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Ion-Associate Solvent Extraction and Separation of Lanthanides(III) with 2,3-Naphthalenediol and Benzyldimethyltetradecylammonium Chloride

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In order to improve the separation factors among lanthanides(III), ion-associate extraction system for them was studied using 2,3-naphthalenediol (H_2L) as a diprotic chelating reagent and benzyldimethyltetradecylammonium chloride (Z^+Cl^-) as an ion-associate reagent at 298 K and the ionic strength of 0.1 (NaCl). Lanthanide ions, Pr^{3+}, Eu^{3+}, and Yb^{3+}, are extracted at weakly acidic pH region as $Z_2^+Na^+[ML_3]^{3-}$. Sufficiently large separation factors among them are obtained. This system has a sharp pH dependence, with a slope of 6 for the plots of $\log\{[M^{3+}]_{(T,o)}/[M^{3+}]\}$ against pH at a constant concentrations of $H_2L_{(o)}$, $Z^+Cl^-_{(o)}$, and NaCl, where the subscripts T and o indicate the total concentration of lanthanide ions and the species in the organic phase, respectively. Details of the extraction system are discussed.

Solvent extraction is one of the promising methods for the separation of rare earth elements. Therefore, extensive studies have been reported, by the use of various kinds of extraction reagents (HR) such as phosphate esters,[1] phosphonate esters,[2] 8-quinolinols,[3—5] and β-diketones.[6,7] Relatively large separation factors among lanthanide(III) were reported by the use of di-(2-ethylhexyl)phosphoric acid (D2EHP),[1] and recently by *N*-phenylhydroxylamines.[8] Ion-associate extraction systems of $Q^+[MR_4]^-$ type, as shown in Eq. 1, are also attractive.

$$M^{3+} + 4HR_{(o)} + Q^+ \overset{K_{ex}}{\rightleftharpoons} Q^+[MR_4]^-_{(o)} + 4H^+ \qquad (1)$$

where subscript (o) refers to the species in the organic phase. But less satisfactory results concerning the separation factors (S.F.) were reported for 8-quinolinol [9] and 2-thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione)[10,11] with quaternary ammonium ion (Q^+), even though the systems extracted lanthanides(III) from more acidic pH region than their $[MR_3(HR)_n]$ and $[MR_3]$ type extraction systems.

In order to search for a possibility to realize large separation factors by the use of ion-associate extraction system, it is worthwhile to study a system in which the formation of higher order ion-associate, as well as the release of a larger number of protons than 4, will take place, because such kinds of works have been rarely reported in the research field of lanthanides(III) extraction, other than those in a strongly alkaline media.[12] Therefore, attention has been paid for a bidentate diprotic chelating reagent (H_2R). The dependence for a proton concentration is expected to be sixth order for the extraction of trivalent metal ions as an ion-associate of $Q_3^+[MR_3]^{3-}$, as shown in Eq. 2.

$$M^{3+} + 3H_2R_{(o)} + 3Q^+ \overset{K_{ex}}{\rightleftharpoons} Q_3^+[MR_3]^{3-}_{(o)} + 6H^+ \qquad (2)$$

Pyrocatechol and its derivatives are attractive reagents to form anionic chelates, which have 0, 0 coordination structure with two proton dissociation per one ligand along with the complex formation. The chelates can be extracted as ion-associate with appropriate counter cations, for example, for gallium(III), $Q_3^+[MR_3]^{3-}$ with pyrocatechols and quaternary ammonium cation into toluene,[13] and for lanthanides(III) and actinides (III), $Na_3^+[MR_3]^{3-}$ with 4-(1-methyl-1-octhylnonyl)pyrocatechol into kerosene,[12] from 3 mol dm^{-3} aqueous sodium hydroxide solution, respectively. These features prompt us to study on the ion-associate extraction of lanthanides(III) from the weakly acidic conditions with the special reference to the extraction stoichiometry and the separation factors. As a result, the largest separation factors are obtained for Eu^{3+}/Pr^{3+} of $10^{2.4}$ and Yb^{3+}/Eu^{3+} of $10^{3.3}$ with 2,3-naphthalenediol (DHN, H_2L) and benzyldimethyltetradecylammonium chloride (Zephiramine, Z^+Cl^-) system, among the reported values including those of D2EHP.

Experimental

Apparatus: A Seiko plasmaspectrometer sps-1200 (ICP-AES) was used for the determination of lanthanide ions in the aqueous solution. An Iwaki KM type shaker was applied for mixing the aqueous and the organic phase. A Hitachi Centrifuge 05P-21 was used for the quick phase separation. A Hitachi Horiba M-7E pH meter calibrated daily with pH standard solutions was used for pH measurement.

Materials: Aqueous solutions of Pr^{3+}, Eu^{3+}, and Yb^{3+} were prepared by dissolving their chloride salts with a small amount of hydrochloric acid, and were standardized by complexometric titration using Xylenol Orange as an indicator. 2,3-Naphthalenediol (Lancaster Synthesis Ltd.) was used after recrystallization from methanol water mixture. Among pyrocatechol derivatives, DHN was chosen, because of its toughness to the air oxidation. Zephiramine (Dojindo Lab.) was used without further purification. Chloroform was used after distillation and saturation with water. All other reagents used were of analytical grade.

Extraction Procedure: An aliquot of 10 cm^3 of aqueous solution containing 1×10^{-4} mol dm^{-3} of lanthanide ion was prepared in a 30 cm^3 glass vial fitted with a polyethylene cap. Its pH was adjusted by acetate buffer solution, and the ionic strength was controlled to 0.1 with sodium chloride.[14] The solution was shaken with 10 cm^3 of chloroform containing DHN and Zephiramine at regulated room temperature of 298 K. Shaking for 30 min was sufficient for the equilibration in each conditions used. Then, the mixture was centrifuged for 10 min at 1500 rpm. After the phase separation, lanthanide ion in the aqueous phase was measured by ICP-AES, using calibration curves with their matrix matching. The amount of extracted lanthanides(III) was calculated from material balance. Any precipitates were not observed during the operation.

Result and Discussion

When an ion-associate, $Z_x^+Na_y^+[ML_w]^{(3-2w)+}$, is responsible for the extraction of lanthanide ions with DHN and Zephiramine, the equilibria are written as:

$$M^{3+} + wH_2L_{(o)} + xZ^+Cl^-_{(o)} + yNa^+ \overset{K_{ex(w,x,y)}}{\rightleftharpoons} Z_x^+Na_y^+[ML_w]^{(3-2w)+}_{(o)} + 2wH^+ + xCl^- \quad (3)$$

with

$$K_{ex(w,x,y)} = \frac{[Z_x^+Na_y^+(ML_w)^{(3-2w)+}]_{(o)}[H^+]^{2w}[Cl^-]^x}{[M^{3+}][H_2L]^w_{(o)}[Z^+Cl^-]^x_{(o)}[Na^+]^y} \quad (4)$$

The side reaction coefficients for the lanthanide ion in the aqueous phase, α_M, those for $H_2L_{(o)}$ and $Z^+Cl^-_{(o)}$ in the organic phase, $\alpha_{H_2L_{(o)}}$ and $\alpha_{Z^+Cl^-_{(o)}}$, respectively, are given as follows:

$$\alpha_M = ([M^{3+}] + \sum_n [M(OH)_n] + \sum_{n'} [MCl_{n'}] + \sum_w [ML_w]) / [M^{3+}],$$

$$\alpha_{H_2L_{(o)}} = ([H_2L] + [HL^-] + [L^{2-}] + [H_2L]_{(o)})/[H_2L]_{(o)},$$

$$\alpha_{Z^+Cl^-_{(o)}} = ([Z^+] + [Z^+Cl^-] + [Z^+Cl^-]_{(o)})/[Z^+Cl^-]_{(o)}$$

where the charge of the complexes in the equation for α_M were omitted, and the terms $[Z^+HL^-]$, $[Z^+HL^-]_{(o)}$, $[Z_2^+L^{2-}]$, and $[Z_2^+L^{2-}]_{(o)}$, are neglected for $\alpha_{H_2L_{(o)}}$ and $\alpha_{Z^+Cl^-_{(o)}}$, because these were not found by the observation of absorption spectra of H_2L–Z^+Cl^- extraction system.

Under the conditions used, the values of $\alpha_{H_2L_{(o)}}$ and $\alpha_{Z^+Cl^-_{(o)}}$ are assigned to 1, based on the following facts: The acid dissociation constants are $K_{a_1} = 10^{-8.7}$ and $K_{a_2} = 10^{-12.5}$.[15] The distribution constant of H_2L between the aqueous phase and the organic phase was estimated to be over 10^2. Ion-associate extraction constant of Z^+Cl^- is sufficiently large ($K_{ex} = 10^{5.11}$).[16]

From these side reaction coefficients and distribution ratio of M^{3+}, shown in Eq. 5,

$$D = \frac{[Z_x^+Na_y^+(ML_w)^{(3-2w)+}]_{(o)}}{\alpha_M[M^{3+}]} \quad (5)$$

Eq. 4 can be re-written as

$$\log K_{ex(w,x,y)} = \log D - 2w\text{pH} - w\log[H_2L]_{(o)} - x\log[Z^+Cl^-]_{(o)} + x\log[Cl^-] - y\log[Na^+] + \log\alpha_M \quad (6)$$

In order to clarify the distribution behavior of lanthanides(III), "slope analysis" was used by plotting the logarithmic value of distribution ratio of lanthanides(III) vs. experimental variables. Distribution ratio with respect to pH are shown in Fig. 1. Each lanthanide ion was extracted in a very narrow proper pH range, respectively. A slope of 6 was obtained for all lanthanides(III) tested, which indicates that six protons were released during the extraction process. Thus, w is 3 in Eq. 3. Plots of ($\log D - 6$ pH) values vs. logarithmic concentration of H_2L in the organic phase at a constant $Z^+Cl^-_{(o)}$ concentration are shown in Fig. 2. The slope of 3 was obtained for Pr^{3+}, Eu^{3+}, and Yb^{3+}. They showed that three DHN molecules were used in the extraction process. This result also indicates $w=3$, and therefore the charge of the complexes is assigned to be -3. Thus, extracted ion-associates contain the anionic chelate of $[ML_3]^{3-}$.

Then, the number of Zephiramine cations used to extract the chelate into organic phase was determined. A slope of 2 was obtained for plots of ($\log D - 6$ pH) vs. logarithmic concentration of Z^+Cl^- in the organic phase at a constant $H_2L_{(o)}$ (Fig. 3). This result indicates that two Z^+ ions take part in the extraction system, and x is 2 in Eq. 3. The linear dependences shown in Figs. 1, 2, and 3 reveal the assumption of α coefficients of $H_2L_{(o)}$ and $Z^+Cl^-_{(o)}$ to be 1, as well as the contribution from hydroxo complexes,[17] chloro complexes,[18] and $[ML_w]^{(3-2w)+}$ (w=1,2,3) to α_M being neglected. Thus, Eq. 6 can be written as:

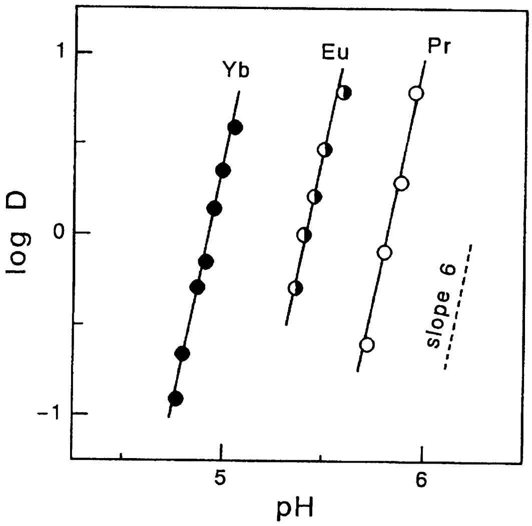

Fig. 1. Distribution ratio of M^{3+} as a function of pH by ion-associate extraction with DHN and Zephiramine. $[M^{3+}] = 1\times10^{-4}$ mol dm^{-3}, $[H_2L]_{(o)} = 1\times10^{-2}$ mol dm^{-3}, $[Z^+Cl^-]_{(o)} = 1\times10^{-3}$ mol dm^{-3}, I=0.1 (NaCl).

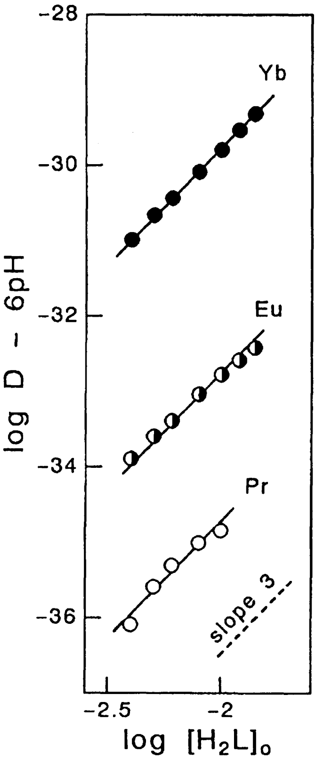

Fig. 2. Plots of $\log D-6\text{pH}$ as a function of $\log[\text{H}_2\text{L}]_{(\text{o})}$. $[\text{M}^{3+}]=1\times10^{-4}$ mol dm^{-3}, $[\text{Z}^+\text{Cl}^-]_{(\text{o})}=1\times10^{-3}$ mol dm^{-3}, $I=0.1$ (NaCl).

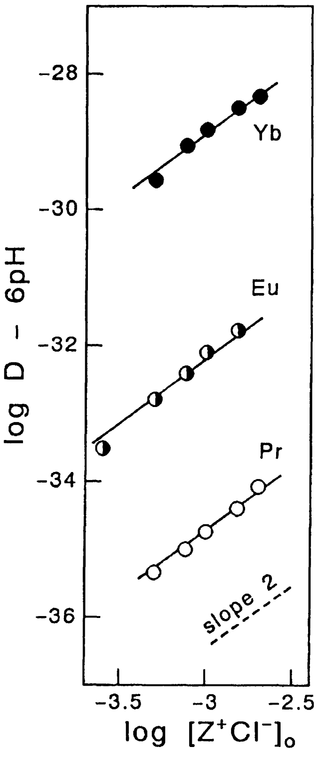

Fig. 3. Plots of $\log D-6\text{pH}$ as a function of $\log[\text{Z}^+\text{Cl}^-]_{(\text{o})}$. $[\text{M}^{3+}]=1\times10^{-4}$ mol dm^{-3}, $[\text{H}_2\text{L}]_{(\text{o})}=1\times10^{-2}$ mol dm^{-3}, $I=0.1$ (NaCl).

$$\begin{aligned}\log K_{\text{ex}(3,2,y)} &= \\ &\log D-6\text{pH}-3\log[\text{H}_2\text{L}]_{(\text{o})}-2\log[\text{Z}^+\text{Cl}^-]_{(\text{o})} \\ &+2\log[\text{Cl}^-]-y\log[\text{Na}^+]+\log\alpha_\text{M} \qquad (7)\end{aligned}$$

As the charge of the anionic chelates is −3, the second order dependence on Z^+ concentration conflicts with the charge balance of the extracted ion-associate. Additional one cationic species should be necessary. In order to confirm this speculation, molar ratio plots of Zephiramine vs. Yb^{3+} for the extraction efficiency is examined (Fig. 4). In this case, Yb^{3+} was used, since it forms the most stable chelate among the lanthanide ions used. About 20% of Yb^{3+} was extracted even in the absence of Zephiramine as shown in Fig. 4. The efficiency increased as a function of Zephiramine concentration and reached to 100% at very close to $[\text{Z}^+\text{Cl}^-]_{(\text{o})}/[\text{Yb}^{3+}]=2$. This result also supports the above speculation. Sodium ion is the only cation existing in the system, except for Z^+ and H^+. Therefore, y must be 1 in Eq. 7. This was confirmed in the following experiments. Under the conditions where a large excess amount of sodium chloride is added, the concentration of sodium ion is nearly equal to that of chloride ion. Therefore, Eq. 7 can be written as:

$$\log D-6\text{pH}=-\log[\text{Na}^+]-\log\alpha_\text{M}+\text{constant} \qquad (8)$$

where constant $=\log K_{\text{ex}(3,2,1)}+3\log[\text{H}_2\text{L}]_{(\text{o})}+2\log[\text{Z}^+\text{Cl}^-]_{(\text{o})}$. Plots of ($\log D-6$ pH) vs. logarithmic total concentration of sodium chloride are examined at constant concentrations of $[\text{H}_2\text{L}]_{(\text{o})}$ and $[\text{Z}^+\text{Cl}^-]_{(\text{o})}$ (Fig. 5). The slope is nearly equal to −1, which indicates that the values of α_M is almost constant and one sodium ion is used as a counter cation in the extraction system, as expected from Eq. 8. The deviation of the

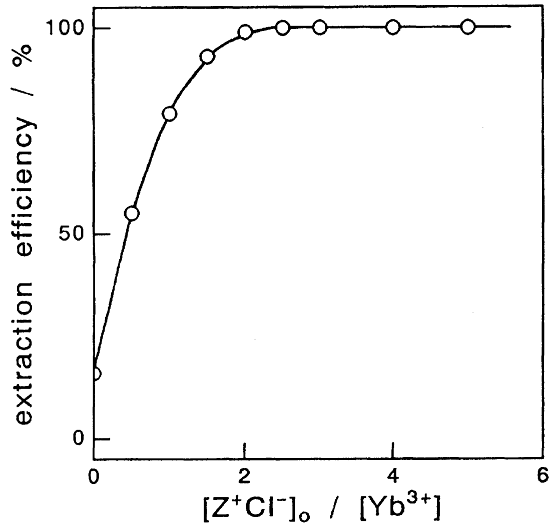

Fig. 4. Extraction efficiency curve of Yb^{3+} as a function of molar ratio of $[\text{Z}^+\text{Cl}^-]_{(\text{o})}$ vs. $[\text{Yb}^{3+}]$. $[\text{Yb}^{3+}]=1\times10^{-4}$ mol dm^{-3}, $[\text{H}_2\text{L}]_{(\text{o})}=1\times10^{-2}$ mol dm^{-3}, $I=0.1$ (NaCl), pH=6.08±0.03.

Table 1. Extraction Constants and Separation Factors of Lanthanides (III).

Reagent	$\log K_{ex}$			log (S.F.)		
	Pr	Eu	Yb	Eu/Pr	Yb/Eu	Yb/Pr
H_2L-Z^+Cl^- [a]	−23.9	−21.5	−18.2	2.4	3.3	5.7
D2EHP[b]	−2.66	−1.47	1.63	1.19	3.10	4.29
HQ[c]	−18.71	−17.20	−15.24	1.51	1.96	3.47
HQ-THA^+Cl^- [d]	−24.13	—	−20.96	—	—	3.17
Kelex-100[e]	−19.45	−17.87	−15.77	1.58	2.10	3.68
HD-PHA[f]	−15.40	−14.38	−11.74	1.02	2.64	3.66
HPMDP[g]	−8.74	−7.27	−5.42	1.47	1.85	3.32
HPMDP-Q^+Cl^- [g]	−5.24	−3.92	−3.60	1.32	0.32	1.64

D2EHP: di(2-ethylhexyl)phosphoric acid, HQ: 8-quinolinol, THA^+Cl^-: tetraheptylammonium chloride, Kelex-100: 7-[1-(2,2,5-trimethylhexyl)allyl]-8-quinolinol, HD-PHA: *N*-(2-hexyldecanoyl)-*N*-phenylhydroxylamine, HPMDP: 1-phenyl-3-methyl-4-dodecanoyl-5-pyrazolone, Q^+Cl^-: methyltrioctylammonium chrolide. a) This work, b) Ref. 1, c) Ref. 3, d) Ref. 9, e) Ref. 5, f) Ref. 8, g) Ref. 7.

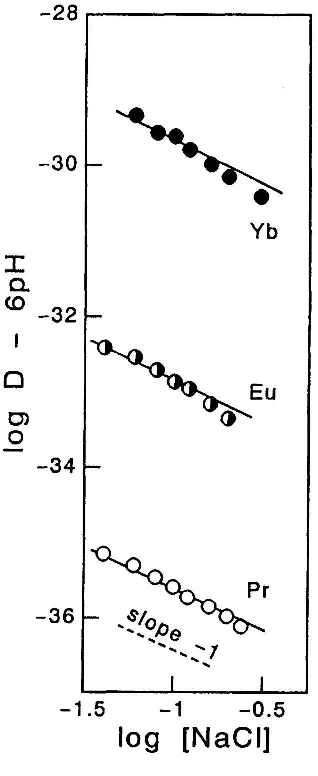

Fig. 5. Plots of $\log D - 6$ pH plots as a function of log[NaCl]. $[M^{3+}] = 1\times10^{-4}$ mol dm^{-3}, $[H_2L]_{(o)} = 1\times10^{-2}$ mol dm^{-3}, $[Z^+Cl^-]_{(o)} = 1\times10^{-3}$ mol dm^{-3}.

plots in the higher sodium chloride concentration area should be attributed to the change of the activity coefficients of ionic species along with the increase in the ionic strength.

Thus, in the presence of sufficient amount of $H_2L_{(o)}$, $Z^+Cl^-_{(o)}$, and sodium chloride, the extraction equilibria Eq. 3 is written as:

$$M^{3+} + 3H_2L_{(o)} + 2Z^+Cl^-_{(o)} + Na^+ \overset{K_{ex(3,2,1)}}{\rightleftharpoons} Z_2^+Na^+[ML_3]^{3-}_{(o)} + 6H^+ + 2Cl^- \quad (9)$$

with

$$K_{ex(3,2,1)} = \frac{[Z_2^+Na^+(ML_3)^{3-}]_{(o)}[H^+]^6[Cl^-]^2}{[M^{3+}][H_2L]^3_{(o)}[Z^+Cl^-]^2_{(o)}[Na^+]} \quad (10)$$

However, Fig. 4 also indicates that a part of lanthanides(III) were also extracted even in the absence of Zephiramine cations, as the species having the stoichiometry of $Na_3^+[ML_3]^{3-}$. This types of ion-associate stoichiometry including sodium ion is not so usual for the lanthanides(III) extraction systems. However, in the case of the extraction system with 4-(1-methyl-1-octhylnonyl)pyrocatechol (H_2R'), $Na_3^+[MR'_3]^{3-}$ types of ion-associate extraction were reported for lanthanides(III) and actinides(III).[12] The large hydrophobic nature of H_2R', which has a large alkyl group of total carbon number of 18, should be responsible for the extraction of the type of ion-associate. In the case of ion-associate extraction system, the large alkyl group is not necessarily placed on the chelating reagent, but it can be placed on the counter ions.[13] Therefore, even though the ion-associate of $Z_2^+Na^+[ML_3]^{3-}$ contains hydrophilic sodium ion, quantitative extraction of the species can be understood, provided that the hydrophobicity of Z^+ ion and H_2L is sufficiently large.

Several kinds of pyrocatechol derivatives, such as pyrocatechol, 4-methylpyrocatechol, 4-chloropyrocatechol, and 4-*t*-butylpyrocatechol were also examined. Among these reagents, DHN can extract lanthanide ions from the most acidic region at the reagent concentration of 1×10^{-2} mol dm^{-3}.

Synergic effects on the extraction system were also examined using 1,10-phenanthroline and trioctylphosphine oxide, but the extraction lines did not show any changes, revealing no synergism.

The extraction constants ($\log K_{ex(3,2,1)}$) for Pr^{3+}, Eu^{3+}, and Yb^{3+} are calculated at the conditions where the extracted species is $Z_2^+Na^+[ML_3]^{3-}$, and the values are summarized in Table 1. Some extraction constants for lanthanides(III) with other reagents are also summarized in Table 1. The separation factors (S.F.) for metal ions M^I and M^{II} (D^I/D^{II}) can be calculated from

$K^{\mathrm{I}}_{\mathrm{ex}}/K^{\mathrm{II}}_{\mathrm{ex}}$, and are also summarized in Table 1. The log (S.F.) values between Pr^{3+} and Eu^{3+}, and between Eu^{3+} and Yb^{3+} in this system are 2.4 and 3.3, respectively. The values are the largest among the reported values for $\mathrm{Eu}^{3+}/\mathrm{Pr}^{3+}$ and for $\mathrm{Yb}^{3+}/\mathrm{Eu}^{3+}$, as shown in Table 1. Therefore, it can be concluded that set of DHN–$\mathrm{Z}^{+}\mathrm{Cl}^{-}$–NaCl provides a very promising extraction system for the separation of lanthanides(III). This conclusion suggests that there is a new way for improving the separation factors among lanthanides(III) by the use of the ion-associate solvent extraction system with hydrophobic large anionic chelates having charge −3 or more.

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