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Synergic Extraction of Rare Earths(III) with 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione and Nitrogen-Involving Polydentate Ligands as Diethylenetriamine and Triethylenetetramine

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The synergic extraction of rare earths(III), i.e. La, Sm, Tb, and Lu, using 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta) and a nitrogen-involving neutral polydentate ligand, such as diethylenetriamine (dien) or triethylenetetramine (trien), was studied between benzene and aqueous phases. The synergic enhancement of this extraction system was attributed to the formation of an adduct, RE(tta)$_3$dien or RE(tta)$_3$trien. The adduct formation constants ($\beta_{\mathrm{S},1}$) were determined. Although $\beta_{\mathrm{S},1}$ decreases with the atomic number of RE(III), the detailed tendency of $\beta_{\mathrm{S},1}$ depends on the number of nitrogen atoms of the polydentate ligands.

The synergic effect has been a well-known phenomenon in solvent extraction, which involves an enhancement of the extraction of a metal ion with an acidic chelating agent by the addition of a neutral ligand. In recent years, the authors have conducted systematic studies[1—5] concerning synergic extraction using various types of nitrogen-involving neutral bidentate ligands, such as ethylenediamine (en), 2,2′-bipyridine (bpy), and 1,10-phenanthroline (phen), finding that synergic extraction provides a new possibility for improving the separation efficiency among rare earths(III). These results are never expected in conventional synergic extraction system using a monodenatate ligand, such as tributyl phosphate.

In the present extraction study we paid the special attention to the synergic effect of polydentate ligands other than the bidentate type, that is, those containing diethylenetriamine (dien) and triethylenetetramine (trien), in order to understand the synergic effect on the separation efficiency. We examined the synergic extraction of several rare earths (La(III), Sm(III), Tb(III), and Lu(III)) with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta) in the presence of such a neutral polydentate aliphatic amine. The partition coefficients of dien and trien between benzene and water were also determiend. By analyzing the extraction equilibrium, the adduct formation constant and the synergic extraction constant could be determined. These results were compared with previous results based on bidentate ligands. The features of the present synergic extraction system using nitrogen-involving neutral polydentate ligands are discussed.

Experimental

Materials and Apparatus. Radioisotopes, ^{140}La, ^{153}Sm, ^{160}Tb, and ^{177}Lu, which are used as tracers, were produced by the neutron irradiation of 0.03—2 mg of the nitrate in a nuclear reactor (JRR-4) of the Japan Atomic Research Institute at a thermal neutron flux 5.5×10^{13} n cm^{-2} s^{-1} for 12 h. Radioactive solutions of rare earths (RE) were prepared by dissolving a known amount of the irradiated sample in 0.1 M nitric acid (1 M=1 mol dm^{-3}), evaporating to dryness, and redissolving in 1×10^{-3} M hydrochloric acid solution before use.

Htta (Dojindo Laboratories, 98% purity) was purified by vacuum sublimation at 30 °C. Polydentate amine was purified by recrystallization of its hydrochloride. Diethylenetriamine trihydrochloride was obtained by adding hydrochloric acid to an ethanol solution of diethylenetriamine (Tokyo Kasei Kogyo Co.), and was recrystallized from aqueous ethanol followed by drying under reduced pressure (mp 234.5—239 °C). Triethylenetetramine tetrahydrochloride (Aldrich Chem. Co., 97% purity) was recrystallized in a hydrochloric acid–ethanol solution followed by drying under reduced pressure (mp 268—271.5 °C). Benzene was stirred with concentrated sulfuric acid, washed with water, and distilled after drying. All other reagents were of reagent grade; the aqueous solution was prepared from double-distilled and deionized (Milli-Q system) water.

The γ-activity of each radioisotope was measured with an NaI(Tl) well-type scintillation detector (BICRON) connected to a single-channel analyzer (NAIG). The pH value of the equilibrated aqueous phase was measured with a glass electrode (Toa Denpa Co. Ltd., HM26S).

Procedure. Extraction of RE(III): An aqueous solution (5 cm^3) containing 1×10^{-5} M RE(III) labelled with its radioisotope, 1×10^{-4}—1×10^{-1} M diethylenetriamine trihydrochloride or 3×10^{-5}—3×10^{-3} M triethylenetetramine tetrahydrochloride, and 1×10^{-2} M sodium citrate to prevent hydrolysis, were placed in a 20 cm^3 centrifuge tube with an SPC stopper. The pH of the aqueous phase was adjusted with 1×10^{-3}—1×10^{-2} M piperazine-*N*,*N*′-bis(2-ethanesulfonic acid) (PIPES, pK_a=6.80) or *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS, pK_a=8.40), and a sodium hydroxide solution. The ionic strength was adjusted to 0.1 with sodium chloride. A benzene solution (5 cm^3) containing 1×10^{-4}—1×10^{-2} M Htta was added, shaken for 1 h at 25 °C and centrifuged. The γ-activity of an aliquot (3 cm^3) of each phase was measured, and the distribution ratio of RE(III) was calculated as the radioactivity ratio. The equilibrium pH of the aqueous phase was measured immediately after phase separation.

Partition Coefficient of Polydentate Amine: An aqueous solution containing a known amount of polydentate amine (0.2 M) was shaken for 30 min with benzene. The pH of the aqueous phase was adjusted to 12—13 by the addition of sodium hydroxide. After phase separation by centrifuging, the distributed amine in the benzene phase was back-extracted into a 1×10^{-3} M HCl solution. The concentration of the amine was determined spectrophotometrically with *p*-chloranil.[6)]

Theoretical

Extraction of RE(III) with Htta. The extraction of a trivalent rare earth metal ion (M^{3+}) with chelating extractant (HA) can be expressed as follows:

$$M^{3+} + 3\overline{HA} \rightleftharpoons \overline{MA_3} + 3H^+ \tag{1}$$

$$K_{ex} = \frac{[\overline{MA_3}][H^+]^3}{[M^{3+}][\overline{HA}]^3}, \tag{2}$$

where the upper bar denotes the organic phase and K_{ex} the extraction constant.

Taking into account of the complex formation with citrate ion (cit^{3-}) in the aqueous phase, the distribution ratio (D_0) of M^{3+} can be expressed as follows:

$$\begin{aligned} D_0 &= \frac{[\overline{MA_3}]}{[M^{3+}] + \Sigma[MA_m{}^{(3-m)+}] + \Sigma[M(cit)_j{}^{(3-3j)+}]} \\ &= \frac{[\overline{MA_3}]}{[M^{3+}](1 + \Sigma\beta_{A,m}[A^-]^m + \Sigma\beta_{cit,j}[cit^{3-}]^j)}, \end{aligned} \tag{3}$$

where $\beta_{A,m}$ and $\beta_{cit,j}$ denote the overall formation constant of $MA_m{}^{(3-m)+}$ and $M(cit)_j{}^{(3-3j)+}$ in the aqueous phase.

In a region where the concentration of A^- is very low, the $\Sigma\beta_{A,m}[A^-]^m$ term is negligible. In the case when the citrate ion is absent and the hydrolysis of M^{3+} is negligible, D_0 can be expressed as

$$D_0 = \frac{[\overline{MA_3}]}{[M^{3+}]} = \frac{K_{ex}P_{HA}{}^3[A^-]^3}{K_{HA}{}^3}, \tag{4}$$

where K_{HA} and P_{HA} denote the acid dissociation constant and the partition coefficient of HA, and A^- the chelating anion in the aqueous phase. D_0 depends on the third power of $[A^-]$.

In the presence of the citrate ion, the metal ion in the aqueous phase is quantitatively complexed with the citrate ion as $M(cit)_j{}^{(3-3j)+}$. D_0 can be expressed by the following equation:

$$\begin{aligned} D_0 &= \frac{[\overline{MA_3}]}{\Sigma[M(cit)_j{}^{(3-3j)+}]} = \frac{K_{ex}P_{HA}{}^3[A^-]^3}{K_{HA}{}^3\Sigma\beta_{cit,\,j}[cit^{3-}]^j} \\ &= \frac{K'_{ex}P_{HA}{}^3[A^-]^3}{K_{HA}{}^3}, \end{aligned} \tag{5}$$

where K'_{ex} is the conditional extraction constant, defined as $K'_{ex}=K_{ex}/(\Sigma\beta_{cit,j}[cit^{3-}]^j)$. D_0 also depends on the third power of $[A^-]$.

Synergic Extraction of RE(III) with Htta and Polydentate Amine. The synergic extraction of M^{3+} with HA and a polydentate amine S can be expressed as follows:

$$M^{3+} + 3\overline{HA} + n\bar{S} \rightleftharpoons \overline{MA_3S_n} + 3H^+ \tag{6}$$

$$K_{ex,S,n} = \frac{[\overline{MA_3S_n}][H^+]^3}{[M^{3+}][\overline{HA}]^3[\bar{S}]^n} = K_{ex}\beta_{S,n}, \tag{7}$$

where $K_{ex,S,n}$ denotes the synergic extraction constant. The distribution ratio (D) of M^{3+} can be expressed as

$$D=\frac{[\overline{MA_3}]+\Sigma[\overline{MA_3S_n}]}{[M^{3+}]+\Sigma[MA_m{}^{(3-m)+}]+\Sigma[M(cit)_j{}^{(3-3j)+}]+\Sigma[MS_k{}^{3+}]}. \tag{8}$$

When $M(cit)_j^{(3-3j)+}$ is dominant in the aqueous phase,

$$\begin{aligned} D &= \frac{[\overline{MA_3}] + \Sigma[\overline{MA_3S_n}]}{\Sigma[M(cit)_j{}^{(3-3j)+}]} \\ &= \frac{[\overline{MA_3}](1 + \Sigma\beta_{S,n}[\bar{S}]^n)}{\Sigma[M(cit)_j{}^{(3-3j)+}]}, \end{aligned} \tag{9}$$

where $\beta_{S,n}$ is the adduct formation constant in the organic phase corresponding to the following equilibrium:

$$\overline{MA_3} + n\bar{S} \rightleftharpoons \overline{MA_3S_n} \tag{10}$$

$$\beta_{S,n} = \frac{[\overline{MA_3S_n}]}{[\overline{MA_3}][\bar{S}]^n}. \tag{11}$$

From Eqs. 5 and 9, the following simple relationship is obtained:

$$D/D_0 = 1 + \Sigma\beta_{S,n}[\bar{S}]^n. \tag{12}$$

If MA_3S_n is the dominant species in the organic phase, D/D_0 depends on the *n*-th power of the equilibrium concentration of free amine in the organic phase, $[\bar{S}]$.

The conditional synergic extraction constant in the presence of the citrate ion ($K'_{ex,S,n}$) is obtained by

$$K'_{ex,S,n} = K'_{ex}\beta_{S,n}. \tag{13}$$

Results and Discussion

Partition Coefficient of Dien and Trien. In general, the distribution ratio (D_S) of a neutral ligand (S) can be expressed as

$$\begin{aligned} D_S &= \frac{[\bar{S}]}{[S] + \Sigma[H_iS^{i+}]} \\ &= \frac{P_S}{1 + \Sigma\{[H^+]^i/(K_{HiS}K_{H(i-1)S}\cdots K_{HS})\}}, \end{aligned} \tag{14}$$

where K_{HiS} denotes the stepswise acid dissociation constant of the protonated amine (H_iS^{i+}) and P_S the partition coefficient of neutral amine ($[\bar{S}]/[S]$). The literature values of K_{HiS} were used, i.e. $pK_{H3S}=4.23$; $pK_{H2S}=9.02$; $pK_{HS}=9.84$ for dien,[7)] $pK_{H4S}=3.27$; $pK_{H3S}=6.59$; $pK_{H2S}=9.07$; $pK_{HS}=9.74$ for trien.[7)] In the region where the H^+ concentration is very low, the $\Sigma\{[H^+]^i/(K_{HiS}K_{H(i-1)S}\cdots K_{HS})\}$ term is negligible in Eq. 14. Hence, D_S is equal to P_S. P_S was determined from D_S at pH 12; $\log P_S=-4.41$ for dien and $\log P_S=-4.64$ for trien. The equilibrium concentration $[\bar{S}]$ of dien or trien in the organic phase was calculated by the following equation:

$$[\bar{S}] = \frac{C_S}{1 + \{1 + \Sigma[H^+]^i/(K_{HiS}K_{H(i-1)S}\cdots K_{HS})\}/P_S}, \tag{15}$$

where C_S denotes the initial concentration of S.

Complexation of RE(III) with Citrate in the Aqueous Phase. By considering the protophilic nature and log P_S value of dien and trien, a noticeable synergic effect can be expected at a relatively high pH region. Therefore, 1×10^{-2} M citric acid was added as a masking agent to prevent the hydrolysis of RE(III). Although complexation of RE(III) with the citrate ion may cause a lowering of the distribution ratio, moderate distribution ratios at around $D=1$ permit a reliable determination of the distribution ratio, i.e. a small fluctuation in the solute concentration measurement of one phase causes a large error in the determination of the distribution ratio in the region where the distribution ratio is extremely high or low. The acid dissociation constants of citric acid (H_3cit) are: $pK_{H3cit}=2.93$; $pK_{H2cit}=4.37$; $pK_{Hcit}=5.64$.[8] From these values, most of the citric acid exists as cit^{3-} under the present experimental conditions of pH 7—9.

In order to identify the chemical species of RE(III) in the aqueous phase in the presence of citric acid, the citric acid concentration dependency of the distribution ratio of Tb(III) with Htta was investigated at a constant initial concentration of Htta and at a fixed pH. The results are given in Fig. 1. The linear plots with a slope of -2 in Fig. 1 at a higher concentration range of cit^{3-}suggest that Tb(III) in the aqueous phase exists predonimantly as a 1:2 complex with cit^{3-}. The existence of $M(cit)_2^{3-}$ is also supported by Ref. 9. In the case when trien is present, a slope of -2 was also observed (Fig. 1). Hence, both in the absence and presence of trien, $M(cit)_2^{3-}$ exists solely in the aqueous phase at 1×10^{-2} M cit^{3-}, where the following extractions are carried out.

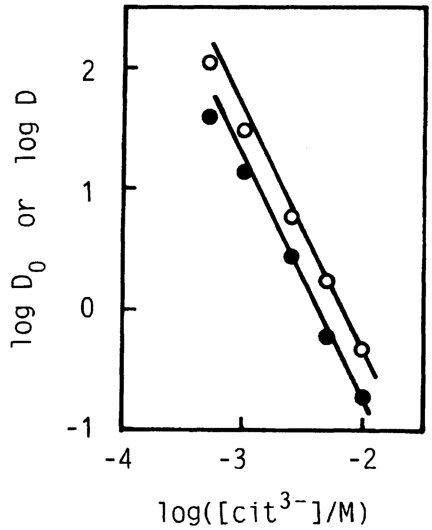

Fig. 1. Dependence of D_0 and D on the concentration of cit^{3-} in the presence (●) and absence (○) of trien in Tb(III)–Htta–benzene system. ○ $[Htta]_{init}=1.3\times10^{-3}$ M, pH 8.1; ● $[Htta]_{init}=1.3\times10^{-3}$ M, $[trien]_{init}=1.0\times10^{-3}$ M, pH 7.9.

Extraction of RE(III) with Htta. The extraction of RE(III), La, Sm, Tb, and Lu, with various Htta concentrations in benzene was carried out; the plots of the logarithmic distribution ratio against the logarithmic tta^- concentration are shown in Fig. 2. The equilibrium tta^- concentration in the aqueous phase was calculated using

$$[A^-]=\frac{C_{HA}}{(P_{HA}+1)[H^+]/K_{HA}+1}, \qquad (16)$$

where C_{HA} denotes the initial Htta concentration. The literature values of K_{HA} and P_{HA} were used, i.e. log $K_{HA}=-6.23$[10] and log $P_{HA}=1.62$.[11] The plots give straight lines with a slope of 3.0 for each RE(III). Therefore, the extracted metal chelate is $RE(tta)_3$. From the plots in Fig. 2, the conditional extraction constants (K'_{ex}) were calculated using Eq. 5 and are listed in Table 1. Also, the formation constant with citrate ($\beta_{cit,2}$) was calculated using Eq. 5 and the extraction constant (K_{ex}),[13] as summarized in Table 1. The K'_{ex} values are very small compared with the K_{ex} value, due to complexing with citric acid in the aqueous phase. The mutual difference in the K'_{ex} values for different RE(III) is small compared with that in K_{ex}. This result is because $\beta_{cit,2}$ increases in the order of the atomic numbers of RE(III) (cf. Eq. 5).

Synergic Extraction of RE(III) with Htta and Polydentate Amine. The synergic extraction of

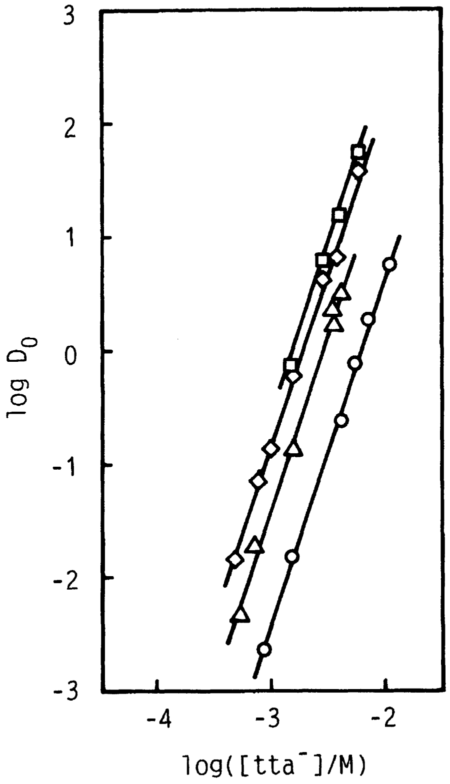

Fig. 2. Dependence of D_0 on the concentration of tta^- in RE(III)–Htta–benzene system. The aqueous phase contains 0.01 M citrate. ○ La, △ Sm, □ Tb, ◇ Lu.

Table 1. Extraction Constants (K_{ex})[a] and Conditional Extraction Conctants (K'_{ex})[b] in RE(III)–Htta–Benzene Systems, and Formation Constants ($\beta_{cit,2}$) of RE(III) Complex with cit^{3-}.

RE(III)	log K_{ex}	log K'_{ex}	log $\beta_{cit,2}$[c]
La	−10.19[d]	−16.89	10.70
Sm	−7.80[d]	−15.74	11.94
Tb	−7.35[d]	−15.16	11.81
Lu	−6.56[d]	−15.35	12.79

a) In the absence of citrate ion. b) In the presence of 0.01 M citrate ion. c) The literature values of log $\beta_{cit,2}$=12.18 (Tb), 13.00 (Lu).[12] d) From our previous work.[13]

RE(III), La, Sm, Tb, and Lu, with various concentrations of Htta and polydentate amine was carried out. Log D is plotted against log [tta^-] in Figs. 3 and 4 for dien and trien, respectively. A large synergic effect can be observed compared with the plots of log D_0 in Fig. 2. The plots in these synergic extraction systems give straight lines with a slope of 3.0 for these RE(III). It is therefore proved that three tta^- anions participate in the synergic extraction of RE(III).

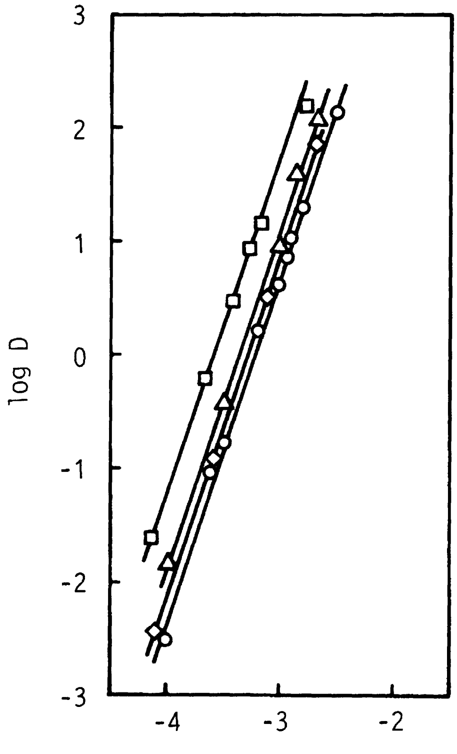

Fig. 3. Dependence of D on the concentration of tta^- in RE(III)–Htta–dien–benzene system. ○ La, $[dien]_{init}=3.5\times10^{-3}$ M, pH 8.3; △ Sm, $[dien]_{init}=1.1\times10^{-2}$ M, pH 7.9; □ Tb, $[dien]_{init}=1.1\times10^{-2}$ M, pH 8.0; ◇ Lu, $[dien]_{init}=9.8\times10^{-3}$ M, pH 8.6.

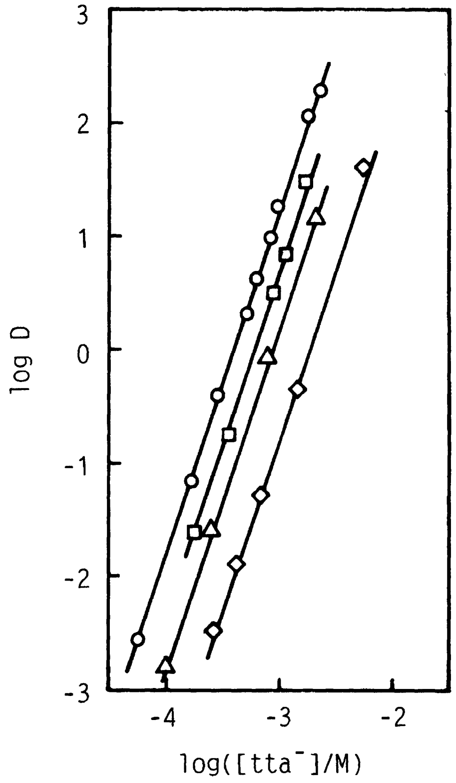

Fig. 4. Dependence of D on the concentration of tta^- in RE(III)–Htta–trien–benzene system. ○ La, $[trien]_{init}=3.1\times10^{-3}$ M, pH 8.0; △ Sm, $[trien]_{init}=1.0\times10^{-3}$ M, pH 8.3; □ Tb, $[trien]_{init}=5.1\times10^{-4}$ M, pH 8.8; ◇ Lu, $[trien]_{init}=2.8\times10^{-3}$ M, pH 7.7.

The plots of log (D/D_0) against log [$\overline{S}$] in the synergic extraction of RE(III) with 1×10^{-4}—1×10^{-2} M Htta and 3×10^{-5}—1×10^{-2} M dien or trien are shown in Figs. 5 and 6 for dien and trien, respectively. The equilibrium concentration of the polydentate amine in the organic phase [$\overline{S}$] was calculated from Eq. 15, and D_0 values were calculated from Eq. 5 using the K'_{ex} values in Table 1. In the Htta–dien system, plots for La, Sm, Tb, and Lu give straight lines with a slope of 1.0. This indicates that the mole ratio of the neutral chelate and dien is 1 : 1 in the adduct. The same relationship was obtained for La, Sm, and Tb in the Htta–trien system, where the slopes are also 1.0, although an enhancement of distribution ratio of Lu was not clearly observed, even upon the addition of 3×10^{-3} M trien.

Some studies concerning synergic extraction have included the association of a chelating agent and a neutral ligand in the organic phase.[14,15] When this association is not negligible, the plots in Figs. 3 and 4 would be lower than the line of slope 3.0 at a higher concentration of Htta,[14,15] or the plots in Figs. 5 and 6 would drop from the line of unity slope in a higher concentration range of S in the organic phase.[14] However, these phenomena were not observed; the association therefore doesn't need to be taken into account for these concentration ranges.

The adduct formation constants ($\beta_{S,1}$) for $RE(tta)_3S$ were calculated from Eq. 12, and are summarized in Ta-

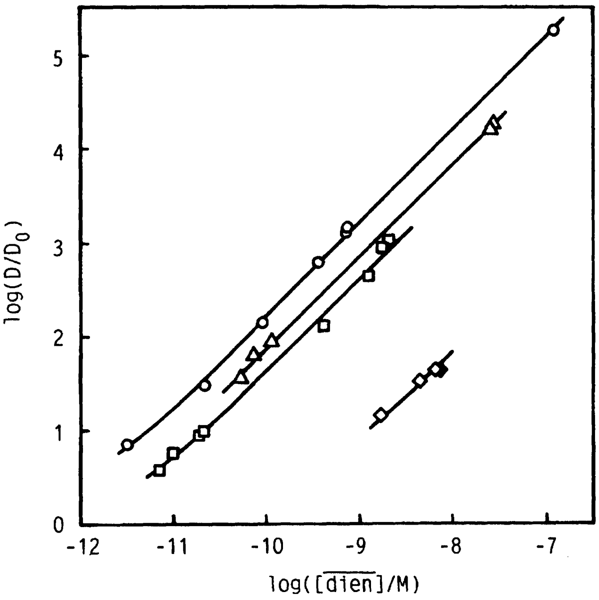

Fig. 5. Dependence of D/D_0 on the concentration of dien in benzene. $[\text{Htta}]_{\text{init}}=1\times10^{-4}$—$1\times10^{-2}$ M; ○ La, △ Sm, □ Tb, ◇ Lu.

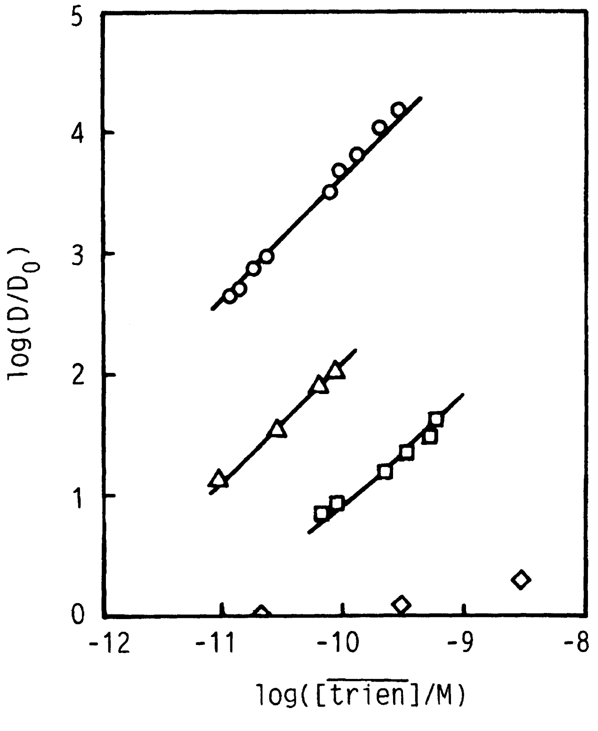

Fig. 6. Dependence of D/D_0 on the concentration of trien in benzene. $[\text{Htta}]_{\text{init}}=1\times10^{-4}$—$1\times10^{-2}$ M; ○ La, △ Sm, □ Tb, ◇ Lu.

ble 2. The synergic extraction constants ($K_{\text{ex,S,1}}$) and the conditional synergic extraction constants ($K'_{\text{ex,S,1}}$) were calculated using Eqs. 7 and 13, respectively, and are also summarized in Table 2.

The adduct formation constants ($\beta_{\text{S,1}}$) for dien and trien are much higher than those for the other nitrogen-involving neutral ligands, ex. $\beta_{\text{S,1}}$ for La(III) with these polydentate amines being about four orders of magnitude greater than that with 1,10-phenanthroline (log $\beta_{\text{S,1}}=8.65$), which was reported as a powerful neutral ligand for synergic extraction.[5]

Table 2. Adduct Formation Constants ($\beta_{\text{S,1}}$), Synergic Extraction Constants ($K_{\text{ex,S,1}}$), and Conditional Synergic Extraction Constants ($K'_{\text{ex,S,1}}$) in RE(III)–Htta–S–Benzene Systems.

S	RE(III)	log $\beta_{\text{S,1}}$	log $K_{\text{ex,S,1}}$	log $K'_{\text{ex,S,1}}$
dien	La	12.22	2.03	−4.67
	Sm	11.86	4.06	−3.88
	Tb	11.61	4.26	−3.55
	Lu	9.82	3.26	−5.53
trien	La	13.64	3.45	−3.25
	Sm	12.08	4.28	−3.66
	Tb	10.86	3.51	−4.30
	Lu	<8.5	<1.9	<−6.9

To understand the typical tendency of $\beta_{\text{S,1}}$ for polydentate amines, we examined the basicity of these amines as well as the availability of the coordination site of the metal chelate RE(tta)$_3$. The adduct formation constants ($\beta_{\text{S,1}}$) for dien is about 10^5-times larger than that for another tridentate nitrogen-involving ligand 2, 2′:6′,2″-terpyridine (p$K_{\text{H2S}}=3.45$; p$K_{\text{HS}}=4.55$,[16] and log $\beta_{\text{S,1}}$=7.16 (La); 6.97 (Sm); 4.75 (Lu)[13]). These differences can be explained by the general understanding that a neutral ligand with a higher basicity produces a higher synergic effect.[17,18] The $\beta_{\text{S,1}}$ values for a series of simple aliphatic amines, i.e. en,[4] dien, and trien, show a marked variation, that is, the $\beta_{\text{S,1}}$ values for La(III) increase in the order en<dien<trien, although three

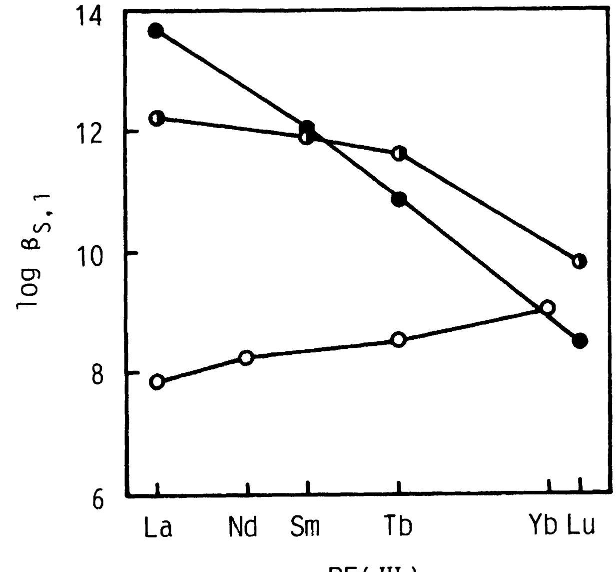

Fig. 7. Plots of $\beta_{\text{S,1}}$ in RE(III)–Htta–S systems in order of RE atomic number. S; ○ en,[4] ◑ dien, ● trien.

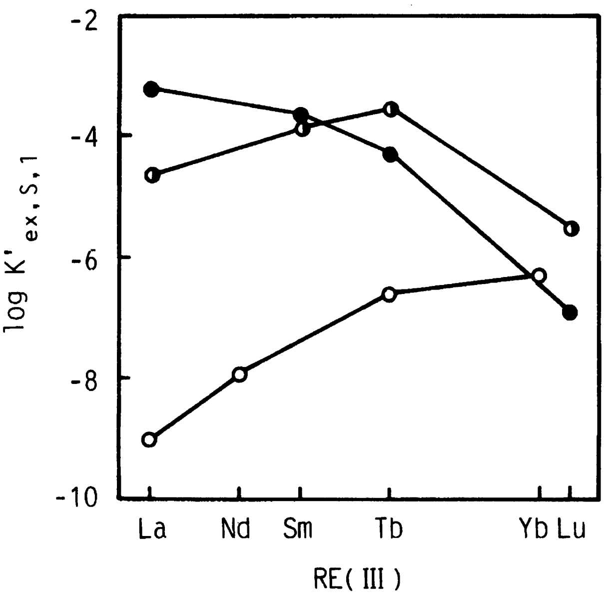

Fig. 8. Plots of $K'_{ex,S,1}$ in RE(III)–Htta–S systems in order of RE atomic number. S; ○ en,[4] ◑ dien, ● trien.

amines seem to be nearly the same level in basicity, $pK_{HS}=9.89$ (en); 9.84 (dien); 9.74 (trien).[7] This result means that the polydentate amine, having a greater number of nitrogen atoms, shows a larger synergic effect as a usual tendency observed in general complex formation. This relation is recognized for light rare earths with a larger ionic radius, such as La(III); however, for Lu(III) with a smaller ionic radius, the $\beta_{S,1}$ value for trien is smaller than those for en and dien, due to an insufficient coordination involving the steric hindrance of the 4 nitrogens in trien. The $\beta_{S,1}$ values are plotted according to the order of the atomic numbers of RE(III) for en, dien and trien in Fig. 7. For the bidentate ligand en, although the $\beta_{S,1}$ values increase simply in the order of the atomic number, for the tridentate ligand dien, the $\beta_{S,1}$ values tend to decrease in the order of the atomic numbers; for the quadridentate trien, the $\beta_{S,1}$ values decrease abruptly in the order of the atomic number. The tendencies concerning the decrement of $\beta_{S,1}$ of dien and trien are more remarkable than that of the bidentate ligand with a large steric hindrance, such as 2,9-dimethylphenanthroline.[5] This also suggests that the number of coordinating nitrogen atoms decreases in the order of the atomic numbers of RE(III) for dien and trien. In the other words, the nitrogen atoms of the ligand would coordinate fully to light rare earths, but insufficiently to heavy rare earths.

The magnitude of the synergic extraction constant ($K'_{ex,S,1}$) is governed by $\beta_{S,1}$, as indicated by Eq. 13. $K'_{ex,S,1}$ is directly related to the extraction efficiency of RE(III). The $K'_{ex,S,1}$ values are plotted against the atomic number of RE(III) in Fig. 8. In the en system, $K'_{ex,S,1}$ increases in the order of the atomic number; in the dien system, $K'_{ex,S,1}$ indicates the maximum at Tb; and in the trien system, it decreases in the order of the atomic number. These results suggest that there is a possibility regarding an improvement in the extraction selectivity to choose the combination of chelating agents and nitrogen-involving neutral ligands.

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