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Solvent Extraction of Europium(III) with Benzoylacetone and Benzoyltrifluoroacetone into Carbon Tetrachloride in the Absence and Presence of Tetrabutylammonium Ions

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The solvent extraction of europium(III) in 0.1 mol dm^{-3} sodium nitrate solutions with benzoylacetone (Hbza) or benzoyltrifluoroacetone (Hbfa) in carbon tetrachloride was measured in the absence and presence of tetrabutylammonium ions (tba$^+$). Although extraction with Hbfa occurred at lower pH than with Hbza, the extraction measured as a function of the β-diketonate ion concentration in the aqueous phase was rather similar. It was also found that extraction with Hbfa was greatly enhanced by the addition of tba$^+$, the effect, however, was negligible with Hbza. The data were analyzed from the stand point that the neutral metal chelate, Eu(bfa)$_3$, was extacted into the organic phase and associated with ion-pairs of the reagents, bfa$^-$tba$^+$, in this phase. It was also found that though extraction of ion-pairs of bfa$^-$ tba$^+$ occurred, that of bza$^-$tba$^+$ was negligible. Thus, the reason for the negligible extraction of the ternary complex, Eu (bza)$_4^-$ tba$^+$, was explained in terms of the negligible extraction of the bza$^-$ tba$^+$, which might associate with Eu(bza)$_3$ in the organic phase.

It was reported in previous papers$^{1-3)}$ that the solvent extraction of cobalt(II), nickel(II), and zinc(II) with β-diketones (denoted HA) containing the CF$_3$– group into carbon tetrachloride was greatly enhanced by the addition of bulky cations, such as tetrabutylammonium ion (tba$^+$). This was explained in terms that in the absence of tba$^+$, only the neutral metal chelate (MA$_2$) was extracted while in its presence; the anionic complex (MA$_3^-$) was also extracted as ion-pairs with the cations (tba$^+$); the extraction of this ion-pair (MA$_3^-$tba$^+$) was much better than that of the neutral complex under identical conditions. It was also pointed out in these previous papers that the solvent extraction of metal ions with acetylacetone and benzoylacetone, which contained no CF$_3$– group, was not affected by the addition of tba$^+$.

In the present work the solvent extraction of europium(III) with benzoylacetone (Hbza, 1-phenyl-1, 3-butanedione) and benzoyltrifluoroacetone (Hbfa, 1-phenyl-4,4,4-trifluoro-1,3-butanedione) into carbon tetrachloride was measured in both the absence and presence of tetrabutylammonium ions. The solvent extraction with Hbza was not affected by tba$^+$, but that with Hbfa was greatly enhanced. By a statistical analysis of the experimental data, it was concluded that the enhancement of extraction with Hbfa was due to the extaction of M(bfa)$_4^-$ tba$^+$; such an extraction of the anionic complex, however, did not occur with Hbza. Furthermore, it was concluded that the reason why no extraction of ion-pairs of the anionic metal complex occurred in the extraction system with Hbza was due to no extraction of the ion-pairs of reagents(bza$^-$tba$^+$); consequently, the addition of this ion-pairs on the M(bza)$_3$ chelate hardly occurred in the organic phase.

Statistical

In the present paper all species in the organic phase are denoted by the subscript "org"; that in the aqueous phase is shown without a subscript. The volume of two liquid phases is assumed to be the same.

The two-phase distribution and acid dissociation equilibrium of HA can be written as follows:

$$\mathrm{HA} \rightleftharpoons \mathrm{HA}_{(\mathrm{org})}\,;\ K_\mathrm{d} = [\mathrm{HA}]_\mathrm{org}[\mathrm{HA}]^{-1} \qquad (1)$$

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

From these equations, the concentration of the extractant anion (A$^-$) can be calculated using

$$[\mathrm{A}^-] = [\mathrm{HA}]_\mathrm{initial} / (1 + (K_\mathrm{d} + 1)[\mathrm{H}^+]\,K_\mathrm{a}^{-1}). \qquad (3)$$

The solvent extraction equilibrium of europium(III), M^{3+}, with a chelating-type extractant in the organic phase can be written as follows:

$$\mathrm{M}^{3+} + 3\mathrm{HA}_{(\mathrm{org})} \rightleftharpoons \mathrm{MA}_{3(\mathrm{org})} + 3\mathrm{H}^+;$$

$$K_{\mathrm{ex}3,0}{}^* = [\mathrm{MA}_3]_\mathrm{org}[\mathrm{H}^+]^3[\mathrm{M}^{3+}]^{-1}[\mathrm{HA}]_\mathrm{org}{}^{-3}. \qquad (4)$$

It can also be written as

$$\mathrm{M}^{3+} + 3\mathrm{A}^- \rightleftharpoons \mathrm{MA}_{3(\mathrm{org})};$$

$$K_{\mathrm{ex}3,0} = [\mathrm{MA}_3]_\mathrm{org}[\mathrm{M}^{3+}]^{-1}[\mathrm{A}^-]^{-3}. \qquad (5)$$

When the anionic chelate (MA$_4^-$) is extracted as ion-pairs with tba$^+$, the equilibrium can be written as follows:

$$\mathrm{M}^{3+} + 4\mathrm{HA}_{(\mathrm{org})} + \mathrm{tba}^+ \rightleftharpoons \mathrm{MA}_4{}^-\mathrm{tba}^+{}_{(\mathrm{org})} + 4\mathrm{H}^+;$$

$$K_{\mathrm{ex}4,1}{}^* = [\mathrm{MA}_4{}^-\mathrm{tba}^+]_\mathrm{org}[\mathrm{H}^+]^4[\mathrm{M}^{3+}]^{-1}[\mathrm{HA}]_\mathrm{org}{}^{-4}[\mathrm{tba}^+]^{-1}. \qquad (6)$$

It can also be written as

$$\mathrm{M}^{3+} + 4\mathrm{A}^- + \mathrm{tba}^+ \rightleftharpoons \mathrm{MA}_4{}^-\mathrm{tba}^+{}_{(\mathrm{org})};$$

$$K_{\mathrm{ex4,1}} = [\mathrm{MA_4^-tba^+}]_{\mathrm{org}}[\mathrm{M^{3+}}]^{-1}[\mathrm{A^-}]^{-4}[\mathrm{tba^+}]^{-1}. \quad (7)$$

However, this extraction equilibrium of ion-pairs can also be given in the form that the extraction of neutral chelate given by Eq. 5 occurs, and addition of the ion-pairs of the reagents ($\mathrm{A^-tba^+}$) on the neutral chelate follows in the organic phase. When the extraction equilibrium is written in this way, the following equations can be used:

$$\mathrm{MA_{3(org)}} + \mathrm{A^-tba^+_{(org)}} \rightleftharpoons \mathrm{MA_4^-tba^+_{(org)}};$$

$$K_{\mathrm{org}} = [\mathrm{MA_4^-tba^+}]_{\mathrm{org}}[\mathrm{MA_3}]_{\mathrm{org}}^{-1}[\mathrm{A^-tba^+}]_{\mathrm{org}}^{-1}. \quad (8)$$

The anions of the chelating extractant ($\mathrm{A^-}$) and the bulky cations ($\mathrm{tba^+}$) should be extracted as ion-pairs ($\mathrm{A^-\,tba^+}$); the following equation can be written for this extraction equilibrium:

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

$$K_{\mathrm{exAB}} = [\mathrm{A^-tba^+}]_{\mathrm{org}}[\mathrm{A^-}]^{-1}[\mathrm{tba^+}]^{-1}. \quad (9)$$

It is possible that $\mathrm{A^-}$ forms complexes in the aqueous phase; the distribution ratio should then be written as follows:

$$D_0 = [\mathrm{MA_3}]_{\mathrm{org}} / ([\mathrm{M^{3+}}] + [\mathrm{MA^{2+}}] + [\mathrm{MA_2^+}] + \cdots) \quad (10)$$

$$= K_{\mathrm{ex3,0}}[\mathrm{A^-}]^3 / (1 + \beta_1[\mathrm{A^-}] + \beta_2[\mathrm{A^-}]^2 + \cdots). \quad (11)$$

Here, β_n is the stability constant of the "nth" complex in the aqueous phase, which can be written as:

$$\beta_n = [\mathrm{MA}_n^{3-n}][\mathrm{M^{3+}}]^{-1}[\mathrm{A^-}]^{-n}. \quad (12)$$

For the same reason, the following general equations can be written when the bulky cation ($\mathrm{tba^+}$) is added:

$$D = ([\mathrm{MA_3}]_{\mathrm{org}} + [\mathrm{MA_4^-tba^+}]_{\mathrm{org}})$$

$$/ ([\mathrm{M^{3+}}] + [\mathrm{MA^{2+}}] + [\mathrm{MA_2^+}] + \cdots) \quad (13)$$

$$= (K_{\mathrm{ex3,0}}[\mathrm{A^-}]^3 + K_{\mathrm{ex4,1}}[\mathrm{A^-}]^4[\mathrm{tba^+}])$$

$$/ (1 + \beta_1[\mathrm{A^-}] + \beta_2[\mathrm{A^-}]^2 + \cdots). \quad (14)$$

The data in the absence of $\mathrm{tba^+}$ can be analyzed statistically on the basis of Eq. 11.

When the concentration ($[\mathrm{A^-}]$) is identical, the following equations can be introduced from Eqs. 5, 7, 11, and 14:

$$D / D_0 = 1 + K_{\mathrm{ex4,1}} K_{\mathrm{ex3,0}}^{-1}[\mathrm{A^-}][\mathrm{tba^+}] \quad (15)$$

$$= 1 + K_{\mathrm{org}} K_{\mathrm{exAB}}[\mathrm{A^-}][\mathrm{tba^+}]. \quad (16)$$

However, in many cases $D >> D_0$, and Eqs. 13 and 14 may approximately be written as:

$$D_{\mathrm{f}} = [\mathrm{MA_4^-tba^+}]_{\mathrm{org}}$$

$$/ ([\mathrm{M^{3+}}] + [\mathrm{MA^{2+}}] + [\mathrm{MA_2^+}] + \cdots) \quad (17)$$

$$= K_{\mathrm{ex4,1}}[\mathrm{A^-}]^4[\mathrm{tba^+}]$$

$$/ (1 + \beta_1[\mathrm{A^-}] + \beta_2[\mathrm{A^-}]^2 + \cdots). \quad (18)$$

In the presence of $\mathrm{tba^+}$, the free $\mathrm{tba^+}$ concentration is found to be

$$[\mathrm{tba^+}]_{\mathrm{initial}} = [\mathrm{tba^+}] + [\mathrm{MA_4^-tba^+}]_{\mathrm{org}} + [\mathrm{A^-tba^+}]_{\mathrm{org}} \quad (19)$$

$$[\mathrm{tba^+}] = ([\mathrm{tba^+}]_{\mathrm{initial}} - [\mathrm{MA_4^-tba^+}]_{\mathrm{org}})$$

$$/ (1 + K_{\mathrm{exAB}}[\mathrm{A^-}]). \quad (20)$$

When $[\mathrm{A^-}]$ is identical, the following equation can be introduced from Eqs. 5, 7, 8, 9, 11, and 18:

$$D_{\mathrm{f}} / D_0 = K_{\mathrm{ex4,1}} K_{\mathrm{ex3,0}}^{-1}[\mathrm{A^-}][\mathrm{tba^+}] \quad (21)$$

$$= K_{\mathrm{org}} K_{\mathrm{exAB}}[\mathrm{A^-}][\mathrm{tba^+}]. \quad (22)$$

As can be seen from Eq. 22, the enhancement of metal extraction by the addition of $\mathrm{tba^+}$ is dependent on the quantity $[\mathrm{A^-}]$ multiplied by $[\mathrm{tba^+}]$. However, the enhancement of extraction, D_{f}/D_0, can be given more clearly on the basis of the association of the extracted neutral chelate ($\mathrm{MA_3}$) with one ion-pair of the reagents ($\mathrm{A^-\,tba^+}$) in the organic phase. By using this statistical treatment, the enhancement of metal extraction by extracting the $\mathrm{MA_4^-tba^+}$ species is essentially dependent on the formation constant of the $\mathrm{MA_4^-\,tba^+}$ species in Eq. 8, and the extraction constant of the ion-pairs of the ligand anion and the bulky cation ($\mathrm{A^-\,tba^+}$) in Eq. 9.

Experimental

All of the reagents were of reagent grade. The benzoylacetone, benzoyltrifluoroacetone and tetrabutylammonium chloride were obtained from Tokyo Kasei Co. Aqueous solutions of europium(III) were supplied by Wako Pure Chemical Industries, Ltd. The solvent extraction was carried out in a thermostated room at 298 K. Stoppered glass tubes (capacity 50 $\mathrm{cm^3}$) were used for the agitation of the two liquid phases. The aqueous phase was 0.1 $\mathrm{mol\,dm^{-3}}$ sodium nitrate solution buffered by acetate. The organic phase was carbon tetrachloride containing Hbza or Hbfa.

The extraction of europium(III) was measured as follows. A 10 $\mathrm{cm^3}$ portion of the aqueous phase containing 1×10^{-4} mol $\mathrm{dm^{-3}}$ of $\mathrm{Eu^{3+}}$ was placed in a tube. When the effect of the $\mathrm{A^-}$ concentration on the distribution ratio was measured, the pH of the aqueous phase was adjusted at various values by keeping the Hbza or Hbfa concentration in the organic phase nearly constant. When the effect of the $\mathrm{tba^+}$ concentration on the distribution ratio was determined, various amounts of $\mathrm{tba^+}$ was added into the aqueous phase. Then, a 10 $\mathrm{cm^3}$ portion of a carbon tetrachloride solution of Hbfa was added. The two liquid phases in the tube were agitated with a mechanical shaker for 1 h. The two phases were then centrifuged off. A 4 cm^3 portion of the organic phase was transferred into another tube, and the metal ion extracted into this organic phase was washed by 0.1 mol dm^{-3} nitric acid. The content of metal in this solution and in the equilibrated aqueous phase was determined by an ICP-AES (Seiko Instruments Inc. SPS-1200AR). The pH of the equilibrated aqueous phase was measured using a pH meter (Tokyo TOA Electronics Ltd. HM-30S).

The extraction of ion-pairs of bza$^-$ or bfa$^-$ with tba$^+$ into the organic phase was determined by spectrophotometry. A portion of a 0.1 mol dm^{-3} sodium nitrate solution containing an amount of tba$^+$ and buffered at a certain pH was placed in a tube, and a carbon tetrachloride solution of Hbfa or Hbza added. The two phases were agitated for 30 min and centrifuged. The organic phase was transferred into another tube and washed by a 0.05 mol dm^{-3} nitric acid. The thus-obtained aqueous phase was transferred into another tube; after the pH was measured, the solution was neutralized by a sodium hydroxide solution. After an excess amount of sodium picrate (at initial 2×10^{-3} mol dm^{-3}) was added to this neutralized aqueous phase, it was agitated with the same volume of chloroform in order to extract the tba$^+$ quantitatively as ion-pairs of picrate ions. The tba$^+$, thus extracted, was determined from the absorption of the picrate ion at 359 nm.

Results

Data concerning the solvent extraction of ion-pairs of benzoyltrifluoroacetonate ions with tetrabutylammonium ions are given in Table 1. From these,the extraction constant of the ion-pairs of the reagents (K_{exAB} in Eq.9) was obtained to be $10^{1.3}$. However, the extraction of ion-pairs of the benzoylacetonate ions with tetrabutylammonium ions was found to be negligible. From the highest value of [A$^-$] and the detection limit of the picrate ions in the chloroform phase in these experiments, the value of K_{exAB} for bza$^-$ tba$^+$ was estimated to be lower than 10^{-1}.

The solvent extraction equilibrium of europium(III) in 0.1 mol dm^{-3} sodium nitrate solutions was determined in the pH range from 2 to 7 when $[\mathrm{HA}]_{\mathrm{org}}$ was 0.1 mol dm^{-3} in both the absence and presence of 1×10^{-3} mol dm^{-3} tba$^+$. As can be seen from Fig. 1, extraction with benzoylacetone (Hbza) was not enhanced at all by the 1×10^{-3} mol dm^{-3} tba$^+$, but that with benzoyltrifluoroacetone (Hbfe) was greatly enhanced by adding this amount of tba$^+$. As can be seen from Fig. 1, the extraction curves in the absence of tba$^+$ deviate from a straight line with a slope of +3. This is assumed to be caused by the formation of metal chelates in the aqueous phase. The stability constants (β_n) were determined by a successive-approximation method by using a least-squares computer program. The obtained values are listed in Table 2.

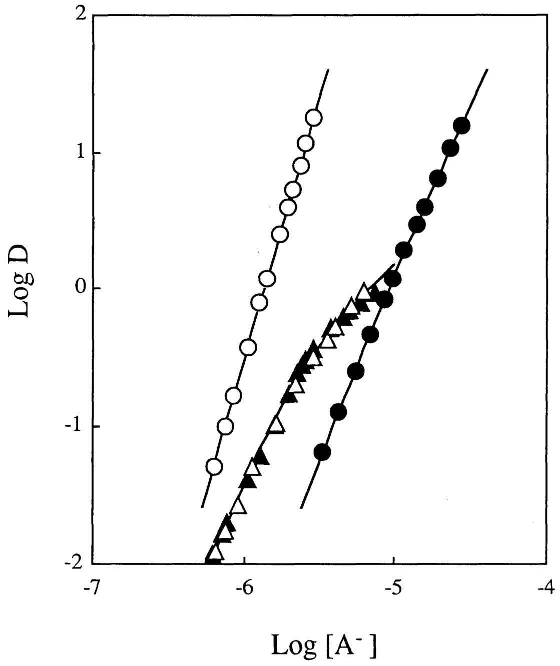

Fig. 1. Distribution ratio of europium(III) as a function of the concentration of dissociated benzoylacetonate anion (▲, △) and benzoyltrifluoroacetonate anion (●, ○). Org. phase: carbon tetrachloride containing 0.1 mol dm^{-3} of one of these β-diketones. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution containing no tetrabutylammonium ions (closed symbols) and 1.0×10^{-3} mol dm^{-3} tetrabutylammonium ions at initial (open symbols). The lines are calculated by Eq. 14, using the value given in Table 2.

The enhancement of extraction with benzoyltrifluoroacetone by the addition of tba$^+$ was determined as a function of the tba$^+$ concentration calculated using Eq. 20 when the concentration of bfa$^-$ was approximately kept constant by keeping the $[\mathrm{HA}]_{\mathrm{org,initial}}$ at 0.1 mol dm^{-3} and

Table 1. Solvent Extraction Data of Tetrabutylammonium and Benzoyltrifluoroacetonate Ions as Ion-Pairs

$[\mathrm{tba}^+]_{\mathrm{initial}}$	pH	[bfa$^-$]	[tba$^+$]	$[\mathrm{tba}^+]_{\mathrm{org}}$	K_{exAB}
1×10^{-3}	6.70	1.83×10^{-3}	9.77×10^{-3}	3.61×10^{-5}	$10^{1.30}$
2×10^{-3}	6.81	2.40×10^{-3}	1.93×10^{-3}	9.03×10^{-5}	$10^{1.29}$
2×10^{-3}	6.88	2.80×10^{-3}	2.19×10^{-3}	1.17×10^{-5}	$10^{1.28}$
3×10^{-3}	6.98	3.50×10^{-3}	2.91×10^{-3}	1.78×10^{-4}	$10^{1.24}$
3×10^{-3}	7.05	4.09×10^{-3}	2.78×10^{-3}	2.08×10^{-4}	$10^{1.26}$
4×10^{-3}	7.06	4.18×10^{-3}	3.76×10^{-3}	2.81×10^{-4}	$10^{1.25}$

a) Org. phase: carbon tetrachloride initially containing 0.1 mol dm^{-3} Hbfa. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution. b) $K_{\mathrm{exAB}}\mathrm{av}=10^{1.27}$.

Table 2. Equilibrium Constants for Solvent Extraction of Europium(III) with Benzoylacetone and Benzoyltrifluoroacetone in the Absence and Presence of Tetrabutylammonium Ions

	pK_a[b]	Log K_d[b]	Log $K_{ex3,0}$	Log $K_{ex4,1}$	Log β_1	Log β_2	Log K_{exAB}	Log K_{org}
Hbza	8.39	2.81	16.7	—	3.17	11.5	—	—
Hbfa	6.03	2.39	15.3	26.5	4.81	—	1.27	9.93

a) Org. phase: carbon tetrachloride containing 0.1 mol dm^{-3} of one of these β-diketones. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution. b) Taken from Ref. 4 but the aqueous phase in this previous study was 0.1 mol dm^{-3} NaClO$_4$.

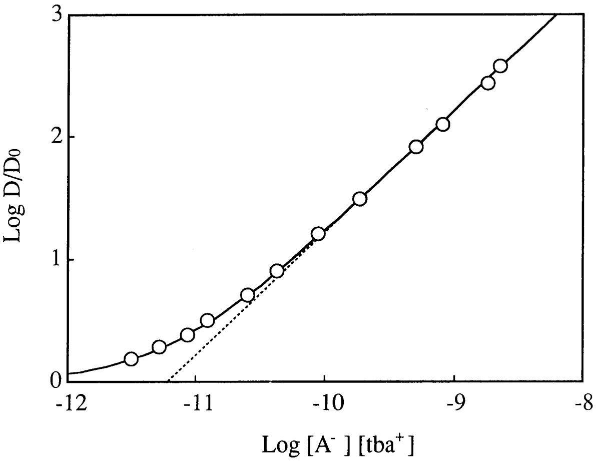

Fig. 2. Increase in the distribution ratio of europium(III) in the extraction systems with benzoyltrifluoroacetone (HA) by addition of tetrabutylammonium (tba$^+$) as a function of the quantity [A$^-$][tba$^+$] in the aqueous phase. Org. phase: carbon tetrachloride containing 0.1 mol dm^{-3} HA. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution at pH 3.9 and contains various amount of tba$^+$. The value of log[A$^-$][tba$^+$] was calculated using Eq. 9.

pH at 3.9 The data are given in Fig. 2. The curve shown in Fig. 2 was drawn using the following equation, which was introduced from Eqs. 5, 7,11, and 18. Here, D (in the presence of tba$^+$) and D_0 (in the absence of tba$^+$) are the distribution ratio when [A$^-$] is identical:

$$Y = \log D/D_0 = \log(1 + K_{ex4,1}K_{ex3,0}^{-1}[A^-][tba^+]). \quad (23)$$

The two asymptotes, one of which is the X-axis in Fig. 2, should indicate the following two lines:

$$Y(\lim[tba^+] \rightarrow \infty) = \log K_{ex4,1}K_{ex3,0}^{-1}[A^-][tba^+] \quad (24)$$

and

$$Y(\lim[tba^+] \rightarrow 0) = 0. \quad (25)$$

The value of log $K_{ex4,1}$ $K_{ex3,0}^{-1}$ can also be obtained from the intercept of the asymptote of the plot logD/D_0 vs. log [tba$^+$] with the X-axis, as can be seen from Eq. 24. The value (11.2) agreed well with that calculated using the two extraction constants given in Table 2.

Discussion

It is noted that the addition of tba$^+$ enhances solvent extraction with Hbfa, though the effect is negligible with Hbza. Similar results were also found regarding the extraction of zinc(II).[2] In this previous paper it was pointed out that although the anionic complexes (Zn A$_3^-$) with acetylacetone and benzoylacetone in the aqueous phase were more stable than those with trifluoroacetylacetone and benzoyltrifluoroacetone, the ion-pairs of the former complexes with tba$^+$ could not pass through the interface of the two liquid phases due to certain reasons. Although no evidence for the formation of the MA$_4^-$ complex in the aqueous phase can be found from the plot given in Fig. 1, it should be reasonable to assume that the Eu(bza)$_4^-$ complex is more stable than the Eu(bfa)$_4^-$ complex, since Hbza is a weaker acid than Hbfa. When the extraction of the ion-pairs is given by

$$MA_4^- + tba^+ \rightleftharpoons MA_4^-tba^+_{(org)}, \quad (26)$$

the extraction of the ternary complex at a certain extractant anion concentration ([A$^-$]) should be more favorable with Hbza if the extractabilities of the MA$_4^-$ complexes are nearly similar.

The fact that the extraction of the bza$^-$ tba$^+$ ion-pairs is negligible seems to provide an explanation for why no enhancement of the extraction of europium(III) with Hbfa occurs by tba$^+$. As can be seen from Eqs. 9 and 16, no enhancement can be expected if $K_{ex_{AB}}$ is very small, except when K_{org} is very large.

The distribution constant of Hbza is better than that of Hbfa, as can be seen from Table 2; the size of these molecules should not be very much different. Thus, a much better extraction of ion-pairs bfa$^-$ tba$^+$ than bza$^-$ tba$^+$ can not be explained only by the effect of the size of ion-pairs. No explanation seems to be possible at present for this great difference in the extractability of the ion-pairs of reagents.

An analogy concerning the difference in the acceptability of A$^-$ in the ion-pairs A$^-$ tba$^+$ by the MA$_3$ complex was pointed out regarding the synergistic extraction of the neutral complex when the organic phase contained a solvating ligand, such as trioctylphosphine oxide (TOPO).[2] The metal bfa$^-$ chelate should accept several neutral ligands more easily than the neutral bza$^-$ chelate of the same metal ion in the organic phase, as was pointed out in several papers (for example, in Refs. 5 and 6). It could be reasonably assumed from a previous study[5] that the $Eu(bza)_3$ undergoes much less coordination in the organic phase, not only with the neutral ligands (such as TOPO), but also with the bidentate ligand (bza^-) compared to $Eu(bfa)_3$ with TOPO or bfa^-. It can also be assumed that K_{org} in Eq. 8 of $Eu(bza)_3$ should be smaller than that of $Eu(bfa)_3$. However, the negligible extraction of the bza^- tba^+ ion-pairs explains the negligible extraction of the anionic complex with tba^+, as can be seen from Eq. 8.

In some solvent extraction systems of metal ions (M^{m+}) with a chelating extractant (HA) the extraction of a self-adduct (written as $MA_m(HA)_n$) where n is an integer occurs. This was found in the solvent extraction systems of europium (III) with 2-thenoyltrifluoroacetone (Htta) and in a carbon tetrachloride system when the Htta concentration was very high; however, the formation equilbrium of self-adduct,

$$MA_{3(org)} + HA_{(org)} \rightleftharpoons MA_3(HA)_{(org)} \tag{27}$$

could not be determined.[7] Thus, in this previous paper the species ($M(tta)_3(Htta)$) was assumed to be negligible when the Htta concentration was 0.1 mol dm^{-3} or lower. Some experiments were also carried out in the present study regarding this problem. The $\log D$ vs. $\log [A^-]$ plot of europium(III) extraction when the HA concentration in the organic phase was 0.2 to 0.04 mol dm^{-3} with benzoylacetone and 0.1 to 0.02 mol dm^{-3} with benzoyltrifluoroacetone was essentially independent on the concentration ($[HA]_{org}$). This indicates that the formation of a self-adduct in Eq. 27 should be negligible under the conditions of the present study.

As can be seen from Table 1, the extraction constant (K_{exAB}) in Eq. 9 is not dependent on the tba^+ concentration within the limit of experimental error. This should indicate that the formation of an aggregate, such as $(A^- tba^+)_n$, or the dissociation of the extracted ion-pairs in the organic phase should be negligible.

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