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Solvent Extraction of Several Divalent Metal Ions with Benzoyltrifluoroacetone and 2-Thenoyltrifluoroacetone into Chloroform in the Presence of Tetrabutylammonium Ions

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The solvent extractions of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) (M^{2+}) in 0.1 mol dm^{-3} sodium nitrate solutions with benzoyltrifluoroacetone and 2-thenoyltrifluoroacetone (HA) into chloroform were studied in the absence and presence of tetrabutylammonium ions (tba^+). The addition of tba^+ enhanced the extraction, except that of copper(II). This enhancement could be explained in terms of the extraction of the ternary complex, $MA_3^- tba^+$, in addition to the neutral complex, MA_2. The data were treated on the basis of the formation equilibrium of the ternary complex from the neutral complex, MA_2, with the extracted ion-pairs of the reagents, $A^- tba^+$, in the organic phase. It was concluded that the association constants of MnA_2, FeA_2, CoA_2, NiA_2, and CdA_2 with the ion-pair, $A^- tba^+$, are not very much different from each other. However, that of ZnA_2 is lower than those of the five divalent metal complexes. This trend is similar to that found among the adduct metal complexes of β-diketonates with trioctylphosphine oxide (TOPO) in synergistic extraction systems.

It has been reported in previous papers[1—3] that the solvent extraction of cobalt(II), nickel(II), and zinc(II) (M^{2+}) with benzoyltrifluoroacetone (Hbfa, 1-phenyl-4,4,4-trifluoro-1,3-butanedione) into carbon tetrachloride is enhanced by the addition of bulky cations, such as tetrabutylammonium ions (tba^+); this could be explained in terms of the extraction of not only the neutral complex, $M(bfa)_2$, but also of the ion-pair of the anionic complex with the cation, $M(bfa)_3^- tba^+$ (ternary complex). It was also pointed out that the degree of extraction of such ternary complexes is dependent on the β-diketone employed.[1,2] The solvent extraction of metal ions as anionic β-diketonate complexes together with bulky cations was further studied systematically with rare earth ions.[4—8] It was also found that extraction of the ternary complex with a certain β-diketone and a bulky cation is different with each rare earth ion. The order of extraction with 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione) was better in the order scandium(III) > lutetium(III) > europium(III) > neodymium(III) > praseodymium(III) > lanthanum(III), but enhancement of the extraction by tba^+ was nearly the same with lanthanum(III) to europium(III) and to some extent lower with lutetium(III); enhancement was negligible in the case of scandium(III). The solvent extraction of alkaline earth ions with Hbfa together with tba^+ has also been reported,[9] and the enhancement of extraction by the addition of tba^+ was found to be greater in the order magnesium(II) > calcium(II) > strontium(II) > barium(II), which is the same as that found regarding the extractability of the neutral complexes of these ions. It was pointed out in these previous studies that the extraction of anionic complexes as ion-pairs with bulky cations could be treated as the overall effect of: (i) the extraction of M^{m+} as MA_m, (ii) the extraction of A^- as ion-pairs with tba^+, and (iii) the association of the MA_m with $A^- tba^+$ in the organic phase. It was also pointed out in these papers that the experimental data when ternary complexes were extracted could be treated statistically in a similar manner as those when adduct metal complexes were extracted (synergistic extraction).

The present study was carried out in order to learn about the solvent extraction of the divalent transition metal ions and zinc(II) and cadmium(II) with two β-diketones, Hbfa as well as Htta, as well as the enhancement of extraction due to the anionic complex extracted as ion-pairs with tba^+. The results were compared with the previous data concerning the synergistic enhancement of these metal complexes; the similarity of ternary complex extraction and synergistic extraction was also considered.

Experimental

All of the reagents and the experimental procedures were similar to those in previous studies,[9] except for iron(II). The organic phase was chloroform initially containing 0.1 mol dm^{-3} Hbfa or Htta; the aqueous phase was a 0.1 mol dm^{-3} sodium nitrate solution initially containing 1×10^{-5} mol dm^{-3} of the metal ions. These metal ions were supplied by Wako Pure Chemical Industries, Ltd. The two phases were agitated for 30 min. When the metal ion was iron(II), an aqueous phase of 1×10^{-2} mol dm^{-3} ascorbic acid was added. This aqueous solution was agitated with chloroform containing Hbfa or Htta for 60 s. This time for two-phase agitation was found to be sufficient to reach the solvent-extraction equilibrium. However, when the agitation was carried out for a shorter time than this, the results were not always reproducible; when it was continued for a longer time, the color of the organic phase became pale yellow, which indicated the formation of the tris(β-diketonato)iron(III) complex by oxidation of the iron(II) with atmospheric oxygen in the organic phase. The metal ion in both phases was determined by either inductive-couple plasma atomic emission spectrometry or atomic absorption spectrometry.

Results

A statistical treatment of the experimental data was carried out in a similar manner to that in a previous paper[9] and, thus, only the main equations are given.

The distribution ratio of metal ions, $[\mathrm{M(II)}]_{\mathrm{org,total}}/[\mathrm{M(II)}]_{\mathrm{aq,total}}$, in the absence ($D_0$) and presence of tba^+ (D_t) can be written as:

$$D_0 = K_{\mathrm{ex}2,0}[\mathrm{A}^-]^2 / \left(1+\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2+\cdots\right) \quad (1)$$

and

$$\begin{aligned} D_\mathrm{t} &= K_{\mathrm{ex}2,0}[\mathrm{A}^-]^2 + K_{\mathrm{ex}3,1}[\mathrm{A}^-]^3[\mathrm{tba}^+] \\ &\quad / \left(1+\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2+\cdots\right) \quad (2) \\ &= K_{\mathrm{ex}2,0}[\mathrm{A}^-]^2\left(1+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A}^-][\mathrm{tba}^+]\right) \\ &\quad / \left(1+\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2+\cdots\right), \quad (3) \end{aligned}$$

where

$$K_{\mathrm{ex}2,0} = [\mathrm{MA}_2]_{\mathrm{org}}[\mathrm{M}^{2+}]^{-1}[\mathrm{A}^-]^{-2}, \quad (4)$$

$$K_{\mathrm{ex}3,1} = [\mathrm{MA}_3{}^-\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{M}^{2+}]^{-1}[\mathrm{A}^-]^{-3}[\mathrm{tba}^+]^{-1}, \quad (5)$$

$$K_{\mathrm{org}} = [\mathrm{MA}_3{}^-\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{MA}_2]_{\mathrm{org}}{}^{-1}[\mathrm{A}^-\mathrm{tba}^+]_{\mathrm{org}}{}^{-1}, \quad (6)$$

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

and

$$\beta_n = [\mathrm{MA}_n{}^{2-n}][\mathrm{M}^{2+}]^{-1}[\mathrm{A}^-]^{-n}. \quad (8)$$

The concentrations of A^- and tba^+ were calculated according to the following equations in the same manner as described in Ref. 6 to Ref. 9:

$$[\mathrm{A}^-] = [\mathrm{HA}]_{\mathrm{initial}} / \left\{1+(K_\mathrm{d}+1)[\mathrm{H}^+]K_\mathrm{a}{}^{-1}\right\} \quad (9)$$

and

$$[\mathrm{tba}^+] = [\mathrm{tba}^+]_{\mathrm{initial}} / \left(1+K_{\mathrm{exAB}}[\mathrm{A}^-]+K_{\mathrm{exXB}}[\mathrm{X}^-]\right), \quad (10)$$

where $K_\mathrm{d}=[\mathrm{HA}]_{\mathrm{org}}[\mathrm{HA}]^{-1}$, $K_\mathrm{a}=[\mathrm{H}^+][\mathrm{A}^-][\mathrm{HA}]^{-1}$, X^- is the anion of the background salt in the aqueous phase, and $K_{\mathrm{exXB}}=[\mathrm{X}^-\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{X}^-]^{-1}[\mathrm{tba}^+]^{-1}$. Equation 9 could approximately be used even when metal ions and tba^+ were present, since $[\mathrm{HA}]_{\mathrm{org,initial}}$ is always much higher than $[\mathrm{M(II)}]_{\mathrm{initial}}$ and $[\mathrm{tba}^+]_{\mathrm{initial}}$. When the concentration of A^- in the aqueous phase is determined in an experiment in the presence of tba^+, the value of D_0 under the same A^- concentration was calculated by Eq. 1, which introduced the value of the equilibrium constants obtained by separate experiments. The enhancement of extraction obtained from these data can be given by the following equations:

$$\begin{aligned} D_\mathrm{t}/D_0 &= 1+K_{\mathrm{ex}3,1}K_{\mathrm{ex}2,0}{}^{-1}[\mathrm{A}^-][\mathrm{tba}^+]. \quad (11) \\ &= 1+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A}^-][\mathrm{tba}^+]. \quad (12) \end{aligned}$$

Figure 1a gives the extraction curves of the metal ions with Hbfa in both the absence and presence of 1×10^{-3} mol dm^{-3} tba^+ (at initial). Figure 1b gives those with Htta, also in both the absence and presence of 1×10^{-3} mol dm^{-3} tba^+ (at initial). Although the solvent extraction of nickel(II) with Htta was attempted, the results were not reproducible and the recovery of the metal ion was not quantitative for unknown reasons. Thus, no data for nickel(II) extraction with Htta are given in Fig. 1b. Figures 2a and 2b give the enhancement of extraction as a function of $[\mathrm{bfa}^-][\mathrm{tba}^+]$ and $[\mathrm{tta}^-][\mathrm{tba}^+]$, respectively, by keeping $[\mathrm{HA}]_{\mathrm{org,initial}}$ at 0.1 mol dm^{-3}. As can be seen from Eqs. 11 and 12, the extraction is dependent on the quantity $[\mathrm{A}^-][\mathrm{tba}^+]$ and, thus, the data were analyzed on the basis of Eqs. 11 and 12.

The data given in Figs. 1a and 1b and Figs. 2a and 2b were statistically analyzed on the basis of Eq. 1 to Eq. 5 and Eqs. 11 and 12, respectively, by a successive-approximation approach using a least-squares computer program. The values of K_{exAB} of bfa^- and tta^-, employed for the statistically analysis were $10^{4.0}$ and $10^{4.1}$ (Refs. 6 and 8). The values of the stability and extraction constants thus obtained are listed in Table 1. The solid lines in Figs. 1a, 1b, 2a, and 2b were calculated by using these constants. Since they fit well with the data, the values of the constants given in Table 1 should be reasonable.

Discussion

In the present study chloroform was employed as the solvent. In general, this solvent is better for the extraction of ion-pairs than is carbon tetrachloride. This general tendency was also found for the extraction of anionic complexes as ion-pairs with tba^+, as can be seen from Table 1: the extraction constant of the ion-pair, $K_{\mathrm{ex}3,1}$, given by Eq. 5 is more than one order larger into chloroform than into carbon tetrachloride with cobalt(II), nickel(II), or zinc(II). This effect of the solvent is just opposite to that found with the formation of the adduct chelate in a synergistic extraction system: the formation constant of the adduct is usually more than one order higher in carbon tetrachloride than in chloroform (for example Ref. 10). In a previous study,[6] this difference in the extraction of a ternary complex into carbon tetrachloride and chloroform was explained in terms that the association of the neutral complex with the ion-pair of the reagents is more favorable in carbon tetrachloride than in chloroform, just as in the adducts formation of a neutral complex with solvating ligands,

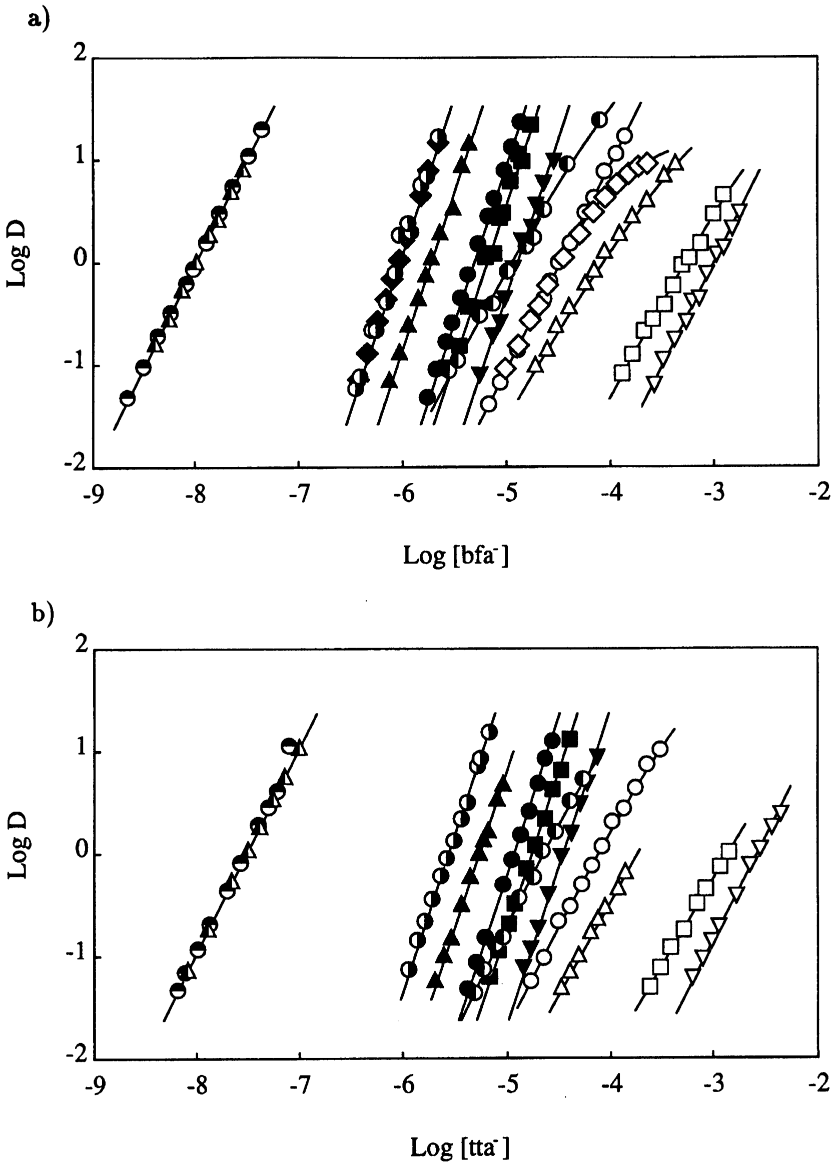

Fig. 1. Distribution ratio of the metal ions as a function of (a) benzoyltrifluoroacetonate anion or (b) 2-thenoyltrifluoroacetonate anion concentration in the absence and presence of tetrabutylammonium ions. Org. phase: chloroform initially containing 0.1 mol dm^{-3} benzoyltrifluoroacetone or 2-thenoyltrifluoroacetone. Aq phase: 0.1 mol dm^{-3} sodium nitrate containing no tba$^+$ and initially containing 1×10^{-3} mol dm^{-3} tba$^+$. The metal ions are Mn(II) (□), Fe(II) (◐), Co(II) (△), Ni(II) (◇), Cu(II) (▲), Zn(II) (○), and Cd(II) (▽) in the absence of tba$^+$ and Mn(II) (■), Fe(II) (◑), Co(II) (▲), Ni(II) (◆), Cu(II) (⊖), Zn(II) (●), and Cd(II) (▼) in the presence of tba$^+$. The nickel(II) with Htta were not reproducible because the recovery was not very quantitative. The solid lines were calculated by Eqs. 1 and 2 using the values given in Table 1.

such as tributylphosphate (TBP) or trioctylphosphine oxide (TOPO). However, extraction of the neutral complex as well as that of the reagents as ion-pairs are more favorable into chloroform. These two effects are opposite. However, since the latter effect is larger than the former, the over-all effect of these appears to be that the extraction of a ternary complex is more favorable in chloroform than in carbon tetrachloride.

It is noted that although the two-phase partition coefficient, K_d ($=[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}]$) of Hbfa ($10^{2.84}$),[11] is one order higher than that of Htta ($10^{1.85}$),[11] the extraction constants of the β-diketonate anions with tba$^+$ into the solvent are nearly the same. As can be seen from Eq. 12, the similar value of K_{exAB} and the rather small difference in the K_{org} should result in a small difference in the enhancement of metal extraction with Hbfa and with Htta in the presence of a certain amount of tba$^+$. The difference in the extractability of the ternary complex given by $K_{\mathrm{ex3,1}}$ in Eq. 5 is thus mainly due to the rather large difference in the extractability of the neutral complex, $K_{\mathrm{ex2,0}}$, in Eq. 4. It was found in previous studies that the solvent extraction of zinc(II)[1]

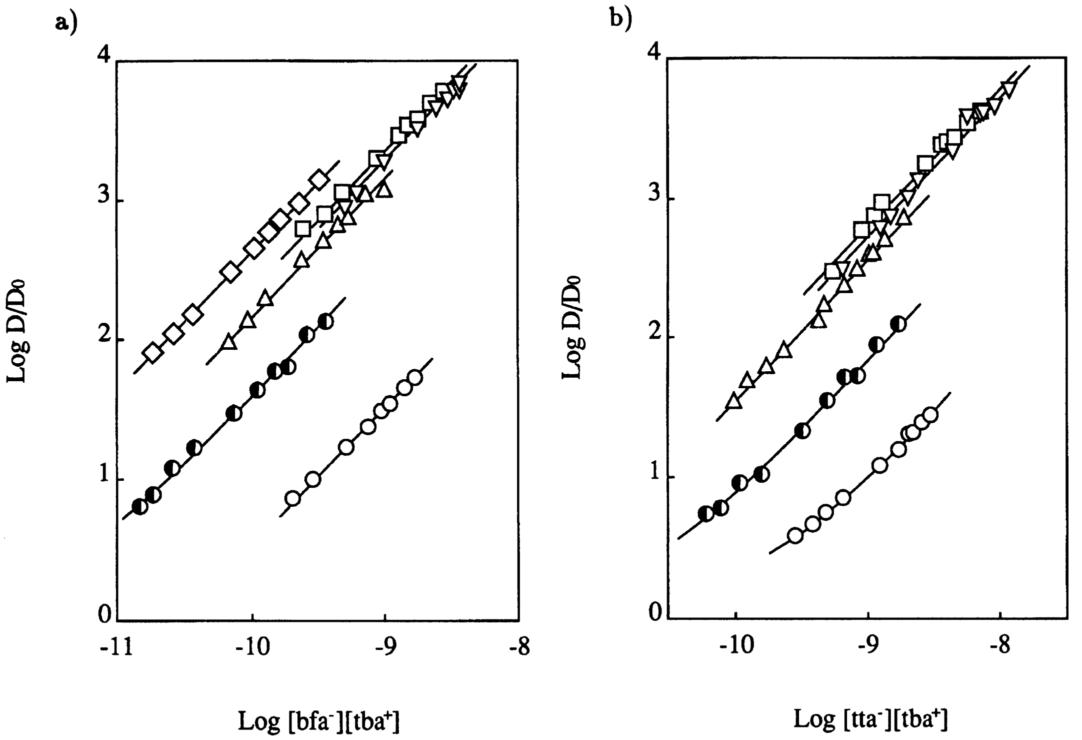

Fig. 2. Increase in the distribution ratio of the metal ions as a function of the quantity, $[A^-]$ multiplied by $[tba^+]$, in the aqueous phase. Org. phase: chloroform initially containing 0.1 mol dm^{-3} (a) benzoyltrifluoroacetone or (b) 2-thenoyltrifluoroacetone. The metal ions are Mn(II) (□), Fe(II) (◐), Co(II) (△), Ni(II) (◇), Zn(II) (○), and Cd(II) (▽). The solid lines were calculated by Eq. 10 using the values given in Table 1.

Table 1. Summary of the Equilibrium Constants
Org. phase: chloroform containing 0.1 mol dm^{-3} Hbfa or Htta. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution.

	Hbfa					Htta			
	log $K_{ex2,0}$	log β_1	log β_2	log $K_{ex3,1}$	log K_{org}	log $K_{ex2,0}$	log β_1	log $K_{ex3,1}$	log K_{org}
Mn(II)	6.8	3.1	—	19.1	8.3	6.0	2.9	17.8	7.7
Fe(II)	10.0	4.2	8.0	21.6	7.6	9.3	(3.4)[c]	20.2	6.8
Co(II)	8.5 (7.2)[d]	4.1 (3.1)[d]	— (5.2)[d]	20.7 (18.9)[d]	8.2 (10.9)[d]	7.7	3.5	19.3	7.5
Ni(II)	9.0 (7.6)[d]	3.1 (3.5)[d]	7.9 (6.9)[d]	21.6 (20.0)[d]	8.6 (11.6)[d]	—[a]	—[a]	—[a]	—[a]
Cd(II)	6.0	—	—	18.2	8.2	5.2	—	16.9	7.6
Zn(II)	9.0 (7.7)[d]	— (2.6)[d]	— (5.0)[d]	19.5 (17.7)[d]	6.5 (9.2)[d]	8.3	(3.3)[c]	18.3	5.9
Cu(II)	16.0	—	—	—	—	15.1	—	—	—

a) Recovery of the nickel(II) was too poor to confirm this species. b) log K_{exAB} of Hbfa and Htta employed for the calculation were 4.0 and 4.1, respectively. These were taken from Refs. 3 and 5. c) Error is too large. d) The values in the parenthesis are those in carbon tetrachloride taken from Ref. 1 to Ref. 3. The values of K_{exAB} used for the calculation of these data: from 1 mol dm^{-3} sodium nitrate to carbon tetrachloride is $10^{0.78}$ (unpublished data).

and cobalt(II)[2] with benzoylacetone (Hbza, 1-phenyl-1,3-butanedione) was not enhanced by the addition of tba^+. The same type of observation was also made regarding europium(III) extractions.[4,8]

The difference in the formation equilibrium of an anionic complex as ion-pairs with tba^+ can be known from a comparison of the K_{org} values, as can be seen from Eqs. 3 and 6. The association of the neutral complex, MA_2, with the ion-pair of the reagents, A^-tba^+, observed may be summarized as follows: (i) the copper(II) complexes do not form a ternary complex; (ii) although zinc(II) complexes form a ternary complex, the formation constant is much smaller than the other five divalent metal complexes with the same ligand; and (iii) the formation constant of the ternary complex from the neutral complex of manganese(II), iron(II), cobalt(II), nickel(II), and cadmium(II) are rather similar to each other, though the values of the iron(II) complexes are slightly smaller than those of the other complexes. As was pointed out, the ability of the metal complex in the organic phase to accept the ion-pair of the reagents seems to be rather similar to that to accept a solvating-type ligand, TOPO. Table 2 summarizes the adduct formation constant of benzoyltrifluoroacetonate complexes

Table 2. Summary of the Formation Constants of the Adducts with TOPO
Aq phase: 1 M $NaClO_4$. Org. phase: carbon tetrachloride containing Hbfa.

	$\log \beta_{(\mathrm{org})1}$	$\log \beta_{(\mathrm{org})2}$	Remarks
Mn(II)	6.1	10.4	#
Co(II)	6.2	9.3	##
Ni(II)	5.2	9.0	###
Zn(II)	6.7	—[a)]	##
Cd(II)	—[b)]	10.4	####

Taken from Ref. 22. ## Taken from Ref. 23. ### Taken from Ref. 24. #### Taken from Ref. 25.
a) No evidence of the second adduct $ZnA_3(TOPO)_2$.
b) Error is too large to confirm this species.

of metal ions with TOPO in carbon tetrachloride. However, in order to compare the equilibrium for the formation of the anionic complex and the adduct, it should be noticed that in the anionic complex, the added ligand is bidentate and the complex is charged, but in the TOPO adducts the added ligand is unidentate and the formed species is non-charged. The situation concerning the formation of an anionic complex is to some extent similar to that of a neutral adduct complex with a bidentate neutral ligand, such as heterocyclic amines.[12—20] As can be seen from Table 2, although the second TOPO adduct of $Zn(bfa)_2$ is unstable, the stability of the second adduct of the other four divalent metal benzoyltrifluoroacetonate is not very much different. Although no very clear explanation can be given for the lower stability of the zinc(II) adduct complex, the lower stability of the anionic zinc(II) complex (as shown by the value of K_{org}) agrees with the relatively lower stability of the zinc(II) adduct complexes in synergistic extraction systems.[16,17] The adduct formation constant of $Cu(bfa)_2$ with TOPO was reported to be much lower than that of the other metal complexes.[21] A similar tendency was also found concerning the stability of the adduct complexes of these metal ions with tributylphosphate[10] or 1,10-phenanthroline.[16] This should show that the copper(II) complex has no great ability to form complexes of higher coordination number. This explains the fact that no extraction of the anionic complex of copper(II) with tba^+ was found.

As was pointed out in a previous study,[8] the magnitude of formation constant, K_{org}, is affected by the overall effect of the acceptability of the neutral complex for an additional ligand, and the ability of the chelate anion as a donor to the neutral complex. Since the donor is the same for all anionic complexes, the similar values of K_{org} should indicate that the acceptability of the neutral complexes is rather similar to each other.

It was reported[9] that the solvent extraction of alkaline earth ions with Hbfa into carbon tetrachloride is better in the order magnesium(II) > calcium(II) > stronitium(II) > barium(II), and that the formation constant of the anionic complex from the neutral complex is also larger in this order. Thus, the separation of these metal ions is better in the presence of tba^+ than in its absence. The results from the present study (that although the solvent extraction of metal ions with Hbfa in the absence of tba^+ is different, the values of K_{org} are rather similar) show that the separation of these metal ions is not improved when tba^+ is added. This is similar to the case that the values of K_{org} of the tris-2-thenoyltrifluoroacetonate complexes of lanthanum(III), praseodymium(III), neodymium(III), and europium(III) are rather similar to each other and, thus, the separation of these metal ions by solvent extraction with Hbfa or Htta is not improved by the addition of tba^+.

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