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Solvent Extraction of Europium(III) Anionic Complexes with Several β-Diketones as Ion-Pairs with Tetrabutylammonium into Chloroform

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The solvent extractions of europium(III) in 0.1 mol dm^{-3} sodium nitrate solutions with acetylacetone (Hacac), benzoylacetone (Hbza), benzoyltrifluoroacetone (Hbfa), trifluoroacetylacetone (Htfa), and hexafluoroacetylacetone (Hhfa) into chloroform were measured in both the absence and presence of tetrabutylammonium (tba$^+$). From the results and those with 2-thenoyltrifluoroacetone (Htta) in a previous study it was concluded that extractions with the CF$_3$– containing β-diketones, Hbfa, Htfa, Hhfa, and Htta are greatly enhanced by the addition of tba$^+$. This could be explained in terms of the extraction of a ternary complex, EuA_4^- tba$^+$ (A^- is a β-diketonate ion). However, extractions with Hacac and Hbza were nearly the same when tba$^+$ was added. The enhancement of extraction was statistically treated by assuming an association of EuA_3 and A^-tba$^+$ in the organic phase. The equilibrium constants for an association with different β-diketones were compared, and the reasons for the difference in the association equilibrium as well as the enhancement of extraction are described.

In previous studies,[1—4] the solvent extraction of europium(III) with benzoylacetone (Hbza, 1-phenyl-1,3-butanedione), benzoyltrifluoroacetone (Hbfa, 1-phenyl-4,4,4-trifluoro-1,3-butanedione), and 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione) in the absence and presence of quarternary ammoniums (base$^+$) was studied. It was found that extraction with Hbfa and Htta was greatly enhanced by the addition of a quarternary ammonium, and that this could be explained in terms of extraction of the anionic complex, EuA_4^-base$^+$, in addition to the neutral complex, EuA_3 (where A^- is the β-diketonate ion). In these studies, the extraction equilibrium of the ternary complex is treated both as the extraction of EuA_4^- with the base$^+$ in the aqueous phase and as an association of the EuA_3 with the ion-pairs, A^-base$^+$, in the organic phase. Furthermore, a similarity in the association equilibrium of a neutral complex with an ion-pair and that with neutral ligand molecules, such as tributylphosphate (TBP) in the organic phase in synergistic extraction systems, was pointed out. Since such a synergistic enhancement of the extraction of trivalent lanthanoids with a β-diketone and a certain given neutral ligand is different when the β-diketone is different,[5] it is also assumed that the association of a neutral complex with extracted ion-pairs of the reagents is probably different when the β-diketone is different. It has already been reported that extraction with Hbfa into carbon tetrachloride was greatly enhanced by the addition of tetrabutylammonium (tba$^+$), but that with Hbza it was not enhanced by the same cation under similar experimental conditions.[1] Such a difference in the extractability of the ternary complex when the β-diketone was different was reported for cobalt(II), nickel(II), and zinc(II).[6—8] It was pointed out that the enhancement in the extraction of these metal ions in the presence of tba$^+$ was negligible with acetylacetone (Hacac, 2,4-pentanedione) or Hbza, but was very marked with Hbfa, Htta, trifluoroacetylacetone (Htfa, 1,1,1-trifluoro-2,4-pentanedione), and hexafluoroacetylacetone (Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione).

In the present study, the difference in the enhancement of extraction of europium(III) with six β-diketones by additions of tba$^+$ was investigated. The β-diketones were Hacac, Hbza, Hbfa, Htta, Htfa, and Hhfa. Chloroform was chosen as the solvent in order to compare the results with those of a synergistic enhancement in the same diluent in a previous study.[5]

Statistical

In the present paper, all chemical species in the organic phase are denoted by the subscript "org", and that in the aqueous phase are shown without a subscript. The volumes of the two liquid phases are assumed to be the same. Since most of the statistical treatments were similar to those described in previous paper,[1—4] only the main equations, as well as those which were not previously given, are presented in the present paper.

With the chelating extractant, the following equations can be written:

$$HA \rightleftharpoons HA_{(org)};\; K_d = [HA]_{org}[HA]^{-1}, \qquad (1)$$

$$HA \rightleftharpoons H^+ + A^-;\; K_a = [H^+][A^-][HA]^{-1}, \qquad (2)$$

and

$$[A^-] = [HA]_{initial}/\{1 + (K_d + 1)[H^+]K_a^{-1}\}. \qquad (3)$$

The equilibrium for the extraction of europium(III) with HA in the absence and presence of tba$^+$ can be written as:

$$Eu^{3+} + 3A^- \rightleftharpoons EuA_{3(org)};$$

$$K_{ex3,0} = [EuA_3]_{org}[Eu^{3+}]^{-1}[A^-]^{-3} \qquad (4)$$

$$Eu^{3+} + 4A^- + tba^+ \rightleftharpoons EuA_4^- tba^+_{(org)};$$

$$K_{\mathrm{ex4,1}} = [\mathrm{EuA_4^-tba^+}]_{\mathrm{org}}[\mathrm{Eu^{3+}}]^{-1}[\mathrm{A^-}]^{-4}[\mathrm{tba^+}]^{-1}. \quad (5)$$

For the extraction of the ion-pairs, $\mathrm{EuA_4^-tba^+}$, the following equations can be written:

$$\mathrm{EuA_{3(org)}} + \mathrm{A^-tba^+_{(org)}} \rightleftharpoons \mathrm{EuA_4^-tba^+_{(org)}};$$

$$K_{\mathrm{org}} = [\mathrm{EuA_4^-tba^+}]_{\mathrm{org}}[\mathrm{EuA_3}]_{\mathrm{org}}^{-1}[\mathrm{A^-tba^+}]_{\mathrm{org}}^{-1}. \quad (6)$$

For the extraction of $\mathrm{A^-}$ and the anion of background salt, $\mathrm{X^-}$, as ion-pair with $\mathrm{tba^+}$, the following equations can be written:

$$\mathrm{A^-} + \mathrm{tba^+} \rightleftharpoons \mathrm{A^-tba^+_{(org)}};$$

$$K_{\mathrm{exAB}} = [\mathrm{A^-tba^+}]_{\mathrm{org}}[\mathrm{A^-}]^{-1}[\mathrm{tba^+}]^{-1} \quad (7)$$

$$\mathrm{X^-} + \mathrm{tba^+} \rightleftharpoons \mathrm{X^-tba^+_{(org)}};$$

$$K_{\mathrm{exXB}} = [\mathrm{X^-tba^+}]_{\mathrm{org}}[\mathrm{X^-}]^{-1}[\mathrm{tba^+}]^{-1}. \quad (8)$$

In the absence of the metal ions, the distribution ratio of the $\mathrm{tba^+}$, D_{tba}, can be introduced from Eqs. 7 and 8 as

$$\begin{aligned} D_{\mathrm{tba}} &= [\mathrm{tba^+}]_{\mathrm{org,total}}/[\mathrm{tba^+}] \\ &= ([\mathrm{A^-tba^+}]_{\mathrm{org}} + [\mathrm{X^-tba^+}]_{\mathrm{org}})/[\mathrm{tba^+}] \\ &= K_{\mathrm{exAB}}[\mathrm{A^-}] + K_{\mathrm{exXB}}[\mathrm{X^-}]. \quad (9) \end{aligned}$$

The distribution ratio of europium(III) extracted with $\mathrm{A^-}$ in the absence (D_0) and presence (D) of $\mathrm{tba^+}$ can be written as follows:

$$\begin{aligned} D_0 &= [\mathrm{EuA_3}]_{\mathrm{org}}/([\mathrm{Eu^{3+}}] + [\mathrm{EuA^{2+}}] + [\mathrm{EuA_2^+}] + \cdots) \quad (10) \\ &= K_{\mathrm{ex3,0}}[\mathrm{A^-}]^3/(1 + \beta_1[\mathrm{A^-}] + \beta_2[\mathrm{A^-}]^2 + \cdots), \quad (11) \end{aligned}$$

$$\begin{aligned} D &= ([\mathrm{EuA_3}]_{\mathrm{org}} + [\mathrm{EuA_4^-tba^+}]_{\mathrm{org}}) \\ &\quad /([\mathrm{Eu^{3+}}] + [\mathrm{EuA^{2+}}] + [\mathrm{EuA_2^+}] + \cdots) \quad (12) \\ &= (K_{\mathrm{ex3,0}}[\mathrm{A^-}]^3 + K_{\mathrm{ex4,1}}[\mathrm{A^-}]^4[\mathrm{tba^+}]) \\ &\quad /(1 + \beta_1[\mathrm{A^-}] + \beta_2[\mathrm{A^-}]^2 + \cdots), \quad (13) \end{aligned}$$

where β_n is the stability constant,

$$\beta_n = [\mathrm{EuA}_n^{3-n}][\mathrm{Eu^{3+}}]^{-1}[\mathrm{A^-}]^{-n}.$$

When the concentration of $\mathrm{A^-}$ in the aqueous phase is identical, the following equations can be introduced from Eqs. 4, 5, 6, 7, 11, and 13:

$$\begin{aligned} D/D_0 &= 1 + K_{\mathrm{ex4,1}}K_{\mathrm{ex3,0}}^{-1}[\mathrm{A^-}][\mathrm{tba^+}] \quad (14) \\ &= 1 + K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A^-}][\mathrm{tba^+}] \quad (15) \end{aligned}$$

In the presence of $\mathrm{tba^+}$, its free concentration can be written as follows:

$$\begin{aligned} [\mathrm{tba^+}]_{\mathrm{initial}} &= [\mathrm{tba^+}] + [\mathrm{EuA_4^-tba^+}]_{\mathrm{org}} \\ &\quad + [\mathrm{A^-tba^+}]_{\mathrm{org}} + [\mathrm{X^-tba^+}]_{\mathrm{org}} \quad (16) \end{aligned}$$

$$\begin{aligned} [\mathrm{tba^+}] &= ([\mathrm{tba^+}]_{\mathrm{initial}} - [\mathrm{EuA_4^-tba^+}]_{\mathrm{org}}) \\ &\quad /(1 + K_{\mathrm{exAB}}[\mathrm{A^-}] + K_{\mathrm{exAB}}[\mathrm{X^-}]). \quad (17) \end{aligned}$$

The synergistic extraction of europium(III) with the chelating extractant and a neutral ligand, L, can be written when the concentration of $\mathrm{A^-}$ in the aqueous phase is identical as follows:

$$\begin{aligned} D &= ([\mathrm{EuA_3}]_{\mathrm{org}} + [\mathrm{EuA_3L}]_{\mathrm{org}} + [\mathrm{EuA_3L_2}]_{\mathrm{org}} + \cdots) \\ &\quad /([\mathrm{Eu^{3+}}] + [\mathrm{EuA^{2+}}] + [\mathrm{EuA_2^+}] + \cdots), \quad (18) \end{aligned}$$

$$\mathrm{EuA_{3(org)}} + n\mathrm{L_{(org)}} \rightleftharpoons \mathrm{EuA_3L}_{n\mathrm{(org)}};$$

$$\beta_{(\mathrm{org})n} = [\mathrm{EuA_3L}_n]_{\mathrm{org}}[\mathrm{EuA_3}]_{\mathrm{org}}^{-1}[\mathrm{L}]_{\mathrm{org}}^{-n}, \quad (19)$$

$$D/D_0 = 1 + \beta_{(\mathrm{org})1}[\mathrm{L}]_{\mathrm{org}} + \beta_{(\mathrm{org})2}[\mathrm{L}]_{\mathrm{org}}^2 + \cdots. \quad (20)$$

Experimental

All of the reagents and the experimental procedures were similar to those used in previous studies,[1—4] except that acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone were used as well as benzoylacetone and benzoyltrifluoroacetylacetone. The acetylacetone was obtained from Dojindo Laboratories. The benzoylacetone, benzoyltrifluoroacetone, trifluoroacetylacetone, and hexafluoroacetylacetone were obtained from Tokyo Kasei Co. The water contents in the β-diketones and tetrabutylammonium chloride were determined by Karl Fischer's titration method.

Results

The equilibrium constant for the solvent extraction of a β-diketonate ion with $\mathrm{tba^+}$, K_{exAB} in Eq. 7, was determined when the aqueous phase was 0.1 mol dm^{-3} sodium chloride. This background salt was chosen because the extraction of the $\mathrm{NO_3^-tba^+}$ ion-pairs was much better than the $\mathrm{Cl^-tba^+}$ ion-pairs, as can be seen from the following constants[3] and the extracted $\mathrm{NO_3^-tba^+}$ interfered from a determination of the $\mathrm{A^-tba^+}$ ion-pairs:

$$K_{\mathrm{exXB}} = [\mathrm{NO_3^-tba^+}]_{\mathrm{org}}[\mathrm{tba^+}]^{-1}[\mathrm{NO_3^-}]^{-1} = 10^{1.3}$$

and

$$K_{\mathrm{exXB}} = [\mathrm{Cl^-tba^+}]_{\mathrm{org}}[\mathrm{tba^+}]^{-1}[\mathrm{Cl^-}]^{-1} = 10^{0.1}.$$

The difference in the K_{exAB} when the aqueous phase was 0.1 mol dm^{-3} sodium nitrate and sodium chloride was negligible with Htta.[3,4] It is thus assumed that the values of K_{exAB} obtained when the aqueous phase was 0.1 mol dm^{-3} sodium chloride could be used for an analysis of the extraction data of europium(III) from 0.1 mol dm^{-3} sodium nitrate in the present study.

Figure 1 gives the distribution ratio of $\mathrm{tba^+}$ in Eq. 9, determined as a function of the concentration of the β-diketonate ion. As can be seen from Fig. 1, the extraction of ion-pairs, $\mathrm{acac^-tba^+}$, is negligible: The extraction of $\mathrm{tba^+}$ in this system is due to $\mathrm{Cl^-tba^+}$. The small decrease in $\log D_{\mathrm{tba}}$ in the highest $\mathrm{acac^-}$ concentration range was concluded to be due to that by a replacement of the $\mathrm{Cl^-}$ by $\mathrm{OH^-}$ in this region: The extraction of $\mathrm{OH^-tba^+}$ is inferior to that of $\mathrm{Cl^-tba^+}$. The extraction of $\mathrm{bza^-tba^+}$ ion-pairs into chloroform

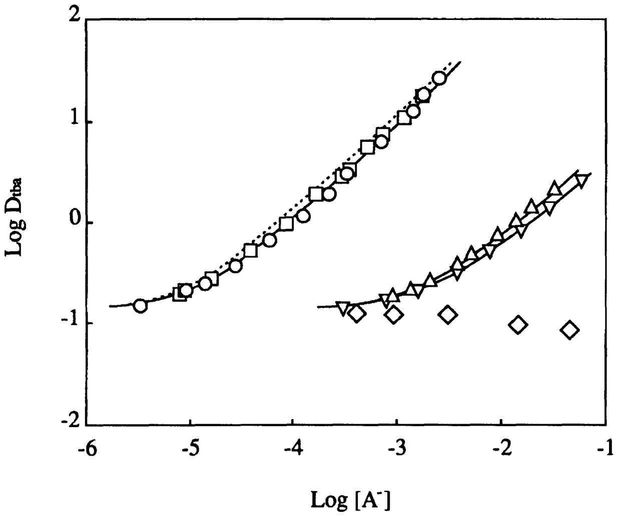

Fig. 1. Distribution ratio of tetrabutylammonium ions as a function of the concentration of dissociated β-diketonate anions.
Aq phase: 0.1 mol dm^{-3} sodium chloride solution initially containing 1×10^{-3} mol dm^{-3} tba$^+$.
Org. phase: chloroform initially containing 1×10^{-2} or 0.1 mol dm^{-3} of Hacac (◇), Hbza (▽), Hbfa (○), Htfa (△), and Hhfa (□).
The dotted line gives the results when β-diketone is Htta in Ref. 3. The lines are calculated by Eq. 9, using the values given in Table 1.

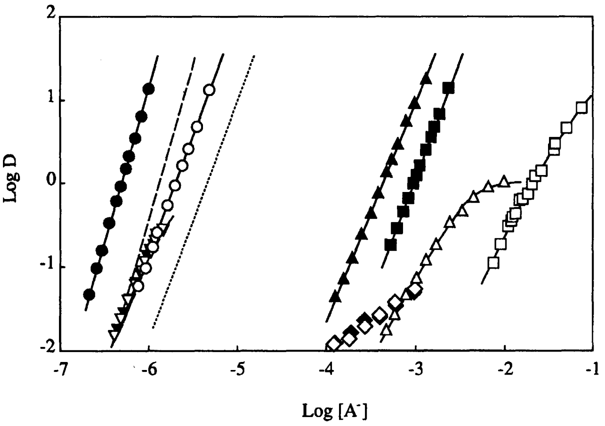

Fig. 2. Distribution ratio of europium(III) as a function of the concentration of dissociated β-diketonate anions.
Aq phase: 0.1 mol dm^{-3} sodium nitrate solution containing no tetrabutylammonium ions (open symbols) and 1×10^{-3} mol dm^{-3} tetrabutylammonium ions at initial (closed symbols).
Org. phase: chloroform containing 0.1 mol dm^{-3} H-acac (◇,◆), Hbza (▽,▼), Hbfa (○,●), Htfa (△,▲), and Hhfa (□,■).
The dotted and broken lines are plots, respectively, in the absence and presence of tba$^+$, when the β-diketone is Htta in Ref. 3. The lines are calculated by Eqs. 11 and 13 by using the values given in Table 1.

is measurable in the highest bza$^-$ concentration region, though it was negligible when the solvent was carbon tetrachloride.[1)] It can also be seen from Fig. 1 that the extraction of tba$^+$ with bfa$^-$, tta$^-$, and hfa$^-$ is rather similar to each other, and that with bza$^-$ is also rather similar with that with tfa$^-$. The values of K_{exAB} obtained from these data are listed in Table 1. The extraction curves in Fig. 1 were calculated using Eq. 9, which introduced the values of K_{exAB} in Table 1 and the K_{exXB} given above. The data with Htta are taken from Ref. 3

The extraction curves of europium(III) with 0.1 mol dm^{-3} of one of the β-diketones (at initial) in the organic phase in the absence (open symbols) and presence (closed symbols) of 1×10^{-3} mol dm^{-3} (at initial) tba$^+$ are given in Fig. 2. A plot when the β-diketone was Htta in Ref. 3 is also given in Fig. 2. A statistical analysis of the data in the absence and presence of tba$^+$ was carried out on the basis of Eqs. 11 and 13. It was concluded from the analysis that the first, second, and third complexes, EuA^{2+}, EuA$_2^+$, and EuA$_3$, should be taken into account with some β-diketones. The values of the stability constants, β_1, β_2, and β_3, and extraction constant, $K_{\mathrm{ex3,0}}$ in Eq. 4 and $K_{\mathrm{ex4,1}}$ in Eq. 5, were calculated by using a least-squares computer program. The values are listed in Table 1. Each solid line in Fig. 2 was calculated on the basis of Eq. 13 by using the values given in Table 1. From these data, the formation constant of the EuA$_4^-$tba$^+$ species from the EuA$_3$ species in the organic phase, K_{org} in Eq. 6, was also calculated. The obtained values are listed in Table 1. As can be seen from Fig. 2, extraction with Hacac and Hbza was not affected by the addition of 1×10^{-3} mol dm^{-3} of tba$^+$. However, the extraction of europium(III) with the β-diketone with one or two CF$_3$– groups is very much enhanced by the addition of tba$^+$. Since the free concentration of tba$^+$ is very much different in each extraction system at different concentrations of A$^-$, a direct comparison of these experimental data is difficult.

Discussion

As can be seen from Fig. 2, the enhancement in the extraction by the addition of 1×10^{-3} mol dm^{-3} (at initial) tba$^+$, is very much different when the extractant is different. However, as was pointed out,[2)] this difference is very much affected by the concentration of dissociated β-diketonate ions in the aqueous phase, A$^-$. The enhancement of extraction in Fig. 2 is largest with Hhfa; that with Htta is much smaller than Hhfa, and the degree of enhancement is not very much different between Hbfa and Htfa.

Extraction by the β-Diketones Containing No CF$_3$– Group. As can be seen from Table 1, the association constant of the EuA$_3$ complex with the A$^-$tba$^+$ ion-pairs in the organic phase, K_{org}, is not very much different among Hbfa, Htta, Htfa, and Hhfa, although no association was found with Hacac and Hbza. Such a

Table 1. Equilibrium Constants for Solvent Extraction of Europium(III) with β-Diketones in the Absence and Presence of Tetrabutylammonium Ions
Org. phase: chloroform containing 0.1 mol dm^{-3} of one of these β-diketones.
Aq phase: 0.1 mol dm^{-3} sodium nitrate solution (when K_{exAB} is determined 0.1 mol dm^{-3} sodium chloride solution).

	log $K_a^{a)}$	log $K_d^{a)}$	log $K_{ex3,0}$	log $K_{ex4,1}$	log β_1	log β_2	log β_3	log K_{org}	log K_{exAB}
Hacac	−8.67	1.36	—c)	—c)	—c)	—c)	—c)	—c)	—c)
Hbza	−8.39	1.64	17.5	—c)	3.4	11.6	—d)	—c)	1.7
Hbfa	−6.03	2.84	17.1	28.7	4.6	—d)	—d)	7.6	4.0
Htta	−6.33	1.85	16.1b)	27.1b)	4.5b)	—d)	—d)	6.9b)	4.1b)
Htfa	−6.13	0.27	9.8	18.5	4.9	6.9	9.6	6.9	1.8
Hhfa	−4.46	−1.75	5.4	16.2	1.1	3.4	—d)	6.8	4.0

a) Taken from Ref. 10 but the aqueous phase in this previous study was 0.1 mol dm^{-3} $NaClO_4$. b) Taken from Ref. 3. c) Can not be determined. d) No evidence for the second complex, EuA_2^+, or the third complex, EuA_3, in the aqueous phase.

smaller effect on the extractions with Hacac and Hbza was also found in the adduct formation of these β-diketones of europium(III) with neutral ligand molecules, such as tributylphosphate (TBP) in the organic phase in a previous paper.5) The equilibrium constants for the adduct formation of these β-diketonate complexes with TBP in this previous paper are summarized in Table 2. In this previous paper, it was mentioned that the europium(III) complexes with Hbfa, Htta, and Htfa in chloroform formed stable adducts with one or two molecules of TBP, and that the formation constant of the EuA_3TBP, $\beta_{(org)1}$, and of the $EuA_3(TBP)_2$, $\beta_{(org)2}$, in Eq. 19, are somewhat similar to those three β-diketones. However, europium(III) complexes with Hacac and Hbza formed an adduct with only one TBP molecule, and the formation constant of the EuA_3TBP is much smaller than the other β-diketones. As already described, the negligible enhancement of the extraction with Hbza into carbon tetrachloride by an addition of tba^+ can be explained in terms of the very poor extraction of the bza^-tba^+ ion-pairs.1) It was also assumed from this synergistic enhancement that the association constant, K_{org}, should not be very large with the Eu(bza)$_3$ complex with bza^-, as well as with the Eu(acac)$_3$ complex with $acac^-$.

Extraction by the β-Diketones Containing One CF_3- Group. The smaller value of the slope of the extraction curve with Hacac and Htfa in the absence of tba^+ is caused by the formation of complexes with the extractant in the aqueous phase. This is due to the fact that the liquid–liquid distribution constant of the reagent, K_d, and that of the complex, K_{dm}, with these two reagents are lower than those with the other β-diketones. It can be assumed that the value of the stability constant of the complex in the aqueous phase, β_1, and that of formation constant of the anionic complex in the organic phase, K_{org}, may not be different from Hbfa, Htta, and Htfa. This is because the pK_a of these reagents are similar, and the structures of the complexes are also similar. As can be seen from Fig. 2, Htfa is not an effective extractant for europium(III), but it is a good extractant when tba^+ is added. This is quite similar to the fact that a chelating extractant could be an effective extractant in the presence of a neutral ligand, which causes a synergistic effect.9) Since the Eu(tfa)$_3$ should be much less extractable than the Eu(bfa)$_3$ and Eu(tta)$_3$, a much higher extractant anion concentration is necessary for extraction with Htfa than with Hbfa and Htta. As was pointed out,2) extraction at a higher extractant anion concentration should be more favorable for the extraction of a ternary complex. As can be seen from Eq. 15, the enhancement of extraction is dependent on the quantity $[A^-][tba^+]$; it can be seen from Eqs. 1, 2, and 3 that when the initial acid concentration is the same, the pH in the aqueous phase is the same, and that the values of the acid dissociation constant, pK_a, are similar, the concentration of the β-diketonate anion in the aqueous phase is higher if the two-phase distribution constant of the acid, K_d, is lower. Thus, among such β-diketones, the value of $[A^-][tba^+]$, which is essential for the formation of the $EuA_4^-tba^+$ species, is higher under otherwise similar conditions when K_d is higher. From this standpoint, tfa^- should be favorable, since the value of K_{org} is not very much different from these three CF_3- containing β-diketones. As can be seen from Eq. 15, the enhancement is dependent on the value of K_{exAB}; and as can be

Table 2. Formation Constants of the Adducts of Europium(III) β-Diketonates with TBP Taken from Ref. 5

	log $\beta_{(org)1}$	log $\beta_{(org)2}$
Hacac	1.9	—a)
Hbaz	1.6	—a)
Hbfa	3.3	5.3
Htta	3.3	5.3
Htfa	3.6	4.6
Hhfa	—b)	—b)

a) No evidence of the second adduct EuA_3L_2 is observed.
b) Not determined.

seen from Table 1, the K_{exAB} of tfa^- is more than two orders lower than that of bfa^- or tta^-. Thus, although extraction at a higher concentration of A^- is favorable for a ternary complex, a lower K_{exAB} is unfavorable for the ternary complex: The overall effect of these two causes a relatevely small difference in the enhancement of extraction with these three β-diketones, as can be seen from Fig. 2. The addition of tba^+ enhances the extraction with Htfa very markedly. This is because the upper limit of the extraction is given by K_{dm} in the following equation:

$$K_{\text{dm}} = [\text{EuA}_3]_{\text{org}}[\text{EuA}_3]^{-1} \tag{21}$$

$$= K_{\text{ex3,0}}\beta_3^{-1}. \tag{22}$$

The value of K_{dm} for the Eu(tfa)_3 is assumed to be $10^{0.2}$. However, by extracting the ternary complex, the maximum extraction can be greatly enhanced, as can be seen from Eq. 15. This is because the ternary complex, $\text{Eu(tfa)}_4^-\text{tba}^+$, is much bulkier than the Eu(tfa)_3 complex.

Extraction by the β-Diketones Containing Two CF_3– Groups. The largest enhancement of extraction by the addition of tba^+ in Fig. 2 occurs with Hhfa. However, this is an apparent effect. This is due to the fact that extraction with Hhfa takes place in the highest A^- concentration region. As it can be seen from Eq. 15, a larger enhancement occurs in the higher A^- concentration region when the free concentration of tba^+ is similar and the association constant, K_{org}, is similar.

The association constant of TBP or trioctylphosphine oxide (TOPO) on the hfa^- complexes with some metal ions is much higher than that on the bfa^- complexes or tta^- complexes in the organic phase.[11] The association constant of the Eu(hfa)_3 complex with hfa^-tba^+ ion-pairs in the organic phase is, however, similar to that of Eu(tta)_3 complex with tta^-tba^+ ion-pairs, and is even somewhat lower than that of the Eu(bfa)_3 complex with bfa^-tba^+ ion-pairs. The values of K_{org} in Table 1 show that the higher enhancement of the Hhfa extraction by an addition of 1×10^{-3} mol dm^{-3} (at initial) tba^+ is not because the Eu(hfa)_3 complex is a very good acceptor of additional ligands in the organic phase than the other complexes. This is different from observations with a synergistic enhancement. One explanation for this may be as follows. Although Eu(hfa)_3 would be a good acceptor of a further coordination with such a ligand as TBP or TOPO than the Eu(bfa)_3 or Eu(tta)_3, the hfa^- ion should be a less effective donor than the bfa^- or tta^- ion, as it can be assumed from the lower stability constants of metal hfa^- complexes in the aqueous phase than those with metal bfa^- and tta^- complexes of the some metal ions.[6,7] The property as a better acceptor of Eu(hfa)_3 than Eu(bfa)_3 or Eu(tta)_3 can only be seen with a certain donor, such as TBP or TOPO. However, when the ability as a donor of hfa^-tba^+ is much weaker than the bfa^-tba^+ or tta^-tba^+, this favorable property for the association should be canceled out by the unfavorable property, the anion is a less effective donor. Thus, these two opposite factors cause a much smaller difference in the formation of the higher coordination complex than is observed with a synergistic enhancement.

Conclusion

As can be seen from the above, the extraction of the ternary complex of europium(III) with the β-diketones and tba^+ is very much different when the β-diketone is different, and, as can be seen from a comparison of the ternary complexes with hfa^-tba^+ and with bfa^-tba^+, the enhancement is different from that observed in synergistic extraction systems. Since the formation of the anionic complex of europium(III) in the aqueous phase with these β-diketones cannot be determined, a treatment of the experimental data on the basis of equilibrium of the association of the neutral complex and the ion-pair of the reagents in the organic phase is especially useful.

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