Inorganica Chimica Acta, 114 (1986) 101–107

Effect of an Acidic Chelating Agent in the Synergic Extraction Systems of Rare Earth(III)-β-diketones-2,2′-bipyridine

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Received June 26, 1985

Abstract

The extraction of rare earth elements (RE), La(III), Sm(III), Tb(III), Tm(III) and Lu(III), with four β-diketones (HA), hexafluoroacetylacetone (Hhfa), pivaloyltrifluoroacetone (Hpta), benzoylacetone (Hba) and acetylacetone (Hacac), in the presence or absence of 2,2′-bipyridine (bpy) in benzene was studied. The extraction constants (K_{ex}) for RE(III) with Hhfa, Hpta and Hacac were determined and compared with each other. The order of K_{ex} is Hacac < Hpta < Hhfa. The synergic enhancement observed in the presence of bpy is attributed to the 1:1 adduct formation such as $RE(A)_3bpy$, except for the La(III)–Hhfa system, in which $La(hfa)_3(bpy)_2$ was also observed. The adduct formation constant, $\beta_{s,1}$, for the β-diketones was in the order of Hacac < Hba < Hpta < Hhfa, which is in the same order as their acid dissociation constants. The trend of $\beta_{s,1}$ with the atomic number of RE is obviously different with different β-diketones; the $\beta_{s,1}$ for Hacac and Hba tends to decrease with increasing atomic numbers of RE, but those for Hpta and Hhfa increase.

Introduction

The synergic extraction of metals with an acidic chelating agent and a neutral ligand has been widely investigated. The synergism occurs generally by the formation of mixed ligand complexes between the metal chelate and the neutral ligand in the organic phase. The synergic enhancement has been qualitatively discussed in terms of metal, chelating agent, neutral ligand and diluent. However, most of the studies of synergic extraction have been carried out on systems involving unidentate neutral ligands, such as tributylphosphate (tbp) and trioctylphosphine oxide (topo), but few have used bidentate ligands.

In our laboratory, the synergic extraction of bivalent transition metals with β-diketone and bidentate neutral ligands, such as 1,10-phenanthroline (phen), 2,9-dimethylphenanthroline and 2,2′-bipyridine (bpy), have been studied [1, 2], and recently that of rare earth elements (RE) with acetylacetone (Hacac) and phen was thoroughly investigated [3, 4]. In order to clarify the role of the acidic chelating agent in the synergic extraction of RE(III) with β-diketones and bidentate neutral ligand, in the present paper, the extraction behavior of RE(III) with a series of β-diketones is examined in the presence or absence of bpy in benzene. Four β-diketones, hexafluoroacetylacetone (Hhfa), pivaloyltrifluoroacetone (Hpta), benzoylacetone (Hba) and Hacac are chosen. The composition of the adduct and the adduct formation constant are determined and compared with each other.

Experimental

Materials and Apparatus

Radioisotopes ^{140}La, ^{153}Sm, ^{160}Tb and ^{177}Lu, used as tracers, were produced by the neutron irradiation of 0.5–5 mg of oxide or nitrate in the nuclear reactor (JRR-4) of the Japan Atomic Research Institute at a thermal neutron flux of 5.5×10^{13} n cm^{-2} s^{-1} for 6 h. ^{168}Tm was produced by 30–60 MeV bremsstrahlung irradiation of its oxide with a linear electron accelerator at Tohoku University. The radioactive solution of RE was prepared by dissolving a known amount of the irradiated sample in hydrochloric acid, evaporating to dryness, and redissolving in 10^{-3} M perchloric acid solution before use.

Acetylacetone was washed with diluted ammonia solution and distilled twice after drying. Hexafluoroacetylacetone was distilled in the presence of phosphorus pentoxide. Reagent grade benzoylacetone, pivaloyltrifluoroacetone and 2,2′-bipyridine were used as obtained. Benzene was stirred with concentrated sulfonic acid, washed with water and distilled after drying. Unless otherwise stated, reagents used were of guaranteed reagent grade.

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0020-1693/86/$3.50

The γ-activity of each radioisotope was measured with an NaI(Tl) well-type scintillation detector connected with a single-channel analyzer. The extraction vial was shaken with a mechanical shaker at 330 strokes per minute. The pH value of the equilibrated aqueous phase was measured with a glass electrode.

Procedure

An aqueous solution (6 ml) containing 10^{-7}–10^{-5} M RE(III) labelled with its radioisotope was placed in a 30 ml centrifuge tube with a ground glass stopper. In the benzoylacetone system, 10^{-3}–10^{-2} M sodium citrate was added to prevent hydrolysis at an extraction pH range appropriate for this chelating agent. A benzene solution (6 ml) containing 10^{-4}–10^{-1} M acidic chelating agent and 10^{-5}–10^{-2} M 2,2′-bipyridine was added and shaken for 1–3 h at 25 °C and centrifuged. An aliquot was taken from each phase, the γ-activity was measured, and the distribution ratio of the metal was calculated as the radioactivity ratio. The pH value of the aqueous phase was adjusted with 5×10^{-3}–10^{-2} M piperazine-*N,N′*-bis-(2-ethanesulfonic acid) and sodium hydroxide solution, and the equilibrium pH was measured immediately after shaking. Ionic strength was adjusted to 0.1 with sodium perchlorate.

Theoretical

The distribution ratio (D_0) of a tervalent cation, M^{3+}, with a chelating extractant, HA, can be expressed as follows;

$$D_0 = \frac{[\overline{MA_3}]}{[M^{3+}] + \Sigma[MA_n{}^{3-n}]} = \frac{P_M\beta_3[A^-]^3}{1 + \Sigma\beta_n[A^-]^n} \qquad (1)$$

where the bar denotes the organic phase, β_n the formation constant of $MA_n{}^{3-n}$ in the aqueous phase, P_M the partition coefficient of MA_3, and A^- the chelating anion in the aqueous phase. In the very low concentration region of A^-, the successive chelates, $MA_n{}^{3-n}$, will be negligible; hence D_0 depends simply on the third power of $[A^-]$. For the sake of convenience, the extraction constant, K_{ex}, is given for the following equilibrium:

$$M^{3+} + 3\overline{HA} \rightleftharpoons \overline{MA_3} + 3H^+ : K_{ex} \qquad (2)$$

The K_{ex} is a mixed constant and can be expressed by a combination of K_{HA}, P_{HA}, P_M and β_3 as

$$K_{ex} = \left(\frac{K_{HA}}{P_{HA}}\right)^3 P_M\beta_3 = \left(\frac{K_{HA}}{P_{HA}}\right)^3 \frac{D_0}{[A^-]^3} \qquad (3)$$

where K_{HA} and P_{HA} denote the acid dissociation constant and the partition coefficient of HA, respectively. Sometimes accurate data for P_M and β_3 are not available, but the product $P_M\beta_3$ can be replaced by the experimental data of D_0 and $[A^-]$, as is understood from the limiting equation of eqn. (1); hence we can determine K_{ex} by the final form of eqn. (3).

In the synergic extraction of M^{3+} with HA and a neutral ligands, S, the distribution ratio D can be expressed as follows:

$$D = \frac{[\overline{MA_3}] + \Sigma[\overline{MA_3S_m}]}{[M^{3+}] + \Sigma[MA_n{}^{3-n}]}$$

$$= \frac{P_M\beta_3[A^-]^3(1 + \Sigma\beta_{s,m}[\overline{S}]^m)}{1 + \Sigma\beta_n[A^-]^n} \qquad (4)$$

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

$$\overline{MA_3} + m\overline{S} \rightleftharpoons \overline{MA_3S_m} : \beta_{s,m} \qquad (5)$$

From eqns. (1) and (4), the following simple relation is obtained:

$$D/D_0 = 1 + \Sigma\beta_{s,m}[\overline{S}]^m \qquad (6)$$

If MA_3S_m is the only dominant species in the organic phase, D/D_0 will depend on the mth power of $[\overline{S}]$.

Results and Discussion

Extraction with Hhfa and Synergic Extraction with Hhfa and bpy

The extraction of La(III), Sm(III) and Lu(III) with various initial concentrations of Hhfa in benzene was carried out at different pHs, and the plots of the distribution ratio against the logarithimic concentration of hfa^- in the aqueous phase are given in Fig. 1. The

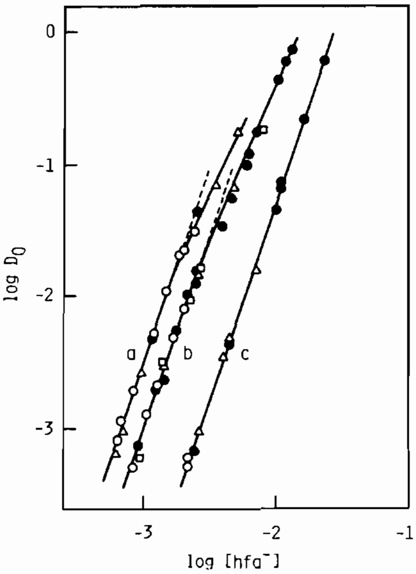

Fig. 1. Distribution ratio of RE(III) as a function of the concentration of hfa^-. (a) Lu, (b) Sm, (c) La. $[Hhfa]_{init}$; ●: 10^{-1} M, □: 5×10^{-2} M, △: 3×10^{-2} M, ○: 10^{-2} M.

TABLE I. Extraction Constants (K_{ex}) and Adduct Formation Constants (β_s) in RE(III)–HA–bpy Systems

HA	RE(III)	$\log K_{ex}$	$\log \beta_{s,1}$
Hhfa	La	−2.91	5.61^a
	Sm	−1.66	6.21
	Lu	−1.20	7.11
Hpta	La	−12.65	5.40
	Sm	−10.06	6.36
	Lu	−8.39	6.42
Hba	La	–^{b}	4.21
	Sm	–^{b}	4.28
	Tb	–^{b}	4.27
	Lu	–^{b}	3.21
Hacac	La	−20.12^c	3.26
	Tm	−15.20^c	2.40

^{a}La: $\log \beta_{s,2} = 8.88$. ^{b}The exact value was not determined due to the presence of citrate (see text). ^{c}Calculated value from eqn. (2), using the experimental values of P_M [6] and the quoted values of K_{HA} [13], P_{HA} [14] and β_3 [15].

equilibrium concentration of hfa$^-$ in the aqueous phase was calculated as follows:

$$[A^-] = \frac{C_{HA}}{(P_{HA} + 1)[H^+]/K_{HA} + 1} \qquad (7)$$

where C_{HA} denotes the initial concentration. The literature values of K_{HA} and P_{HA} were adopted, *i.e.*, $\log K_{HA} = -4.46$ and $\log P_{HA} = -1.91$ for benzene [5]. The plots for La(III) are independent of the initial concentration of Hhfa and give a straight line with a slope of three; thus, the extracted chelate is $La(hfa)_3$, as expected. The plots for Sm(III) and Lu(III) give straight lines with a slope of three in the lower concentration region of hfa$^-$, which means that $Sm(hfa)_3$ and $Lu(hfa)_3$ are extracted. In the higher concentration region of hfa$^-$, these plots are negatively deviated from the straight lines. This may be due to the noticeable formation of an intermediate chelate of RE(III) with hfa$^-$ in the aqueous phase, such as $RE(hfa)^{2+}$. A contribution of the intermediate chelate may be more noticeable for heavy RE(III) than for light RE(III), becuase the successive formation constant is larger for heavy RE(III) than for light RE(III) [6]. The extraction constant, K_{ex}, was calculated from eqn. (3), by taking these plots on a straight line with a slope of three; the results are listed in Table I.

The synergic extractions of La(III), Sm(III) and Lu(III) with Hhfa and various concentrations of bpy in benzene were carried out, and the plots of $\log D/D_0$ against $\log [\overline{bpy}]$ are shown in Fig. 2. The equilibrium concentration of bpy in the organic phase was calculated from the following equation:

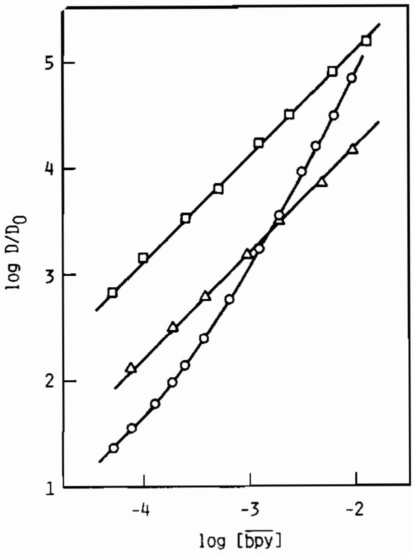

Fig. 2. Effect of the concentration of bpy in the organic phase on the synergic extraction of RE(III) together with Hhfa. ○: La, 10^{-2} M Hhfa, pH 3.6, △: Sm, 5×10^{-3} M Hhfa, pH 3.7, □: Lu, 5×10^{-3} M Hhfa, pH 3.6.

$$[\overline{S}] = \frac{C_S}{1 + (1 + [H^+]/K_{HS})/P_S} \qquad (8)$$

where C_S denotes the initial concentration of bpy in the organic phase, P_S is the partition coefficient of bpy, and K_{HS} the acid dissociation constant of the protonated bpy. The values of P_S and K_{HS} have been obtained experimentally in a previous work [7], *i.e.*, $\log P_S = 2.05$ for benzene and $\log K_{HS} = -4.50$. The plots for Sm(III) and Lu(III) give straight lines with the slope of unity. This indicates that the mole ratio of the chelate to bpy in the adduct is 1:1, and no evidence for the formation of a higher adduct such as $RE(hfa)_3(bpy)_2$ is observed. Similar 1:1 adduct formation between a tris-β-diketonate chelate of RE(III) and a neutral bidentate ligand was reported previously in the RE(III)–Hacac–phen system [3, 4] and the Tm(III)–thenoyltrifluoroacetone (Htta)–bpy, –phen systems [7]. On the other hand, the plots for La(III) in Fig. 2 give a curved line, which comes close to an asymptote to a line with a slope of two in the higher concentration of bpy, and with a slope of unity in the lower concentration range. This suggests that the mole ratio of chelate to bpy in the adduct is 1:1 and 1:2. The formation of the 1:2 adduct between the tris-β-diketonate chelate of RE(III) and a neutral bidentate ligand has not been observed in our previous studies [3, 4, 7] or in another available report [8]. Kassierer and Kertes noted a formation of the 1:2 adduct in the La(III), Nd(III), Gd(III) and Lu(III)–Htta–phen and –bpy systems by simple slope analysis [9], but they pay no attention to the partition of neutral ligands and do not get reasonable value for the slope; hence, their simple conclusion based on such ambiguous data and discussion is not plausible.

In order to confirm that the addition of a basic bidentate neutral ligand does not alter the stoichiometry of the central chelate, in other words, to confirm the number of moles of the acidic chelating ligand in the adduct, the synergic extraction of La(III) was carried out with various concentrations of Hhfa and with the higher concentration of bpy in which the 1:2 adduct may be dominantly formed. In eqn. (4), when the concentration of A^- is very low, the successive chelate can be neglected, so that D depends on the third power of $[A^-]$. The plots of $\log D$ against $\log[\text{hfa}^-]$ are shown in Fig. 3. A straight line with a slope of three is obtained; thus, the 1:2 adduct involves three moles of hfa^- as $\text{La(hfa)}_3\text{(bpy)}_2$. The 1:1 adduct between the tris-β-diketonate chelate of RE(III) and a bidentate ligand, e.g., $\text{Nd(tta)}_3\text{bpy}$, has been isolated and analyzed by X-ray crystallography to be an eight-coordination complex with a distorted square antiprismatic geometry [10]. In $\text{La(hfa)}_3\text{(bpy)}_2$, if two bpy molecules coordinate directly to the central metal of the chelate as a bidentate ligand, the coordination number of La(III) may be ten. No crystallographic study of a comparable mixed ligand complex with ten-coordination has been reported, but the structures of some decacoordination compounds of RE(III) have been determined by X-ray analysis, such as $\text{La(NO}_3)_3\text{(bpy)}_2$ [11], where NO_3^- acts as a bidentate ligand, and $\text{La(Hedta)(H}_2\text{O)}_4\cdot 3\text{H}_2\text{O}$ [12], where edta is the ethylenediaminetetraacetate anion. Therefore, the formation of $\text{La(hfa)}_3\text{(bpy)}_2$ with decacoordination may be understandable. The adduct formation constants are calculated from eqn. (6) and are listed in Table I.

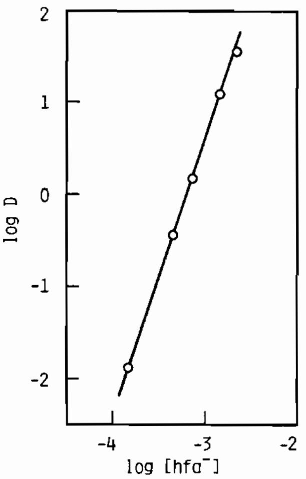

Fig. 3. Effect of the concentration of hfa^- on the distribution ratio of La(III) in the synergic extraction together with bpy. bpy: 1×10^{-2} M, pH 3.7.

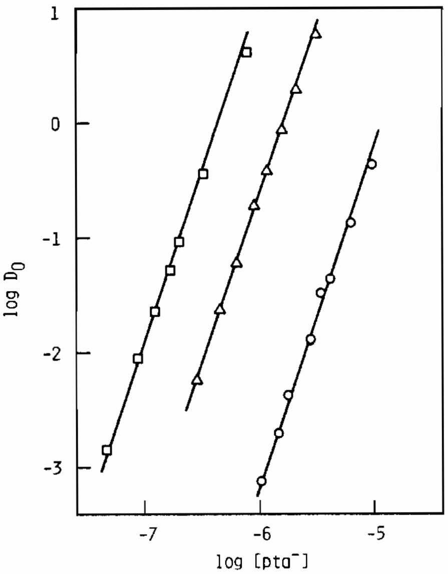

Fig. 4. Distribution ratio of RE(III) as a function of the concentration of pta^-. $[\text{Hpta}]_{\text{init}} = 10^{-3}$ M. ○: La, △: Sm, □: Lu.

Extraction with Hpta and Synergic Extraction with Hpta and bpy

The extraction of La(III), Sm(III) and Lu(III) with Hpta in benzene was carried out, and the plots of $\log D_0$ against $\log [\text{pta}^-]$ are shown in Fig. 4. The concentration of pta^- in the aqueous phase was calculated from eqn. (7) using the quoted values of $\log P_{\text{HA}} = 2.15$ and $\log K_{\text{HA}} = -7.01$ [5]. The plot of each RE(III) gives a straight line with a slope of three, corresponding to RE(pta)_3.

The synergic extractions of La(III), Sm(III) and Lu(III) with Hpta and bpy in benzene were carried out, and the plots of $\log D/D_0$ against $\log [\overline{\text{bpy}}]$ are shown in Fig. 5. The plot for each RE(III) gives a straight line with a slope of unity, and it suggests that the single mixed ligand complex, $\text{RE(pta)}_3\text{bpy}$, is formed. The extraction constants and the adduct formation constants are calculated and listed in Table I.

Extraction with Hba and Synergic Extraction with Hba and bpy

The extraction of La(III) with 10^{-2} M Hba in benzene was carried out, but the percentage extraction of La(III) was less than 3% even at pH 10. The total radioactivity in the aqueous and organic phases at pH 8–10 was less than 6% of the initial radioactivity of labelled La(III) added before shaking. This means that a large part of the La(III) was lost by the hydrolysis of La(III) in the aqueous phase at such a high pH range. Thus, in order to prevent the hydrolysis of RE(III), the extraction study with Hba was carried out in the presence of citrate. The

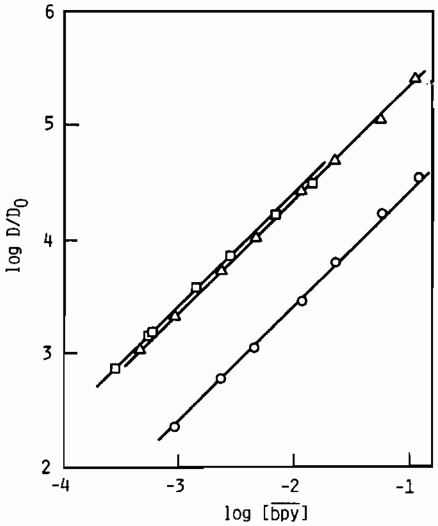

Fig. 5. Effect of the concentration of bpy in the organic phase on the synergic extraction of RE(III) with Hpta. $[\mathrm{Hpta}]_{\mathrm{init}} = 10^{-3}$ M. ○: La, pH 6.2, △: Sm, pH 5.0, □: Lu, pH 4.5.

distribution ratio of RE(III), denoted by M^{3+}, with Hba, HA, in the presence of citrate, C^{3-}, may be represented as

$$D_0 = \frac{[\overline{MA_3}]}{[M^{3+}] + \Sigma[MA_n{}^{3-n}] + \Sigma[MC_y{}^{3-3y}]}$$

$$= \frac{P_M\beta_3[A^-]^3}{1 + \Sigma\beta_n[A^-]^n + \Sigma\beta_{C,y}[C^{3-}]^y} \qquad (9)$$

where $\beta_{C,y}$ denotes the formation constant of $MC_y{}^{3-3y}$. When a neutral ligand, S, is added, the distribution ratio of M^{3+} is written as

$$D = \frac{[\overline{MA_3}] + \Sigma[\overline{MA_3S_m}]}{[M^{3+}] + \Sigma[MA_n{}^{3-n}] + \Sigma[MC_y{}^{3-3y}]}$$

$$= \frac{P_M\beta_3[A^-]^3(1 + \Sigma\beta_{s,m}[\overline{S}]^m)}{1 + \Sigma\beta_n[A^-]^n + \Sigma\beta_{C,y}[C^{3-}]^y} \qquad (10)$$

From both eqns. (9) and (10), we can arrive at the same equation as eqn. (6). Namely, the adduct formation constant can be calculated from the distribution ratio, D_0 and D, at the same concentration of Hba, citrate and hydrogen ions.

The extractions of La(III), Sm(III), Tb(III) and Lu(III) with Hba in the absence or the presence of bpy in benzene were carried out. The plots of log D/D_0 against log $[\overline{\mathrm{bpy}}]$ are shown in Fig. 6. The plot for each RE(III) gives a straight line with a slope of unity. It suggests that a single adduct, $\mathrm{RE(ba)_3}$-bpy, is formed. An extraction possibility of the mixed ligand complex of RE(III) with bpy and citrate, e.g., RE(citrate)(bpy), might be considered, but no extraction of Lu(III) under similar experimental conditions, *i.e.*, 2×10^{-2} M citrate and pH 9.1, was observed in the absence of Hba. In the lower concentration range of bpy, the plots for Lu(III) are positively deviated from a straight line, because of the extraction of the neutral chelate of $\mathrm{Lu(ba)_3}$ together with $\mathrm{Lu(ba)_3bpy}$. The adduct formation constants are calculated and listed in Table I.

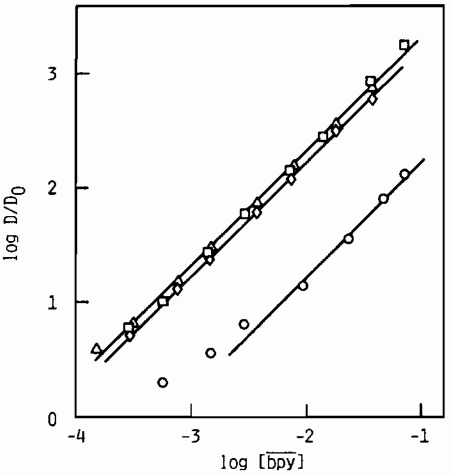

Fig. 6. Effect of the concentration of bpy in the organic phase on the synergic extraction of RE(III) with Hba in the presence of citrate. ◇: La, 2.7×10^{-2} M Hba, 2×10^{-3} M citrate, pH 9.3. △: Sm, 2.7×10^{-2} M Hba, 2×10^{-3} M citrate, pH 8.7. □: Tb, 2×10^{-2} M Hba, 1×10^{-2} M citrate, pH 9.0. ○: Lu, 2×10^{-2} M Hba, 2×10^{-2} M citrate, pH 9.1.

Synergic Extraction with Hacac and bpy

The extraction of some RE(III)s with Hacac in benzene has been reported previously [3, 6], in which the formation of the successive chelates $\mathrm{RE(acac)^{2+}}$, $\mathrm{RE(acac)_2{}^+}$, $\mathrm{RE(acac)_3}$ and $\mathrm{RE(acac)^{4-}}$ in the aqueous phase cannot be neglected. In the present paper, the synergic extraction of La(III) and Tm(III) with Hacac and bpy in benzene is reported. The plots of log D/D_0 against log $[\overline{\mathrm{bpy}}]$ are shown in Fig. 7. In the higher concentration range of bpy, the plots give straight lines with a slope of unity. It suggests that a single adduct, $\mathrm{RE(acac)_3}$-bpy, is formed. The adduct formation constants are calculated and listed in Table I.

Comparison of K_{ex}

The extraction constants in the RE(III)–Hhfa and in RE(III)–Hpta systems were determined experimentally, but a reliable value in the Hba system can not be obtained in the presence of an auxiliary complexing agent such as citrate ion. In the RE(III)–Hacac system, a reliable extraction constant

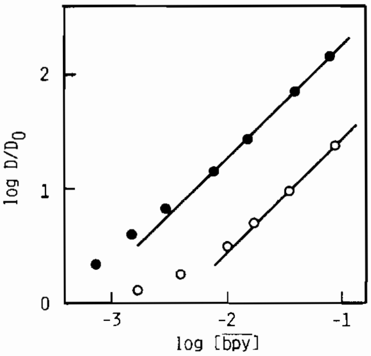

Fig. 7. Effect of the concentration of bpy in the organic phase on the synergic extraction of RE(III) with Hacac. $[\text{Hacac}]_{\text{init}} = 10^{-1}$ M, ●: La, pH 8.5, ○: Tm, pH 6.5.

can not be obtained by a simple extraction technique because of the competitive formation of the successive chelates in the aqueous phase. The extraction constant shown as eqn. (2), however, can be evaluated using the experimental values of P_M and the quoted values of K_{HA}, P_{HA} and β_3; *i.e.*, log P_M = −2.17(La), −2.12(Nd), −1.89(Sm), −1.60(Tb), −0.63(Tm), −0.32(Lu) [6], log K_{HA} = −8.88 [13], log P_{HA} = 0.74 [14], and log β_3 = 10.91(La), 12.60(Nd), 12.95(Sm), 14.04(Tb), 14.29(Tm), 14.68(Lu) [15], hence log K_{ex} = −20.12(La), −18.38(Nd), −17.80(Sm), −16.42(Tb), −15.20(Tm), −14.50(Lu).

The values of K_{ex} are plotted in the order of the atomic number of RE in Fig. 8. For a series of chelating extractants, the K_{ex} values for given RE(III) elements with different β-diketones vary greatly and increase in the order of Hacac < Hpta < Hhfa.

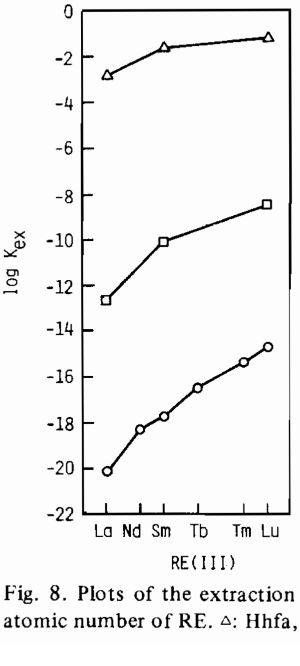

Fig. 8. Plots of the extraction constants in the order of the atomic number of RE. △: Hhfa, □: Hpta, ○: Hacac.

The K_{ex} tends to increase with increasing atomic numbers of RE in every β-diketone system. In eqn. (2), the term of (K_{HA}/P_{HA}) is constant for the same β-diketone, so that the trend of β_3 and P_M must be considered. It is easily expected that the values of β_3 increase with increasing atomic numbers of RE. In a previous paper, it was observed that the P_M for various RE(acac)_3 chelates into benzene increases with increasing atomic numbers of RE [6]. The tendency of P_M for a series of rare earth chelates with Hpta and Hhfa is probably similar to that of chelates with Hacac. Therefore, the increase of K_{ex} may be positively attributed to both β_3 and P_M.

Comparison of β_s

The plots of the adduct formation constant for $\text{RE(A)}_3\text{bpy}$ against the atomic number of RE are shown in Fig. 9. The values of $\beta_{s,1}$ for given RE elements with different β-diketones increase in the order of following acidic chelating agents: Hacac < Hba < Hpta < Hhfa. This order is the same as that of K_{HA}, and may be the reverse of the stability constants of the metal chelate RE(A)_3 with these chelating agents. These trends are commonly observed in synergic extraction involving the unidentate neutral ligand; that is, the order of $\beta_{s,1}$ in Cu(II), Zn(II)–Hhfa, Htfa, Hacac–topo, tbp systems is Hacac < Htfa < Hhfa [16], where Htfa denotes trifluoroacetylacetone. However, there is no large difference in $\beta_{s,1}$ for Hhfa and Hpta. This is an unexpected result, considering the large difference in K_{HA} of Hhfa and Hpta. For strict discussion, we have to compare the thermodynamic formation constants instead of the apparent adduct formation constant determined experimentally. The thermodynamic adduct formation constant, β_s^0, is related to the apparent one as follows:

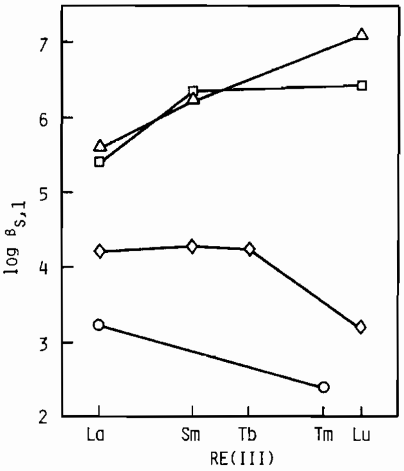

Fig. 9. Plots of the adduct formation constants in the order of the atomic number of RE. △: Hhfa, □: Hpta, ◇: Hba, ○: Hacac.

$$\beta_s{}^0 = \frac{X_{MS}}{X_M X_S} \times \frac{\gamma_{MS}}{\gamma_M \gamma_S} = \beta_s{}^x \times \frac{\gamma_{MS}}{\gamma_M \gamma_S} \tag{14}$$

where $\beta_s{}^x$ denotes the adduct formation constant expressed in mole fraction, γ denotes the activity coefficient, and the subscripts MS, M and S are the adduct, chelate and neutral ligand, respectively. The activity coefficient of a nonelectrolyte solute, γ_c, can be expressed based on regular solution theory [3, 4] as

$$\ln \gamma_{c,o} = \frac{V_c}{RT}(\delta_c - \delta_o)^2 \tag{15}$$

where V and δ are the molar volume and the solubility parameter, respectively. No reliable data for the solubility parameter of the metal chelate with Hhfa and Hpta, δ_M, are available, but δ_M for Hhfa containing the trifluoromethyl groups may be smaller than that for Hpta, by analogy with the solubility parameters of the chelating agents δ_{HA}, which are 10.6 $cal^{1/2}$ $cm^{-3/2}$ for Hacac and 9.6 $cal^{1/2}$ $cm^{-3/2}$ for Htfa [14]. The molar volume of the chelate of Hhfa (molecular weight 208.1) seems to be nearly equal to that of Hpta (molecular weight 196.2). Hence, the γ_M for Hhfa will be smaller than that for Hpta, as expected from eqn. (15), and the term of the activity coefficients in eqn. (14) for Hhfa larger than that for Hpta. This means that the thermodynamic adduct formation constant of the system involving Hhfa is larger than that of the system involving Hpta, even though the apparent β_s for Hhfa and Hpta seems to be nearly equal in Fig. 9.

The relation of β_s to the atomic number of RE is different with different acidic chelating agents (Fig. 9). In Hacac and Hba systems, the β_s of the larger atomic number of RE shows smaller values, but this is not the case in Hpta and Hhfa systems. It has often been reported that the synergic enhancement is smaller for RE of larger atomic number [17]. However, this simple conclusion has been derived from the synergic extraction systems involving the unidentate neutral ligands, but not the bidentate ones. In the present work, the larger synergic enhancement for RE with higher atomic number is clearly observed in the system of the bidentate ligand and a selected chelating agent, Hpta or Hhfa. It has been generally believed that synergic extraction improves the extraction efficiency greatly, but makes the separation of metals worse, in contrast to the extraction with acidic extractants only. In conclusion, the K_{ex} and β_s increase with increasing atomic numbers of RE in Hpta–bpy and Hhfa–bpy systems, and a new possibility for improving the separation efficiency of rare earth elements by synergic extraction is demonstrated.

Acknowledgement

The authors thank Dr. H. Imura for his encouraging interest and for many discussions.

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