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Solvent Extraction of Alkaline Earth Ions with Benzoyltrifluoroacetone into Carbon Tetrachloride in the Absence and Presence of Tetrabutylammonium Ion or Trioctylphosphine Oxide

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The solvent extraction of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} (M^{2+}) in aqueous 0.1 mol dm^{-3} sodium nitrate solutions with benzoyltrifluoroacetone (Hbfa) in carbon tetrachloride was studied in both the absence and presence of tetrabutylammonium ion (tba^+) or trioctylphosphine oxide (TOPO). It was found that not only the $M(bfa)_2$ species, but also the $tba^+M(bfa)_3{}^-$ or the $M(bfa)_2(TOPO)_n$ species (n is 1 to 3), were extracted by the addition of tba^+ or TOPO, and that the extraction was very much enhanced. The equilibria for the extractions were treated as the over-all equilibrium of (i) extraction of the $M(bfa)_2$ chelate and (ii) the association of the ion-pair of the reagents, tba^+bfa^-, or the TOPO molecules with the chelate in the organic phase. The separation of these four metal ions was improved by the addition of tba^+. This was due to the fact that the chelates of smaller M^{2+} associated with the tba^+bfa^- better than those of larger M^{2+} in the organic phase.

In a previous paper[1] it was reported that the solvent extraction of magnesium(II) and calcium(II) in aqueous 1 mol dm^{-3} sodium nitrate solutions into carbon tetrachloride with 1-phenyl-4,4,4-trifluorobutane-1,3-dione(benzoyltrifluoroacetone, Hbfa) was enhanced by the addition of tetraalkylammonium ion (R_4N^+); this was explained as follows. In the absence of R_4N^+, the extracted species was $Na^+M(bfa)_3{}^-$, but in the presence of R_4N^+ the $R_4N^+M(bfa)_3{}^-$ species was also extracted, and the extraction of such ion-pairs with the bulky cations was much better than ion-pairs with Na^+.

It was also reported in another paper[2] that an enhancement of the extraction of a metal ion with a chelating extractant, such as Hbfa by an addition of tetrabutylammonium ion (tba^+), also occurred in the case of europium(III). This extraction equilibrium was statistically treated as the over-all equilibrium of the solvent extraction of non-charged metal chelate ($Eu(bfa)_3$) and its association with the ion-pair of the reagents (tba^+bfa^-) in the organic phase. It was pointed out in this previous paper that this association of the non-charged chelate with the ion-pair of the reagents can be compared with the association of the chelate with a neutral ligand, such as tributylphosphate (TBP) or trioctylphosphine oxide (TOPO), in the organic phase.[3]

In the present paper, the solvent extraction of four alkaline earth ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} (they will be represented by M^{2+})) in 0.1 mol dm^{-3} sodium nitrate solutions with Hbfa into carbon tetrachloride as the $M(bfa)_2$ chelate was studied. The extraction was also measured when tba^+ or TOPO was added to the system and the enhancement of extraction by tba^+ was ascribed to the association of the ion-pairs (tba^+bfa^-) with the $M(bfa)_2$ chelate. This was compared with the synergistic enhancement of the metal chelate extraction by the addition of TOPO molecules on the $M(bfa)_2$ chelate in the organic phase. The 0.1 mol dm^{-3} sodium nitrate solution was chosen as the aqueous phase. This was because from this lower salt concentration solution compared to a previous study,[1] the $M(bfa)_2$ species was extracted and the extraction of the $Na^+M(bfa)_3{}^-$ species was negligible. It was thus possible to consider the association equilibrium between the neutral chelate $M(bfa)_2$ with the ion-pair, tba^+bfa^-, which was not observed in the previous study.

Experimental

The experiments were carried out in an essentially similar manner as in previous studies.[2,5] The solvent-extraction work was performed at 298 K. The concentration of alkaline earth metal in stock solutions was determined by an EDTA titration method. Stoppered glass tubed (capacity 20 cm^3) were used for the solvent-extraction experiments. The aqueous phase was a 0.1 mol dm^{-3} sodium nitrate solution buffered by Hbfa transferred from the organic phase to this phase.[4] The initial concentration of Mg(II) in the aqueous phase was 5×10^{-5} mol dm^{-3} and that of Ca(II), Sr(II), and Ba(II) was 1×10^{-4} mol dm^{-3}. The volume of the two phases was always 5 cm^3. They were agitated for 30 min and centrifuged off. The hydrogen-ion concentration in the aqueous phase was measured by potentiometry. The extracted metal ions in the organic phase were stripped by 1 mol dm^{-3} nitric acid. The alkaline earth metal ions in the aqueous solution were determined by an atomic absorption method.

Statistical

The statistical analysis of the data was carried out in a similar manner as described in previous papers;[2,4,5] only those equations which were used for the data analysis are given here:

$$[\mathrm{Hbfa}]_{\mathrm{org,init}} = [\mathrm{Hbfa}]_{\mathrm{org}} + [\mathrm{Hbfa}] + [\mathrm{bfa}^-] \quad (1)$$

$$[\mathrm{bfa}^-] = [\mathrm{Hbfa}]_{\mathrm{org,init}} / \left(1 + (1 + K_{\mathrm{d}})\, K_{\mathrm{a}}{}^{-1}[\mathrm{H}^+]\right), \quad (2)$$

where $K_a = [H^+][bfa^-][Hbfa]^{-1}$ and $K_d = [Hbfa]_{org}$ $[Hbfa]^{-1}$. The distribution ratio can be written as follows:

$$D_0 = [\mathrm{M(bfa)_2}]_{\mathrm{org}} / \left([\mathrm{M}^{2+}] + [\mathrm{M(bfa)}^+]\ldots\right) = K_{\mathrm{ex2,0}}[\mathrm{bfa}^-]^2 / \left(1 + \sum \beta_n [\mathrm{bfa}^-]^n\right), \quad (3)$$

$$K_{\mathrm{ex2,0}} = [\mathrm{M(bfa)_2}]_{\mathrm{org}}[\mathrm{M}^{2+}]^{-1}[\mathrm{bfa}^-]^{-2} \quad (4)$$

and $\beta_n = [\mathrm{M(bfa)}_n{}^{2-n}][\mathrm{M}^{2+}]^{-1}[\mathrm{bfa}^-]^{-n}$. However, since the metal chelates in the aqueous phase were negligible in all of the systems studied in the present work, they will not be used here.

In the presence of bulky cation (tba^+) the distribution ratio can generally be written as:

$$D = \left([\mathrm{M(bfa)_2}]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{M(bfa)_3}^-]_{\mathrm{org}}\right) / [\mathrm{M}^{2+}] = \left(K_{\mathrm{ex2,0}}[\mathrm{bfa}^-]^2 + K_{\mathrm{ex3,1}}[\mathrm{bfa}^-]^3[\mathrm{tba}^+]\right), \quad (5)$$

$$D[\mathrm{bfa}^-]^{-2} = K_{\mathrm{ex2,0}} + K_{\mathrm{ex3,1}}[\mathrm{bfa}^-][\mathrm{tba}^+] \quad (5\mathrm{a})$$

and

$$K_{\mathrm{ex3,1}} = [\mathrm{tba}^+\mathrm{M(bfa)_3}]_{\mathrm{org}}[\mathrm{M}^{2+}]^{-1}[\mathrm{bfa}^-]^{-3}[\mathrm{tba}^+]^{-1}. \quad (6)$$

The following equation can thus be introduced:

$$D^*/D_0{}^* = 1 + (K_{\mathrm{ex3,1}}/K_{\mathrm{ex2,0}})[\mathrm{bfa}^-][\mathrm{tba}^+], \quad (7)$$

where $D_0{}^*$ is $D_0 \times [\mathrm{bfa}^-]^{-2}$ and D^* is $D \times [\mathrm{bfa}^-]^{-2}$.

The enhancement of extraction can be written more clearly as

$$\mathrm{M(bfa)_{2(org)}} + \mathrm{tba^+bfa^-_{(org)}} \rightleftharpoons \mathrm{tba^+M(bfa)_3{}^-_{(org)}}$$
$$K_{\mathrm{org}} = [\mathrm{tba}^+\mathrm{M(bfa)_3}^-]_{\mathrm{org}}[\mathrm{M(bfa)_2}]_{\mathrm{org}}{}^{-1}[\mathrm{tba}^+\mathrm{bfa}^-]_{\mathrm{org}}{}^{-1} \quad (8)$$

and

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

From Eqs. 4, 5, 6, 7, and 9, the following equations can be written:

$$K_{\mathrm{org}} = K_{\mathrm{ex3,1}} \times K_{\mathrm{ex2,0}}{}^{-1}K_{\mathrm{exAB}}{}^{-1},$$
$$D = K_{\mathrm{ex2,0}}[\mathrm{bfa}^-]^2\left(1 + K_{\mathrm{org}} \times K_{\mathrm{exAB}}[\mathrm{bfa}^-][\mathrm{tba}^+]\right) \quad (10)$$

and

$$D^*/D_0{}^* = 1 + (K_{\mathrm{org}} \times K_{\mathrm{exAB}})[\mathrm{bfa}^-][\mathrm{tba}^+]. \quad (11)$$

When the neutral complex ($\mathrm{M(bfa)_2}$) forms adducts with n molecules of a neutral ligand (L) such as TOPO in the organic phase, the distribution ratio in the presence of L can generally be written when the formation of three adducts are assumed to be:

$$D = \left([\mathrm{M(bfa)_2}]_{\mathrm{org}} + [\mathrm{M(bfa)_2L}]_{\mathrm{org}} + [\mathrm{M(bfa)_2L_2}]_{\mathrm{org}} + [\mathrm{M(bfa)_2L_3}]_{\mathrm{org}}\right)/[\mathrm{M}^{2+}] = K_{\mathrm{ex2,0}}[\mathrm{bfa}^-]^2\left(1 + \beta_{(\mathrm{org})1}[\mathrm{L}]_{\mathrm{org}} + \beta_{(\mathrm{org})2}[\mathrm{L}]_{\mathrm{org}}{}^2 + \beta_{(\mathrm{org})3}[\mathrm{L}]_{\mathrm{org}}{}^3\right), \quad (12)$$

where

$$\beta_{(\mathrm{org})n} = [\mathrm{M(bfa)_2L}_n]_{\mathrm{org}}[\mathrm{M(bfa)_2}]_{\mathrm{org}}{}^{-1}[\mathrm{L}]_{\mathrm{org}}{}^{-n}. \quad (13)$$

The following equation can thus be introduced from Eqs. 3 and 12 where $D_0{}^*$ and D^* are the same as already given:

$$D^*/D_0{}^* = 1 + \beta_{(\mathrm{org})1}[\mathrm{L}]_{\mathrm{org}} + \beta_{(\mathrm{org})2}[\mathrm{L}]_{\mathrm{org}}{}^2 + \beta_{(\mathrm{org})3}[\mathrm{L}]_{\mathrm{org}}{}^3. \quad (14)$$

For these calculations, the concentration at equilibrium should be used; it can be obtained by

$$[\mathrm{tba}^+]_{\mathrm{init}} = [\mathrm{tba}^+] + [\mathrm{tba}^+\mathrm{M(bfa)_3}^-]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{bfa}^-]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{NO_3}^-], \quad (15)$$

$$K_{\mathrm{exXB}} = [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}}[\mathrm{NO_3}^-]^{-1}[\mathrm{tba}^+]^{-1} \quad (16)$$

and

$$[\mathrm{TOPO}]_{\mathrm{org,init}} = [\mathrm{TOPO}]_{\mathrm{org}} + [\mathrm{TOPO}] + [\mathrm{M(bfa)_2TOPO}]_{\mathrm{org}} + 2[\mathrm{M(bfa)_2TOPO_2}]_{\mathrm{org}} + 3[\mathrm{M(bfa)_2TOPO_3}]_{\mathrm{org}} + [\mathrm{Hbfa{\cdot}TOPO}]_{\mathrm{org}}. \quad (17)$$

The concentration of the associated TOPO with Hbfa can be calculated by using

$$K_{\mathrm{ass}} = [\mathrm{Hbfa{\cdot}TOPO}]_{\mathrm{org}}[\mathrm{Hbfa}]^{-1}{}_{\mathrm{org}}[\mathrm{TOPO}]^{-1}{}_{\mathrm{org}}. \quad (18)$$

Results

Figure 1a to Fig. 1d give the extraction curves of Mg(II), Ca(II), Sr(II), and Ba(II). The open circles give the data in the absence of either tba^+ or TOPO. The plots in the absence of tba^+ and TOPO are straight lines with a slope of +2. As can be seen from Eq. 3, this indicates that the complexes with bfa^- in the aqueous phase are negligible with all of the four metal ions. Since the experiments in the presence of tba^+ or TOPO were carried out in the lower concentration range of bfa^-, complexes in the aqueous phase should also be negligible. The data obtained in the absence of tba^+ and TOPO

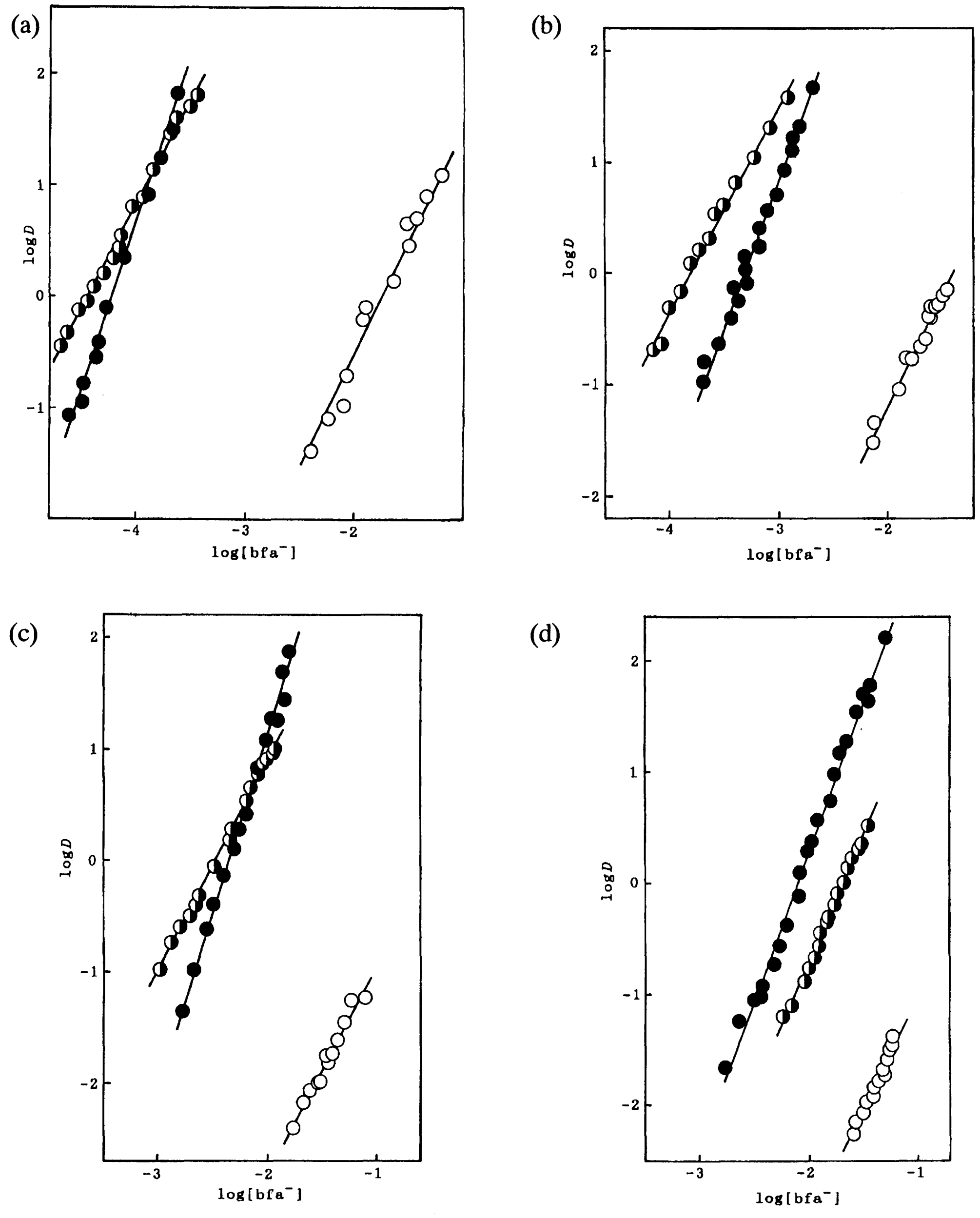

Fig. 1. Extraction curves of (a) Mg(II), (b) Ca(II), (c) Sr(II), and (d) Ba(II) with Hbfa from 0.1 mol dm^{-3} $NaNO_3$ solutions into carbon tetrachloride as a function of the concentration of bfa^- in the aqueous phase in the absence and presence of tba^+ or TOPO. The open symbols show the system containing no tba^+ and TOPO, the closed symbols show $[tba^+]_{init}=1.0\times10^{-3}$ mol dm^{-3} and the semiclosed symbols show $[TOPO]_{org,init}=1.0\times10^{-3}$ mol dm^{-3}. The lines were calculated by using Eqs. 3, 5, and 12 in the manner explained in the text.

were treated on the basis of Eq. 3, and the values of $K_{ex2,0}$ were calculated as given in Table 1. The line for the data in each figure was plotted by introducing the constants given in Table 1 into Eq. 3, while assuming no complex formation in the aqueous phase.

The addition of tba^+ enhanced the extraction of all the four metal ions; the slope of the plot is nearly +3, as is shown in Fig. 1a to Fig. 1d. This is well explained by the extraction of the ion-pair of the anionic complex ($tba^+M(bfa)_3^-$). Figures 2a and 2b give the distribution ratio as a function of the calculated value of $[tba^+][bfa^-]$ in the aqueous phase. As can be seen from Eq. 5a, if the $M(bfa)_2$ species is negligible and $tba^+M(bfa)_3^-$ is only the metal species, the plots given in Figs. 2a and 2b should be straight lines having a slope of +1, as is shown in these figures. The extraction constants of the anionic chelate ($K_{ex3,1}$) in Eq. 6 was calculated for each metal ion from the data given in Fig. 1a to Fig. 1d and in Figs. 2a and 2b by a successive approximation method using a least-squares computer program. In these calculations, the value $K_{exAB}=10^{1.27}$ was used, and the negligible extraction of the ion-pairs of $tba^+NO_3^-$ into

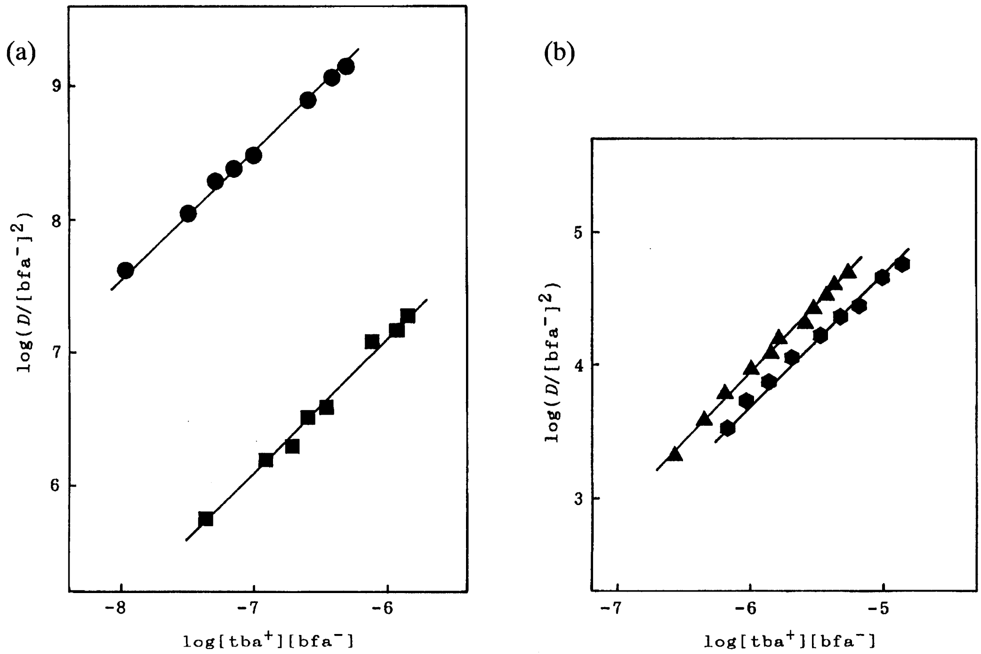

Fig. 2. Extraction of (a) Mg(II) (●) and Ca(II) (■) and (b) Sr(II) (▲) and Ba(II) (⬢) given as a function of the value $[tba^+][bfa^-]$ (cf. Eq. 5a). Org. phase: CCl_4 containing 0.1 mol dm^{-3} Hbfa, aq phase 0.1 mol dm^{-3} $NaNO_3$ containing tba^+ at various concentrations and the $-\log[H^+]$ is in the region from 5.3 to 5.6 for Mg(II), from 5.7 to 6.1 for Ca(II), and from 7.3 to 7.4 for Sr(II) and Ba(II). The curves were calculated by using the set of values given in the text.

Table 1. Summary of the Equilibrium Constants

	Mg(II)	Ca(II)	Sr(II)	Ba(II)	Remarks
i) Extraction of neutral chelate					
$\log K_{ex2,0}$	3.48	2.78	1.10	0.97	a)
ii) Extraction of anionic chelate with tba^+					
$\log K_{ex3,1}$	15.65	12.95	10.15	9.40	b)
$\log K_{org}$	10.90	8.90	7.78	7.16	c)
iii) Extraction of adduct with TOPO					
$\log \beta_{(org)1}$	6.75	6.43	—e)	—e)	d)
$\log \beta_{(org)2}$	11.64	11.21	10.27	8.88	d)
$\log \beta_{(org)3}$	Nil	Nil	Nil	12.67	d)

a) Eq. 4, b) Eq. 6, c) Eqs. 8 and 10, and d) Eq. 13, e) The value is very erroneous and this species is not confirmed.

carbon tetrachloride was assumed.[2)] The free tba^+ concentration was calculated for each experimental point when the constant $K_{ex3,1}$ was determined. The following set of five values can thus be obtained for each experimental point: D, D_{cal} (D calculated by Eq. 5), $[tba^+]_{init}$, $[tba^+]$ at equilibrium (free tba^+ concentration) and $[bfa^-]$. The lines in Fig. 1a to Fig. 1d were drawn by using D_{cal} and $[bfa^-]$. The lines in Figs. 2a and 2b were drawn by using D_{cal} and $[tba^+]$. The association constant of the $M(bfa)_2$ with tba^+bfa^- for each complex (K_{org} in Eq. 8) was calculated from the values of $K_{ex2,0}$, $K_{ex3,1}$, and K_{exAB} on the basis of Eq. 10, as is listed in Table 1.

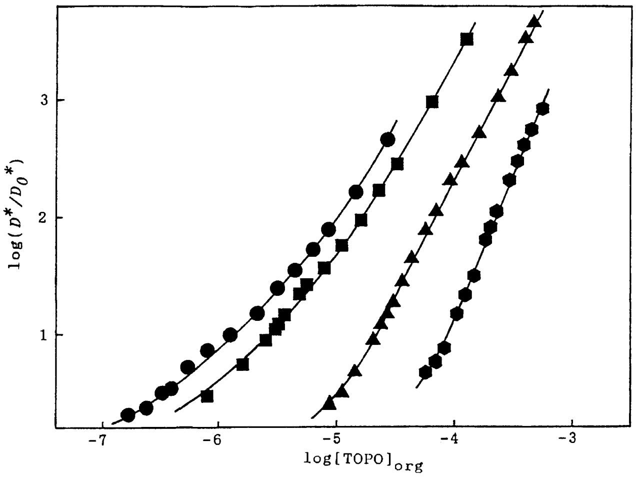

Fig. 3. Values of $D^*/D_0{}^*$ in Eq. 14 of Mg(II) (●), Ca(II) (■), Sr(II) (▲), and Ba(II) (⬢) by extraction with Hbfa as a function of TOPO concentration. Org. phase: CCl_4 containing 0.1 mol dm^{-3} Hbfa, aq phase 0.1 mol dm^{-3} $NaNO_3$. The $-\log[H^+]$ is in the region from 7.2 to 7.4 for Mg(II) and Ca(II), from 8.0 to 8.2 for Sr(II) and Ba(II). The lines were calculated by Eqs. 14 and 17, which are introduced as the values of constants in Table 1 and $10^{0.59}$ as K_{ass} in Eq. 18.

Upon the addition of TOPO, the extraction was also greatly enhanced. This can be seen from Fig. 1a to Fig. 1d. Figure 3 gives the enhancement of the extraction as a function of the TOPO concentration at equilibrium. In a similar manner to that for tba^+, the adduct formation constants ($\beta_{(\mathrm{org})n}$ in Eq. 13) were calculated from these data on the basis of Eq. 14, which was combined with Eq. 17. For the calculation of [Hbfa·TOPO] in Eq. 17, the value of K_{ass} in Eq. 18, which was reported to be $10^{0.59}$ in carbon tetrachloride,[6] was used. It was found from the calculation that the equilibrium concentration of TOPO was much lower than the initial concentration, especially when the TOPO concentration was low: The former was only a few percent of the latter in the lowest concentration range. Although this difference was much smaller when the TOPO concentration was higher, a calculation based on Eq. 17 was always indispensable.

A set of five values (D, D_{cal} (D calculated by Eq. 12), $[\mathrm{TOPO}]_{\mathrm{org,init}}$, $[\mathrm{TOPO}]_{\mathrm{org}}$ (at equilibrium) and $[\mathrm{bfa}^-]$) were obtained for each experimental point. The lines for the semiclosed circles in Fig. 1a to Fig. 1d were drawn by using D_{cal} and $[\mathrm{bfa}^-]$, and the lines in Fig. 3 were drawn by using the calculated $D^*/D_0{}^*$ and $[\mathrm{TOPO}]_{\mathrm{org}}$. It was found that the values of $\beta_{(\mathrm{org})1}$ for $\mathrm{Sr(bfa)_2}$ and $\mathrm{Ba(bfa)_2}$ were erroneous. It was also concluded that the data for barium(II) could be well explained by assuming the formation of a third adduct, $\mathrm{Ba(bfa)_2(TOPO)_3}$, in addition to the second adduct.

Discussion

The constant $K_{\mathrm{ex3,1}}$ shows the over-all equilibrium of the extraction of anionic complex, $\mathrm{M(bfa)_3{}^-}$, together with tba^+. Since the formation of anionic complexes in the aqueous phase can often not be estimated from the extraction data, it is often not possible to know the extractability of the anionic complex given in the following equation even though the anionic complex is actually extracted:

$$K_{\mathrm{ex\ anion}} = [\mathrm{tba^+M(ba)_3{}^-}]_{\mathrm{org}}[\mathrm{tba^+}]^{-1}[\mathrm{M(bfa)_3{}^-}]^{-1}. \quad (19)$$

A discussion based on Eq. 11 enables a general consideration in such cases. The K_{exAB} used in Eq. 11 is the extraction constant of the reagents: It is a general constant as long as this combination of reagents is employed. The K_{org} used in Eq. 11 can be obtained from the experimental data. This shows the acceptability of the neutral chelate, $\mathrm{M(bfa)_2}$, for one more chelating ligand anion, bfa^-, in the organic phase; this should be a good index for comparing the extractability and stability of the anionic complexes in a systematic way. This constant (K_{org}) can be compared with the $\beta_{(\mathrm{org})n}$ in Eq. 13 when the acceptability of the $\mathrm{M(bfa)_2}$ species is considered. From Table 1, it is seen that the both association constants, K_{org} and $\beta_{(\mathrm{org})n}$, are larger in the order $\mathrm{Mg(bfa)_2 > Ca(bfa)_2 > Sr(bfa)_2 > Ba(bfa)_2}$. This should be due to the fact that the ability of the $\mathrm{M(bfa)_2}$ chelate to associate with additional ligands is higher in this order.

As was pointed out, the initial and equilibrium concentrations of TOPO in Fig. 3, were very different. This is because in the lower TOPO concentration range, the proportion of the $[\mathrm{M(bfa)_2TOPO}]_{\mathrm{org}}$ and $[\mathrm{M(bfa)_2(TOPO)_2}]_{\mathrm{org}}$ terms to the total TOPO concentration in Eq. 17 is high. Furthermore, the decrease in the "free" TOPO concentration by its association with Hbfa (given in Eq. 18) is not negligible. From the value of K_{ass} in Eq. 18 of Hbfa with TOPO in carbon tetrachloride, $10^{0.59}$, it can be calculated that the proportion $[\mathrm{Hbfa{\cdot}TOPO}]_{\mathrm{org}}/[\mathrm{TOPO}]_{\mathrm{org}}$ is about 0.4 when $[\mathrm{Hbfa}]_{\mathrm{org}}$ is 0.1 $\mathrm{mol\,dm^{-3}}$. In other words, about 30% of the TOPO which is not combined with the chelate is in the form of the associate with the β-diketone; this part should be excluded from the calculation of free TOPO concentration by using Eq. 17.

From Table 1, it is seen that the association constant of the metal chelate with two TOPO molecules, $\beta_{(\mathrm{org})2}$, is larger in the same order as that of K_{org}. The same order was also found with the synergistic effect of the 2-thenoyltrifluoroacetone (Htta) extraction of these metals with TBP.[7] This seems to be quite reasonable, since these two enhancements of solvent extraction, which are apparently different chemical phenomena, can be treated in similar statistical manner if they are considered in the way that the central metal ion in the neutral complex is associated with two oxygen atoms of the ligand, though TOPO is monodentate and bfa^- is bidentate. However a direct comparison of the values, $\beta_{(\mathrm{org})2}$ and K_{org}, cannot be made, since the dimensions of the constants are different from each other.

The extraction with Hbfa in the absence of tba^+ or TOPO is also better in the same manner, as can be seen from the values of $K_{\mathrm{ex2,0}}$; thus, by extracting the ternary complex, an even better separation of these elements is possible.

The extraction of alkaline earth metal ions as the ternary complexes enables the quantitative extraction of these metal ions from aqueous solutions. In the absence of tba^+, the best extraction with 0.1 $\mathrm{mol\,dm^{-3}}$ Hbfa is about 93% for Mg(II), about 60% for Ca(II), about 7% for Sr(II) and about 6% for Ba(II) (when $[\mathrm{bfa}^-]$ is 0.08 $\mathrm{mol\,dm^{-3}}$). On the other hand, the extraction is calculated from the values of the constants given in Table 1 to be more than 99% ($\log D > 2$) for these metal ions in the presence of 1×10^{-3} $\mathrm{mol\,dm^{-3}}$ of tba^+ (an initial) when $\log[\mathrm{bfa}^-]$ is -3.4 with Mg(II), -2.5 with Ca(II), -1.7 with Sr(II), and -1.4 with Ba(II).

The effect of the addition of TOPO on the mutual separation of these four metal ions is not so marked as that caused by the addition of tba^+, though it greatly enhanced the extraction.

Although the synergistic extraction of alkaline earth ions with a β-diketone and TBP or TOPO has been used for several purposes,[8,9] the estimation of the equilibrium involved does not seem to have been made systematically.

The synergistic enhancement of lanthanoide ions is somewhat different from that of alkaline earth metal ions. Although the extraction with Htta is better in the order of Lu(III)>Eu(III)>La(III), the synergistic effect with TBP or TOPO is larger in the opposite order.[3] Thus, the addition of TBP to the extraction system of trivalent lanthanoide ions greatly improves the extraction, but impairs the separation. The addition of tba^+ to the extraction systems of lanthanoide ions with Htta also enhanced the extraction by extracting the ternary complexes, $tba^+MA_4^-$. However, it was found that the mutual separation was not improved,[5] or, to some extent, even impaired. For this reason, it can be concluded that the addition of tba^+ or TOPO into the extraction systems of alkaline earth ions is more useful than into the extraction systems of lanthanoide ions.

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