coefficients of europium, DDTPA and the complex, respectively, C_{Eu} is here the total concentration of

europium and J_0 is the initial extraction rate of europium. The concentration of hydrogen ion adjacent to the interface, C_{Hi} , is assumed to be equal to the bulk concentration, C_{H0} , because the buffer solution was used.

By using Eqs. (18) and (19), the relation between J_0 and the bulk concentrations of europium, DDTPA and the complex is obtained.

The values of the unknown constants were evaluated from the experimental results for J_0 and the equations derived above by non-linear regression, and are listed in **Table 1** along with the value of K_{ex} . The value of the adsorption equilibrium constant of DDTPA, $K_{HR}=0.10\text{ m}^3/\text{mol}$, which was obtained previously,⁷⁾ was used in the calculation. The values of the mass transfer coefficients are considered to be reasonable. The solid lines shown in Figs. 4, 5 and 6 are calculated from Eqs. (18) and (19). Close agreement between the experimental and the calculated values was obtained. The calculated results when the extraction rate is controlled by diffusion of europium or the complex are also shown in the figures. These results show that the extraction of europium is also explained by the interfacial reaction model accompanied by diffusion, which has been proposed by the authors.

In the interfacial reaction model, the rate-determining step was concluded to be the reaction of the adsorbed 1:2 intermediate complex, EuR_{2ad}^+ , with the extractant in the organic solution, HR_{org} . This point is different from that of the Cu-dodecylbenzene-sulfonamide system.¹⁴⁾ In extraction of trivalent metal ion, a chelate complex formed is generally more bulky than that of divalent metal ion. So the reaction of EuR_{2ad}^+ with HR_{org} is considered to be apt to occur much more than that with the adsorbed extractant, HR_{ad} , at the interface.

Conclusion

Equilibrium and kinetic studies of extraction of europium with didodecylmonothiophosphoric acid were carried out to clarify the extraction mechanism. The following information was obtained.

1) The species extracted into toluene diluent was EuR_3 and the extraction equilibrium constant, $K_{ex}=2.3 \times 10^{-2}$, was obtained.

2) The rate-determining step was the interfacial reaction between the adsorbed 1:2 europium chelate complex and the extractant in the organic solution adjacent to the interface. The overall reaction rate constant, and the mass transfer coefficients for europium, the extractant and the complex were obtained.

Nomenclature

C = concentration [mol/m³]

Table 1. Values of constants for europium extraction

	$K_{ex}=2.3 \times 10^{-2}$	
	$K_{HR}=1.0 \times 10^{-1} \text{ m}^3/\text{mol}^{(7)}$	
	$k_f=5.6 \times 10^{-8} \text{ m}^4/(\text{mol} \cdot \text{s})$	
	$k_{Eu}=8.7 \times 10^{-6} \text{ m/s}$	
	$k_{HR}=8.0 \times 10^{-6} \text{ m/s}$	
	$k_{EuR3}=7.2 \times 10^{-6} \text{ m/s}$	
D	= distribution ratio of europium	[—]
i	= number of acetate anions in europium-acetate complex formed	[—]
J	= extraction rate	[mol/(m ² s)]
j	= j -mer of extracted species	[—]
K_1	= equilibrium constant of Eq. (12)	[—]
K_2	= equilibrium constant of Eq. (13)	[m ⁻¹]
K_{ex}	= extraction equilibrium constant defined by Eq. (5)	[—]
K_{HR}	= adsorption equilibrium constant of extractant	[m ³ /mol]
k_3	= forward reaction rate constant of Eq. (14)	[m ³ /(mol·s)]
k_{-3}	= reverse reaction rate constant of Eq. (14)	[m ⁴ /(mol·s)]
k_f	= overall reaction rate constant	[m ⁴ /(mol·s)]
k	= mass transfer coefficient	[m/s]
r	= reaction rate	[mol/(m ² s)]
S_{HR}	= interfacial area occupied by unit mole of extractant	[m ² /mol]
x	= number of additional molecules of extractant in extracted species	[—]
β_i	= stability constant defined by Eq. (2) ($i=1-3$)	[(m ³ /mol) ^{i}]
θ	= fraction of active site at interface	[—]
[]	= concentration	[mol/m ³]
<Subscripts>		
ad	= adsorbed state	
aq	= aqueous phase	
Eu	= europium	
$EuR3$	= europium complex	
H	= hydrogen ion	
HR	= extractant	
i	= adjacent to interface	
org	= organic phase	
t	= total amount	
v	= vacant site	
0	= initial value	

Literature Cited

- 1) Aguilar, M. and D. H. Liem: *Acta Chem. Scand.*, **A30**, 313 (1976)
- 2) Danesi, P. R. and C. Cianetti: *Separ. Sci. Technol.*, **17**, 969 (1982)
- 3) Danesi, P. R., E. P. Horwitz and P. Rickert: *Separ. Sci. Technol.*, **17**, 1183 (1982)
- 4) Danesi, P. R. and G. F. Vandegrift: *J. Phys. Chem.*, **85**, 3646 (1981)
- 5) Imai, M. and S. Furusaki: *Kagaku Kogaku Ronbunshu*, **13**, 355 (1987)
- 6) Kandil, A. T. and G. R. Choppin: *J. Inorg. Nucl. Chem.*, **37**, 1787 (1975)
- 7) Kondo, K., H. Nishio and F. Nakashio: *J. Chem. Eng. Japan*, **22**, 269 (1989)

- 8) Martell, A. E. and R. M. Smith: "Critical Stability Constants", Vol. 3, Plenum Press, New York (1977)
- 9) Motomizu, S. and H. Freiser: *Solv. Extr. Ion Exch.*, **3**, 637 (1985)
- 10) Nag, K. and M. Chaudhury: *J. Inorg. Nucl. Chem.*, **39**, 1213 (1977)
- 11) Owens, T. C. and M. Smutz: *J. Inorg. Nucl. Chem.*, **30**, 1617 (1968)
- 12) Teramoto, M., T. Sakuramoto, T. Koyama, H. Matsuyama and Y. Miyake: *Separ. Sci. Technol.*, **21**, 229 (1986)
- 13) Yamada, E. and H. Freiser: *Anal. Chem.*, **53**, 2115 (1981)
- 14) Yoshizuka, K., K. Kondo and F. Nakashio: *J. Chem. Eng. Japan*, **18**, 163 (1985)
- 15) Žíkovský, L.: *J. Inorg. Nucl. Chem.*, **35**, 2917 (1973)

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