Synergistic Extraction of Rare Earths(III) with β-Diketone and Nitrogen-Containing Terdentate Ligand, 2,2′:6′,2″-Terpyridine

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The synergistic extraction of rare earth(III) ions (RE: La, Sm, Tb, and Lu) was investigated using a β-diketone (HA), i.e., trifluoroacetylacetone (Htfa) or hexafluoroacetylacetone (Hhfa), in the presence of a terdentate ligand, 2,2′:6′,2″-terpyridine (terpy) into benzene. The formation of complexes such as $RE(A)^{2+}$ or $RE(A)_2^+$ in the aqueous phase was observed. The synergistic enhancement is attributed to the formation of an adduct $RE(A)_3$terpy in the benzene phase. The adduct formation constants ($\beta_{S,1}$) and the synergistic extraction constants were determined. For each RE(III), the $\beta_{S,1}$ value in the Htfa–terpy system is smaller than that in the Hhfa–terpy system. The $\beta_{S,1}$ values decrease with increasing atomic number of RE(III) in the Htfa–terpy system, but the $\beta_{S,1}$ value for La(III) is smaller than that for the other RE(III) in the Hhfa–terpy system.

The synergistic extraction with an acidic chelating reagent and a neutral ligand has been widely investigated. The synergistic enhancement has been discussed with the coordination number of a metal ion, acidity of the chelating reagent and neutral ligand, and polarity of organic solvent. In most of these studies, oxygen-coordinating unidentate ligands, such as tributyl phosphate (tbp) or trioctylphosphane oxide (topo), have been used.

In recent years, nitrogen-coordinating bidentate ligands, such as 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy), have been examined for the first transition elements, rare earths and actinides.[1—4] We first found that these bidentate ligands provided a new possibility for improving the separation efficiency among rare earth (RE(III)) ions, which was never expected by using unidentate ligands, and that this separation efficiency was affected by β-diketones.[5—8] However, the effect of β-diketone on the synergistic extraction with a terdentate neutral ligand has not been studied.

We reported on the synergistic extraction of RE(III)[9,10] and Mn(II)[11] by using 2-thenoyltrifluoroacetone (Htta, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) and nitrogen-containing ter- and quadridentate neutral ligands, 2,2′:6′,2″-terpyridine (terpy), diethylenetriamine and triethylenetetramine. In these synergistic extraction systems, multidentate neutral ligands show larger synergistic effects for lighter RE than for heavy RE.

In the present paper, to clarify the role of the acidic chelating reagent, i.e., β-diketone, in the synergistic extraction of RE(III) with a neutral multidentate ligand, the extraction behavior of RE(III) (La, Sm, Tb, and Lu) with trifluoroacetylacetone (Htfa, 1,1,1-trifluoro-2,4-pentanedione) or hexafluoroacetylacetone (Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) is examined in the presence or absence of a terdentate neutral ligand, terpy.

Experimental

Materials and Apparatus. The radioisotopes, ^{140}La, ^{153}Sm, ^{160}Tb, and ^{177}Lu, used as tracers, were produced by neutron irradiation of 0.03—0.8 mg of metal nitrate (99.99—99.999%) in the JRR-3 or JRR-4 nuclear reactor of the Japan Atomic Research Institute at a thermal neutron flux of 9×10^{13} n·cm^{-2}s^{-1} for 24 h or 5.5×10^{13} n·cm^{-2}s^{-1} for 12 h, respectively. A radioactive solution of each RE(III) was prepared by dissolving a known amount of the irradiated sample in 0.1 M (1 M=1 mol dm^{-3}) nitric acid, adding an aliquot of the standard solution of each RE(III), evaporating to dryness, and dissolving the residue in 1×10^{-3} M perchloric acid.

Htfa (98% purity, Dojindo Laboratories) and Hhfa (99% purity, Aldrich Chem. Co.) were purchased and used without further purification. Terpy (98% purity, Aldrich Chem. Co.) was purified by vacuum sublimation at 40 °C. Benzene was stirred with concentrated sulfuric acid, washed with water and distilled after drying. Other reagents used were of guaranteed reagent grade. The γ-activity of each radioisotope was measured with an NaI(Tl) well-type scintillation detector connected with a single-channel analyzer. The pH of the equilibrated aqueous phase was measured with a glass electrode.

Extraction Procedure. An aqueous solution (5 cm^3) containing 1×10^{-6}—1×10^{-5} M RE(III) labeled with its radioisotope was placed in a 20 cm^3 centrifuge tube.

The pH of the aqueous phase was adjusted to 3—7 with 1×10^{-3}—1×10^{-2} M 2-(*N*-morpholino)ethanesulfonic acid and sodium hydroxide solution. The formation of RE hydroxide can be ignored in this pH range.[12] The ionic strength was fixed to 0.1 M with sodium perchlorate. A benzene solution (5 cm^3) containing 1×10^{-4}—1×10^{-2} M β-diketone and 0—1×10^{-2} M terpy was shaken with the aqueous solution for 1 h at 25 °C and centrifuged. After an aliquot (3 cm^3) was taken from each phase, its γ-activity was measured and the distribution ratio of RE(III) was calculated as the radioactivity ratio. The equilibrium pH was measured immediately after phase separation.

Results and Discussion

Extraction Equilibrium in the Synergistic Extraction System. The extraction constant (K_{ex}), adduct formation constant ($\beta_{S,n}$), and synergistic extraction constant ($K_{ex,S,n}$) are commonly defined.[9,10] The distribution ratio, D_o, of a trivalent metal ion, M^{3+}, with an acidic chelating reagent, HA, is expressed as:

$$D_o=[\overline{MA_3}]/([M^{3+}]+\sum_j[MA_j^{(3-j)+}])$$
$$=K_{ex}P_{HA}^3[A^-]^3/K_{HA}^3(1+\sum_j\beta_{A,j}[A^-]^j), \quad (1)$$

where P_{HA} and K_{HA} are the partition coefficient and acid-dissociation constant of HA, respectively. $\beta_{A,j}$ is the over-all formation constant of $MA_j^{(3-j)+}$ in the aqueous phase and A^- is the acid-dissociated anion of HA. The upper bar indicates the organic phase. In the synergistic extraction of M^{3+} with HA and a neutral ligand, S, the distribution ratio, D, can be expressed as:

$$D=([\overline{MA_3}]+\sum_n[\overline{MA_3S_n}])/([M^{3+}]+\sum_j[MA_j^{(3-j)+}])$$
$$=K_{ex}P_{HA}^3[A^-]^3(1+\sum_n\beta_{S,n}[\overline{S}]^n)$$
$$/K_{HA}^3(1+\sum_j\beta_{A,j}[A^-]^j). \quad (2)$$

From Eqs. 1 and 2 the following equation is obtained:

$$D/D_o=1+\sum_n\beta_{S,n}[\overline{S}]^n. \quad (3)$$

The logarithmic distribution ratios of RE(III) with HA only are plotted against the logarithmic equilibrium concentration of A^- in the aqueous phase and are shown in Figs. 1 and 2 for Htfa and Hhfa, respectively. The $[A^-]$ values are calculated by considering the partition and dissociation of HA as before.[9,10] The literature values are adopted in the calculation of $[A^-]$; pK_{HA} (6.13) and $\log P_{HA}$ (0.04)[13] for Htfa, and pK_{HA} (4.46) and $\log P_{HA}$ (−1.91)[13] for Hhfa. The initial concentration of HA is 100 times higher than those of RE(III) ions; therefore loss of HA due to the complexation can be neglected. Plots in these figures deviate downward from a straight line with a slope of 3 both in the absence and presence of terpy, and the slopes of plots decrease with increase in $[A^-]$. Since the extracted species is $RE(A)_3$

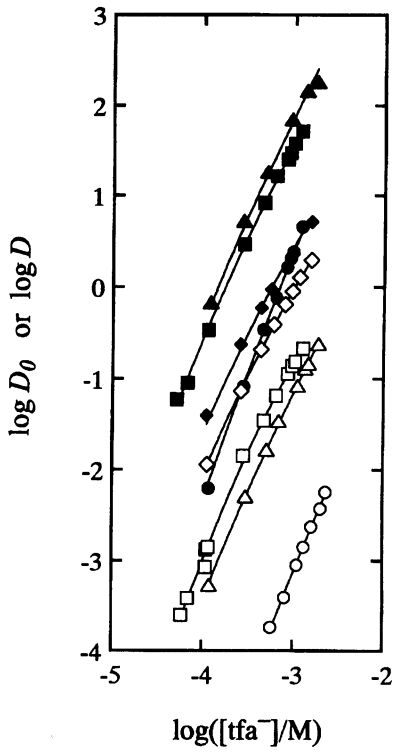

Fig. 1. Distribution ratio of RE(III) as a function of tfa^- concentration in the absence of terpy, ○, La; △, Sm; □, Tb; ◇, Lu, and in the presence of 0.97—1.2×10^{-3} M terpy, ●, La; ▲, Sm; ■, Tb; ◆, Lu.

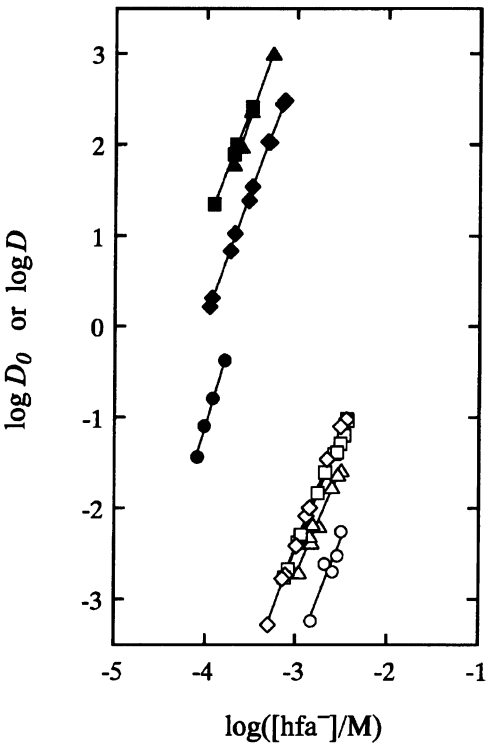

Fig. 2. Distribution ratio of RE(III) as a function of hfa^- concentration in the absence of terpy, ○, La; △, Sm; □, Tb; ◇, Lu, and in the presence of 1.1×10^{-3} M terpy, ●, La; ▲, Sm; ■, Tb; ◆, Lu.

in other RE–β-diketone systems,[7,9,14] the curvatures of the plots are caused by the formation of $RE(A)_j^{(3-j)+}$ in the aqueous phase.

As for La and Sm in the Htfa system, the slope in Fig. 1 is more than 2, and thus only the existence of $RE(tfa)^{2+}$ is suggested. For Tb and Lu, the slope is 1.6 in a higher concentration range of tfa^-, and this indicates that $RE(tfa)^{2+}$ and $RE(tfa)_2^+$ form in the aqueous phase. With Eq. 1 and all the observed D_o data in Fig. 1, the K_{ex} and $\beta_{A,j}$ values were calculated by the non-linear least squares method[15] and are summarized in Table 1. For all cases, correlation coefficients are more than 0.99. The increasing tendency of K_{ex} of Htfa with increasing atomic number (Z) is similar to that of Htta.[9] The increase in $\beta_{A,1}$ and $\beta_{A,2}$ values with increasing Z is observed in other systems, such as acetylacetone,[16] and this tendency can be explained by the lanthanide contraction.

In the Hhfa case, only $RE(hfa)^{2+}$ forms in the aqueous phase, since the slope for every RE(III) is more than 2 in Fig. 2. The K_{ex} and $\beta_{A,j}$ values are also summarized in Table 1. For La, the correlation coefficient is 0.94, while the value is more than 0.99 in the other cases. The difference in the $\beta_{A,1}$ value between REs is small in this system.

The logarithmic distribution ratios with HA and terpy are also plotted against $\log[A^-]$ in Figs. 1 and 2. Large synergistic effects are observed, as compared with the plots of $\log D_o$. The plots obey the lines calculated with Eq. 2 using $\beta_{A,1}$ (and $\beta_{A,2}$), and this implies that terpy has no effect on the formation of $RE(A)_j^{(3-j)+}$ in the aqueous phase.

$\log(D/D_o)$ is plotted against the logarithmic concentration of terpy in the organic phase, $[\overline{terpy}]$, and the result is shown in Fig. 3. The $[\overline{terpy}]$ values are calculated by considering the partition and protonation of terpy.[9] The initial concentration of terpy is 100 times higher than those of RE(III) ions; loss of terpy due to the complexation can therefore be neglected. The adduct

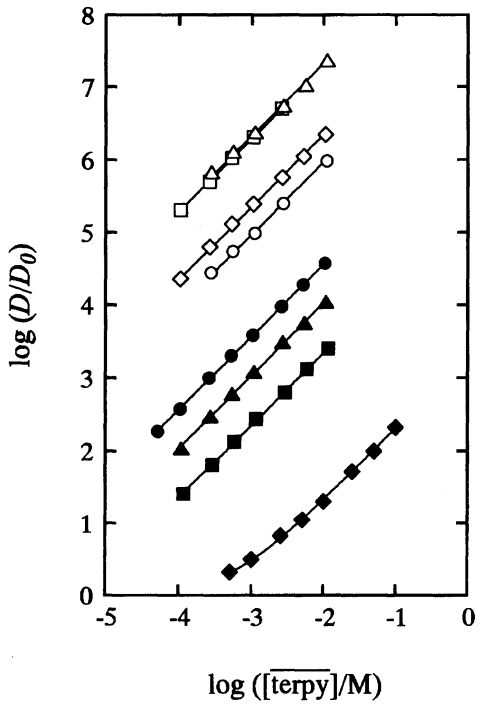

Fig. 3. Effect of the terpy concentration in benzene on the extraction of RE(III) in the Htfa–terpy system, ●, La; ▲, Sm; ■, Tb; ◆, Lu, and in the Hhfa–terpy system, ○, La; △, Sm; □, Tb; ◇, Lu.

formation constants are obtained with Eq. 3. The values of D_o under comparable conditions are calculated with Eq. 1 using K_{ex} and $\beta_{A,j}$. The slope of the plots is 1 for every RE(III); this means that $RE(A)_3$terpy is the dominant extracted species. The adduct formation constants, $\beta_{S,1}$, and the synergistic extraction constants, $K_{ex,S,1}$, are listed in Table 1.

The Adduct Formation Constant. The plots of $\beta_{S,1}$ of $RE(A)_3$terpy against Z are shown in Fig. 4 together with the previous related data. The $\beta_{S,1}$ value for each RE increases in the following order: Htfa< Htta<Hhfa in the β-diketone–terpy system. This order

Table 1. Equilibrium Constants of the Synergistic Extraction of RE(III) in the β-Diketone–Terpy–Benzene System

RE(III)	$\log\beta_{A,1}$	$\log\beta_{A,2}$	$\log K_{ex}$	$\log\beta_{S,1}$	$\log K_{ex,S,1}$
			Htfa–terpy system		
La	2.99±0.10	—[a]	−12.36±0.06	6.57±0.00	−5.79±0.06
Sm	3.94±0.05	—[a]	−9.68±0.04	6.04±0.01	−3.64±0.04
Tb	4.13±0.11	6.59±0.17	−9.31±0.09	5.35±0.01	−3.96±0.09
Lu	4.17±0.05	6.84±0.02	−8.17±0.03	3.31±0.01	−4.86±0.03
			Hhfa–terpy system		
La	2.55±0.98	—[a]	−2.16±0.45	7.98±0.01	5.82±0.45
Sm	2.92±0.31	—[a]	−1.14±0.19	9.33±0.02	8.19±0.19
Tb	2.81±0.08	—[a]	−0.88±0.05	9.29±0.00	8.41±0.05
Lu	2.50±0.09	—[a]	−0.95±0.03	8.36±0.01	7.41±0.03

a) Not observed.

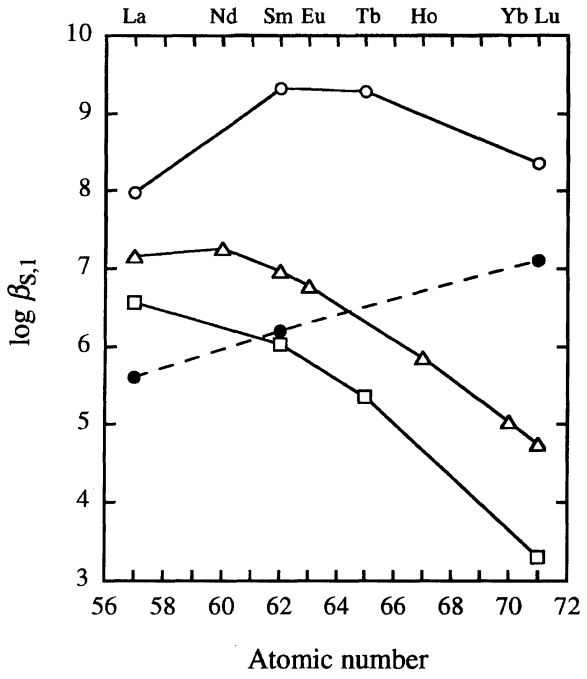

Fig. 4. Plots of $\beta_{S,1}$ against RE atomic number: □, Htfa–terpy; ○, Hhfa–terpy; △, Htta–terpy;[9] ●, Hhfa–bpy.[8]

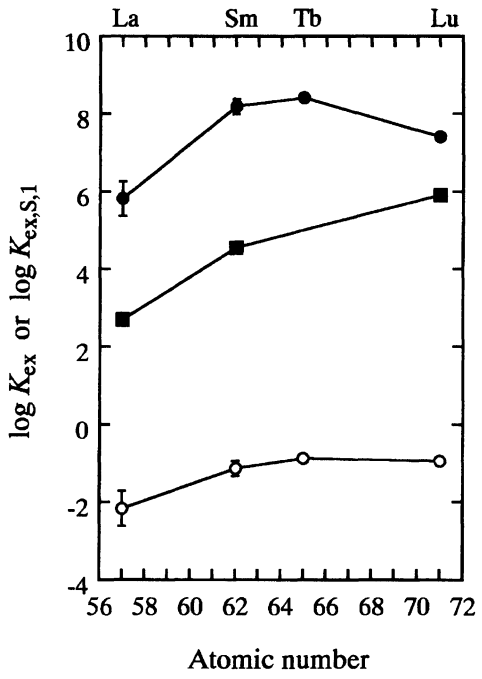

Fig. 5. Plots of K_{ex} and $K_{ex,S,1}$ against RE atomic number: ○, K_{ex} for Hhfa; ■, $K_{ex,S,1}$ for Hhfa–bpy;[8] ●, $K_{ex,S,1}$ for Hhfa–terpy.

can be related to that of K_{HA}, and would be the reverse order of the stability constant of $RE(A)_3$. In fact, $\beta_{A,1}$ of $RE(tfa)^{2+}$ is larger than that of $RE(hfa)^{2+}$ for each RE(III), as shown in Table 1. These trends of β_S are observed in the synergistic extraction using unidentate neutral ligands and bidentate neutral ligands; The order of $\beta_{S,1}$ in the Cu(II), Zn(II)–Hhfa, Htfa, Hacac–topo, tbp system is Hacac<Htfa<Hhfa[17] ($pK_{HA}=8.67$ for Hacac)[13] and the order of $\beta_{S,1}$ in the RE(III)–Hhfa, pivaloyltrifluoroacetone (Hpta, $pK_{HA}=7.01$[13]), benzoylacetone (Hba, $pK_{HA}=8.39$[13]), Hacac–bpy system is Hacac<Hba<Hpta<Hhfa.[8] However, the difference in $\beta_{S,1}$ between Htfa and Htta is an unexpected result, considering the small difference in K_{HA} between Htta and Htfa.

In our previous studies for the Htta system,[10] the $\beta_{S,1}$ values of terpy are larger than those of a bidentate neutral ligand, bpy, for lighter RE, but smaller for the heavy RE. This suggests that three nitrogen atoms of terpy can be bound to the extracted complex of lighter RE in benzene, and that terpy can not function as a terdentate ligand for the complex of heavy RE with smaller ionic size. On the other hand, the decreasing tendency of $\beta_{S,1}$ with increasing Z in the Htfa–terpy system is similar to that in the Htta–terpy system, and the similarity for K_{ex} is also observed. Furthermore, the difference in K_{HA} between Htfa and Htta (pK_{HA} 6.33)[13] is small, and thus the preceding discussion of the coordination in the Htta–terpy system[10] would be also valid in the Htfa–terpy system.

The $\beta_{S,1}$ value for La(III) is smaller than that for the other RE(III) in the Hhfa–terpy system, and the $\beta_{S,1}$ values of terpy are larger than those of bpy[8] in all RE(III), as shown in Fig. 4. This result shows that terpy is bound to the central RE(III) with all the three nitrogen atoms as the terdentate ligand.

Synergistic Extraction Constant. The difference in the extraction constant ($K_{ex,S,1}$) between RE(III) in the Htfa–terpy system is smaller than that (K_{ex}) in the Htfa system. Thus the mutual separation efficiency can not be improved by using the combination of Htfa and terpy. In contrast, the difference in $K_{ex,S,1}$ between La and Sm in the Hhfa–terpy system is larger than that in the K_{ex} values in Hhfa system, as shown in Fig. 5. Thus the mutual separation efficiency as well as the extractability would be improved for lighter RE by using terpy. As compared with a bidentate ligand bpy, the use of terpy in the Hhfa system creates a disadvantage in the mutual separation for middle and heavy RE, but creates an advantage in both the extractability and the mutual separation efficiency for lighter RE(III), such as La and Sm.

In the present study, it is found that this separation efficiency is affected by β-diketones, and that a nitrogen-containing terdentate ligand, terpy, also provides a possibility for improving the separation efficiency among lighter RE(III)s.

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