2242 © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 2242—2250(1993) [Vol. 66, No. 8

Solvent Extraction of Europium(III) with 1-Naphthoic Acid into Chloroform in the Absence and Presence of Tetrabutylammonium Ions or Trioctylphosphine Oxide

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(Received February 4, 1993)

The solvent extraction of europium(III) in 0.1 mol dm^{-3} sodium nitrate solutions with 1-naphthoic acid (HA) into chloroform was studied in the absence and presence of tetrabutylammonium ions (tba$^+$) or trioctylphosphine oxide (TOPO). In the absence of tba$^+$ and TOPO the distribution ratio of europium(III) with 0.1 mol dm^{-3} 1-naphthoic acid was higher when the initial concentration of the metal was higher under otherwise identical conditions. This could be explained in terms of the extraction of a polynuclear species, $Eu_2A_6(HA)_2$, in addition to a mononuclear species, EuA_3HA. Furthermore, by the addition of tba$^+$ or TOPO, the extraction of europium(III) was greatly enhanced. This could be explained in terms of the extraction of the ternary complex, $EuA_4{}^-tba^+$, or the adducts, EuA_3TOPO and $EuA_3(TOPO)_2$, like that found in the extraction of this metal ion with β-diketones. In these systems the extracted anionic complex with tba$^+$ or the adducts with TOPO were only mononuclear, even under conditions in which the polynuclear species were extracted in the absence of these.

In previous papers[1—5] it was reported that the extraction of europium(III) with β-diketones containing the $CF_3{}^-$ group became much better by an addition of tetrabutylammonium ions (tba$^+$). This was explained in terms of the extraction of anionic complexes with four β-diketonate ions (E^-) as ion-pairs with tba$^+$, $EuE_4{}^-tba^+$, since the extraction of this type of ion-pairs was much better than that of the non-charged complexes, EuE_3, under otherwise identical conditions, the extraction was enhanced. This extraction of the ternary complex was treated in previous papers on the basis of the extraction equilibrium of the non-charged chelate, EuE_3, and that of the ion-pairs of the reagents, E^-tba^+, and the association equilibrium of the complex with the ion-pairs of the reagents in the organic phase. Furthermore, it was pointed out that this association of the non-charged chelate with the ion-pair in the organic phase could be compared with adduct formation of the non-charged chelate with non-charged ligands, such as tributylphosphate (TBP) or trioctylphosphine oxide (TOPO), in the organic phase, which also formed metal complexes having higher coordination numbers. The "synergistic effect" of europium(III) was studied with several extractants as well as with several neutral lignds.[6—9] It was reported in a previous paper[8] that the addition of 0.1 mol dm^{-3} TBP enhanced the solvent extraction of europium(III) with 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione) by a factor of 2.5×10^3; that with 1-naphthoic acid was enhanced by a factor of 13; and that with β-isopropyltropolone and 5,7-dichloro-8-quinolinol were enhanced by a factor of 3. Due to the similarity of the ternary complex extraction and the synergistic extraction, it was assumed that the solvent extraction of europium(III) with 1-naphthoic acid (HA) should be enhanced by an addition of the large cations, tba$^+$.

In order to confirm this assumption experimentally, the solvent extraction of europium(III) with 1-naphthoic acid into chloroform in both the absence and presence of tba$^+$ or TOPO was studied. From a statistical analysis of the results, the chemical equilibria in the systems under these conditions were estimated and the similarity of the enhancement of extraction due to the anionic complex species together with the large cations to that due to the synergistic effect was considered.

Statistical

In the present paper, all chemical species in the organic phase are denoted by the subscript "org" and that in the aqueous phase is shown without any subscript. The volumes of the two liquid phases are assumed to be the same.

For the initial concentration of 1-naphthoic acid in the initial organic phase, $[HA]_{org,initial}$, the following relation can be given:

$$[HA]_{org,initial} = [A^-] + [HA] + \Sigma n[(HA)_n]_{org}. \qquad (1)$$

However, since only the monomer and dimer were experimentally found in the organic phase under the conditions employed in the present study, the following simplified equations are given here:

$$[HA]_{org,initial} = [A^-] + [HA] + [HA]_{org} + 2[(HA)_2]_{org}. \qquad (2)$$

The two-phase distribution, the acid dissociation, and the dimerization equilibrium for HA can be written as follows:

$$HA \rightleftharpoons HA_{(org)}; \quad K_d = [HA]_{org}/[HA], \qquad (3)$$

$$HA \rightleftharpoons H^+ + A^-; \quad K_a = [H^+][A^-]/[HA], \qquad (4)$$

and

$$2\mathrm{HA}_{(\mathrm{org})} \rightleftharpoons (\mathrm{HA})_{2(\mathrm{org})};\ K_{\mathrm{dim}} = [(\mathrm{HA})_2]_{\mathrm{org}}/[\mathrm{HA}]_{\mathrm{org}}{}^2. \quad (5)$$

By introducing Eqs. 3, 4, and 5, Eq. 2 can be rewritten as

$$\begin{aligned}[\mathrm{HA}]_{\mathrm{org,initial}} &= [\mathrm{A}^-] + (K_{\mathrm{d}}+1)\,[\mathrm{A}^-][\mathrm{H}^+]/K_{\mathrm{a}} \\ &+ 2K_{\mathrm{dim}}K_{\mathrm{d}}{}^2[\mathrm{A}^-]^2[\mathrm{H}^+]^2/K_{\mathrm{a}}{}^2. \quad (6)\end{aligned}$$

The concentration of the extractant anion, A^-, can be calculated from Eq. 6 as

$$[\mathrm{A}^-] = \left(-b + \sqrt{b^2+4ac}\right)/2a, \quad (7)$$

where $a{=}2K_{\mathrm{dim}}K_{\mathrm{d}}{}^2[\mathrm{H}^+]^2/K_{\mathrm{a}}{}^2$, $b{=}1{+}(K_{\mathrm{d}}{+}1)[\mathrm{H}^+]/K_{\mathrm{a}}$, and $c{=}[\mathrm{HA}]_{\mathrm{org,initial}}$. The above equations could approximately be used even when metal ions were present in the present study, since $[\mathrm{HA}]_{\mathrm{org,initial}}$ is always much higher than $[\mathrm{Eu(III)}]_{\mathrm{initial}}$.

The equilibrium for the extraction of the polynuclear europium(III) complex with only A^- may be written as

$$\begin{aligned}&n\mathrm{Eu}^{3+} + 3n\mathrm{A}^- \rightleftharpoons \mathrm{Eu}_n\mathrm{A}_{3n(\mathrm{org})}; \\ &K_{\mathrm{ex}3n,0,0} = [\mathrm{Eu}_n\mathrm{A}_{3n}]_{\mathrm{org}}/[\mathrm{Eu}^{3+}]^n[\mathrm{A}^-]^{3n}. \quad (8)\end{aligned}$$

When the extracted species is in the $\mathrm{Eu}_n\mathrm{A}_{3n}(\mathrm{HA})_m$ form, the equilibrium can be written as

$$\begin{aligned}&n\mathrm{Eu}^{3+} + 3n\mathrm{A}^- + m(\mathrm{HA})_{(\mathrm{org})} \rightleftharpoons \mathrm{Eu}_n\mathrm{A}_{3n}(\mathrm{HA})_{m(\mathrm{org})}; \\ &K_{\mathrm{ex}3n,m,0} = [\mathrm{Eu}_n\mathrm{A}_{3n}(\mathrm{HA})_m]_{\mathrm{org}} \\ &\qquad /[\mathrm{Eu}^{3+}]^n[\mathrm{A}^-]^{3n}[\mathrm{HA}]_{\mathrm{org}}{}^m. \quad (9)\end{aligned}$$

The distribution ratio of europium(III) can be given by the following equation:

$$\begin{aligned}D_0 &= \frac{[\mathrm{Eu(III)}]_{\mathrm{org,total}}}{[\mathrm{Eu(III)}]_{\mathrm{aq,total}}} = \frac{\sum\limits_n\sum\limits_m n[\mathrm{Eu}_n\mathrm{A}_{3n}(\mathrm{HA})_m]_{\mathrm{org}}}{\sum\limits_p [\mathrm{EuA}_p{}^{3-p}]} \\ &= \frac{\sum\limits_n\sum\limits_m nK_{\mathrm{ex}3n,m,0}[\mathrm{Eu}^{3+}]^{n-1}[\mathrm{A}^-]^{3n}[\mathrm{HA}]_{\mathrm{org}}{}^m}{\sum\limits_p \beta_p[\mathrm{A}^-]^p}, \quad (10)\end{aligned}$$

where β_p is the following stability constant:

$$\beta_p = [\mathrm{EuA}_p{}^{3-p}]/[\mathrm{Eu}^{3+}][\mathrm{A}^-]^p. \quad (11)$$

However, since only $\mathrm{EuA_3HA}$, $\mathrm{Eu_2A_6}$, and $\mathrm{Eu_2A_6(HA)_2}$ were experimentally found in the organic phase, and only Eu^{3+} and EuA^{2+} were found in the aqueous phase under the conditions employed in the present study, the following simplified equations are given here:

$$\begin{aligned}D_0 &= ([\mathrm{EuA_3HA}]_{\mathrm{org}} + 2[\mathrm{Eu_2A_6}]_{\mathrm{org}} + 2[\mathrm{Eu_2A_6(HA)_2}]_{\mathrm{org}}) \\ &\quad /\left([\mathrm{Eu}^{3+}] + [\mathrm{EuA}^{2+}]\right) \quad (12) \\ &= \Big(K_{\mathrm{ex}3,1,0}[\mathrm{A}^-]^3[\mathrm{HA}]_{\mathrm{org}} + 2K_{\mathrm{ex}6,0,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6 \\ &\quad + 2K_{\mathrm{ex}6,2,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6[\mathrm{HA}]_{\mathrm{org}}{}^2\Big) / \left(1+\beta_1[\mathrm{A}^-]\right). \quad (13)\end{aligned}$$

The free concentration of Eu^{3+} in the aqueous phase may be introduced from Eq. 11 as

$$[\mathrm{Eu(III)}]_{\mathrm{aq,total}} = [\mathrm{Eu}^{3+}] + [\mathrm{EuA}^{2+}]$$

and

$$[\mathrm{Eu}^{3+}] = [\mathrm{Eu(III)}]_{\mathrm{aq,total}}/\left(1+\beta_1[\mathrm{A}^-]\right). \quad (14)$$

When tba^+ is added into the system, the extraction of anionic complexes may occur and the chemical form of the tba^+ containing extracted species may be written as $\mathrm{EuA_4}^-\mathrm{tba}^+$. This extraction equilibrium can be written as

$$\begin{aligned}&\mathrm{Eu}^{3+} + 4\mathrm{A}^- + \mathrm{tba}^+ \rightleftharpoons \mathrm{EuA_4}^-\mathrm{tba}^+{}_{(\mathrm{org})}; \\ &K_{\mathrm{ex}4,0,1} = [\mathrm{EuA_4}^-\mathrm{tba}^+]_{\mathrm{org}}/[\mathrm{Eu}^{3+}][\mathrm{A}^-]^4[\mathrm{tba}^+]. \quad (15)\end{aligned}$$

For the formation equilibrium of the ion-pairs, $\mathrm{EuA_4}^-\mathrm{tba}^+$, the following equation may be written:

$$\begin{aligned}&\mathrm{EuA_3HA}_{(\mathrm{org})} + \mathrm{A}^-\mathrm{tba}^+{}_{(\mathrm{org})} \rightleftharpoons \mathrm{EuA_4}^-\mathrm{tba}^+{}_{(\mathrm{org})} + \mathrm{HA}_{(\mathrm{org})}; \\ &K_{\mathrm{org}}{}^* = [\mathrm{EuA_4}^-\mathrm{tba}^+]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{EuA_3HA}]_{\mathrm{org}}[\mathrm{A}^-\mathrm{tba}^+]_{\mathrm{org}}. \\ &\qquad (16)\end{aligned}$$

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

$$\begin{aligned}&\mathrm{A}^- + \mathrm{tba}^+ \rightleftharpoons \mathrm{A}^-\mathrm{tba}^+{}_{(\mathrm{org})}; \\ &K_{\mathrm{exAB}} = [\mathrm{A}^-\mathrm{tba}^+]_{\mathrm{org}}/[\mathrm{A}^-][\mathrm{tba}^+] \quad (17)\end{aligned}$$

$$\begin{aligned}&\mathrm{X}^- + \mathrm{tba}^+ \rightleftharpoons \mathrm{X}^-\mathrm{tba}^+{}_{(\mathrm{org})}; \\ &K_{\mathrm{exXB}} = [\mathrm{X}^-\mathrm{tba}^+]_{\mathrm{org}}/[\mathrm{X}^-][\mathrm{tba}^+]. \quad (18)\end{aligned}$$

The free concentration of tba^+ can be written as

$$\begin{aligned}[\mathrm{tba}^+]_{\mathrm{initial}} &= [\mathrm{tba}^+] + [\mathrm{EuA_4}^-\mathrm{tba}^+]_{\mathrm{org}} \\ &+ [\mathrm{A}^-\mathrm{tba}^+]_{\mathrm{org}} + [\mathrm{X}^-\mathrm{tba}^+]_{\mathrm{org}} \quad (19)\end{aligned}$$

and

$$\begin{aligned}[\mathrm{tba}^+] &= \left([\mathrm{tba}^+]_{\mathrm{initial}} - [\mathrm{EuA_4}^-\mathrm{tba}^+]_{\mathrm{org}}\right) \\ &\quad /\left(1 + K_{\mathrm{exAB}}[\mathrm{A}^-] + K_{\mathrm{exXB}}[\mathrm{X}^-]\right). \quad (20)\end{aligned}$$

The distribution ratio in the presence of tba^+ should be written as

$$\begin{aligned}D &= ([\mathrm{EuA_3HA}]_{\mathrm{org}} + 2[\mathrm{Eu_2A_6}]_{\mathrm{org}} + 2[\mathrm{Eu_2A_6(HA)_2}]_{\mathrm{org}} \\ &+ [\mathrm{EuA_4}^-\mathrm{base}^+]_{\mathrm{org}}\big) / \left([\mathrm{Eu}^{3+}] + [\mathrm{EuA}^{2+}]\right) \quad (21)\end{aligned}$$

$$= \Big(K_{\mathrm{ex}3,1,0}[\mathrm{A}^-]^3[\mathrm{HA}]_{\mathrm{org}} + 2K_{\mathrm{ex}6,0,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6 + 2K_{\mathrm{ex}6,2,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6[\mathrm{HA}]_{\mathrm{org}}{}^2 + K_{\mathrm{ex}4,0,1}[\mathrm{A}^-]^4[\mathrm{tba}^+]\Big) \Big/ \Big(1+\beta_1[\mathrm{A}^-]\Big) \qquad (22)$$

$$= \Big(K_{\mathrm{ex}3,1,0}[\mathrm{A}^-]^3[\mathrm{HA}]_{\mathrm{org}} + 2K_{\mathrm{ex}6,0,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6 + 2K_{\mathrm{ex}6,2,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6[\mathrm{HA}]_{\mathrm{org}}{}^2 + K_{\mathrm{org}}{}^*K_{\mathrm{exAB}}K_{\mathrm{ex}3,1,0}[\mathrm{A}^-]^4[\mathrm{tba}^+]\Big) \Big/ \Big(1+\beta_1[\mathrm{A}^-]\Big). \qquad (23)$$

In the absence of europium(III), the distribution ratio of tba^+, D_{tba}, may be introduced from Eqs. 17 and 18 as

$$\begin{aligned} D_{\mathrm{tba}} &= [\mathrm{tba}^+]_{\mathrm{org,total}}/[\mathrm{tba}^+] \\ &= \Big([\mathrm{A}^-\mathrm{tba}^+]_{\mathrm{org}} + [\mathrm{X}^-\mathrm{tba}^+]_{\mathrm{org}}\Big)/[\mathrm{tba}^+] \\ &= K_{\mathrm{exAB}}[\mathrm{A}^-] + K_{\mathrm{exXB}}[\mathrm{X}^-]. \end{aligned} \qquad (24)$$

When TOPO is added into the system, the extraction of adduct complexes may occur and the chemical form of the TOPO containing extracted species may be given as $\mathrm{EuA_3TOPO}$ and $\mathrm{EuA_3(TOPO)_2}$. For the formation equilibrium of the adduct complexes, $\mathrm{EuA_3(TOPO)}_n$, the following equations may be written:

$$\begin{aligned} &\mathrm{EuA_3HA_{(org)}} + n(\mathrm{TOPO})_{(\mathrm{org})} \rightleftharpoons \mathrm{EuA_3(TOPO)}_{n(\mathrm{org})} + \mathrm{HA_{(org)}}; \\ &\beta_{(\mathrm{org})n}{}^* = [\mathrm{EuA_3(TOPO)}_n]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}} / [\mathrm{EuA_3HA}]_{\mathrm{org}}[\mathrm{TOPO}]_{\mathrm{org}}{}^n. \end{aligned} \qquad (25)$$

The distribution ratio in the presence of TOPO should be written as

$$D = \Big([\mathrm{EuA_3HA}]_{\mathrm{org}} + 2[\mathrm{Eu_2A_6}]_{\mathrm{org}} + 2[\mathrm{Eu_2A_6(HA)_2}]_{\mathrm{org}} + \sum [\mathrm{EuA_3(TOPO)}_n]_{\mathrm{org}}\Big) \Big/ \Big([\mathrm{Eu}^{3+}] + [\mathrm{EuA}^{2+}]\Big) \qquad (26)$$

$$= \Big(K_{\mathrm{ex}3,1,0}[\mathrm{A}^-]^3[\mathrm{HA}]_{\mathrm{org}} + 2K_{\mathrm{ex}6,0,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6 + 2K_{\mathrm{ex}6,2,0}[\mathrm{Eu}^{3+}][\mathrm{A}^-]^6[\mathrm{HA}]_{\mathrm{org}}{}^2 + \sum \beta_{(\mathrm{org})n}{}^*K_{\mathrm{ex}3,1,0}[\mathrm{A}^-]^3[\mathrm{TOPO}]_{\mathrm{org}}{}^n\Big) \Big/ \Big(1+\beta_1[\mathrm{A}^-]\Big). \qquad (27)$$

The association equilibrium of 1-naphthoic acid and TOPO in the organic phase may be written as

$$\begin{aligned} &\mathrm{TOPO_{(org)}} + \mathrm{HA_{(org)}} \rightleftharpoons \mathrm{TOPO{\cdot}HA_{(org)}} \\ &K_{\mathrm{LHA(org)}} = [\mathrm{TOPO{\cdot}HA}]_{\mathrm{org}}/[\mathrm{TOPO}]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}}. \end{aligned} \qquad (28)$$

The free concentration of TOPO can be written as

$$[\mathrm{TOPO}]_{\mathrm{org,initial}} = [\mathrm{TOPO}]_{\mathrm{org}} + [\mathrm{TOPO{\cdot}HA}]_{\mathrm{org}} + \sum n[\mathrm{EuA_3TOPO}_n]_{\mathrm{org}} \qquad (29)$$

$$[\mathrm{TOPO}]_{\mathrm{org}} = \Big([\mathrm{TOPO}]_{\mathrm{org,initial}} - \sum n\,[\mathrm{EuA_3TOPO}_n]_{\mathrm{org}}\Big) \Big/ \Big(1 + K_{\mathrm{LHA(org)}}[\mathrm{HA}]_{\mathrm{org}}\Big). \qquad (30)$$

Since the concentration of TOPO in the aqueous phase should be very low, this term can be excluded as in Eq. 29.

Experimental

All of the reagents and the experimental procedures were similar to those in previous studies,[1—5] except that 1-naphthoic acid (HA), which was obtained from Tokyo Kasei Co., was used as the extractant and trioctylphosphine oxide, which was obtained from Tokyo Kasei Co., was used as the neutral ligand. Since the dissociated acid anion, A^-, was formed from HA by the addition of sodium hydroxide into the aqueous phase and these buffered the solution, no buffering agent was added.

For the determination of the two-phase distribution, the acid dissociation, and the dimerization constant for 1-naphthoic acid, a chloroform solution containing a certain amount of 1-naphthoic acid was agitated with the same volume of 0.1 $\mathrm{mol\,dm^{-3}}$ $\mathrm{Na(OH,NO_3)}$ solution for one hour and then centrifuged off. The two phases were separated and the pH of the aqueous phase was measured. The concentration of dissolving A^- in the aqueous phase was estimated by a similar method to that described in a previous paper.[10]

The determination of the association constant of TOPO and 1-naphthoic acid in the organic phase was determined as follows. A chloroform solution containing 0.1 $\mathrm{mol\,dm^{-3}}$ 1-naphthoic acid and a certain amount of TOPO was agitated with the same volume of aqueous 0.1 $\mathrm{mol\,dm^{-3}}$ sodium nitrate solutions containing 1×10^{-3} $\mathrm{mol\,dm^{-3}}$ sodium hydroxide for 1 h. The two phases were centrifuged off and the pH of the aqueous phase was determined.

Results

Two-Phase Equilibrium of 1-Naphthoic Acid. The equilibrium constants of 1-naphthoic acid in the system were determined as follows. The following relation can be written when C_{OH} is the initial concentration of sodium hydroxide:[10]

$$C_{\mathrm{OH}} + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-]. \qquad (31)$$

Since the pH measured was in the range of 4 to 7, the $[\mathrm{OH}^-]$ should be much smaller than the $[\mathrm{A}^-]$ and, thus, $[\mathrm{A}^-]$ was approximately equal to $C_{\mathrm{OH}}+[\mathrm{H}^+]$. Figure 1 gives a $\log([\mathrm{HA}]_{\mathrm{org,initial}}-[\mathrm{A}^-])$ vs. $\log[\mathrm{A}^-][\mathrm{H}^+]$ plot. The data were treated on the basis of Eq. 6 using a least-squares computer program, and the following values were obtained: $(K_{\mathrm{d}}+1)K_{\mathrm{a}}{}^{-1}=10^{5.54}$ and $K_{\mathrm{dim}}K_{\mathrm{d}}{}^2K_{\mathrm{a}}{}^{-2}=10^{12.81}$. From the literature value of the acid dissociation constant, $\mathrm{p}K_{\mathrm{a}}=3.6$,[11] K_{d} and K_{dim} were calculated, as listed in Table 1. The solid line in Fig. 1 was calculated on the basis of Eq. 6 by using the values for the constants in Table 1. The limiting slope of the plot in Fig. 1 is +2. As can be seen from Eq. 6, although nearly all of the acid in the organic phase is

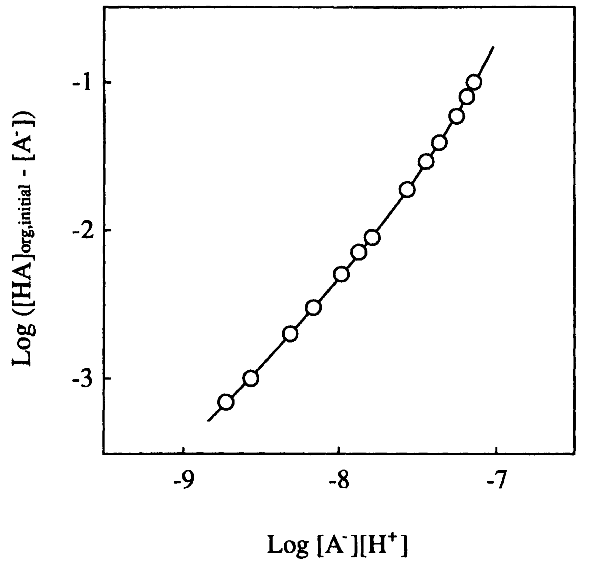

Fig. 1. Relation between log $([HA]_{org,initial}-[A^-])$ and log $[A^-][H^+]$. Org. phase: chloroform containing various amount of 1-naphthoic acid. Aq phase: 0.1 mol dm^{-3} sodium nitrate initially containing 1×10^{-3} mol dm^{-3} sodium hydroxide. The solid line was calculated on the basis of Eq. 6 using the values given in Table 1.

Table 1. Acid Dissociation, the Two-Phase Distribution, and the Dimerization Equilibrium Constant of 1-Naphthoic Acid and Extraction Constant of Tetrabutylammonium as Ion-Pair with 1-Naphthoic acid

Org. phase: chloroform. Aq phase: 0.1 mol dm^{-3} sodium nitrate.

log K_a	log K_d	log K_{dim}	log K_{exAB}
−3.6[a)]	1.9	1.8	3.6

a) Taken from Ref. 11.

in the dimer form in the highest $[HA]_{org,initial}$ region, the lower value of the slope in the lower $[HA]_{org,initial}$ range indicates that the proportion of the monomer to the dimer increases upon a decrease in the acid concentration in the initial organic phase.

Extraction of Tetrabutylammonium Ions with 1-Naphthoic Acid. The extraction constant of tba^+ as ion-pairs with 1-naphthoate ion was determined from the distribution ratio of tba^+ between chloroform and aqueous 0.1 mol dm^{-3} sodium chloride solutions. Sodium chloride solutions were employed for these experiments instead of 0.1 mol dm^{-3} sodium nitrate solutions in order to determine the constant more accurately. This was because (as discussed in a previous paper[3)]) although more than half of the tba^+ in the aqueous phase is extracted from 0.1 mol dm^{-3} sodium nitrate solutions as $NO_3{}^-tba^+$ into chloroform, the extraction from 0.1 mol dm^{-3} sodium chloride solutions is much less and, thus, the effect of background salt on the accuracy of this extraction constant should be much smaller.[3,4)] Figure 2 is a log D_{tbs} vs. log $[A^-]$ plot when the organic phase initially contained 0.1 mol dm^{-3} 1-naphthoic acid and the aqueous phase initially contained 3×10^{-3} to 2×10^{-2} mol dm^{-3} sodium hydroxide and 1×10^{-3} mol dm^{-3} tba^+. The data were treated on the basis of Eq. 24, which introduced the value $K_{exXB}=10^{0.1}$ in Ref. 3 by using a least-squares computer program. The value of K_{exAB} obtained is listed in Table 1. The solid line in Fig. 2 was calculated on the basis of Eq. 24 by using the value given in Table 1.

Association of Trioctylphosphine Oxide with 1-Naphthoic Acid. A 0.1 mol dm^{-3} sodium nitrate solution containing 1×10^{-3} mol dm^{-3} sodium hydroxide, but no europium(III), was agitated with the same volume of chloroform containing 0.1 mol dm^{-3} of 1-naphthoic acid and various amounts of TOPO. The value of the pH of the aqueous phase was determined. The data are given in Table 2. As can be seen from Table 2, the pH was essentially the same when the initial TOPO concentration was lower than 1×10^{-2} mol dm^{-3}. However, when it was higher than this, the pH of the aqueous phase became higher upon the addition of TOPO. These data were treated as follows:

$$
\begin{aligned}
[\mathrm{TOPO{\cdot}HA}]_{org} &= [\mathrm{HA}]_{org,initial} \\
&\quad - \left([\mathrm{A}^-] + [\mathrm{HA}] + [\mathrm{HA}]_{org} + 2[(\mathrm{HA})_2]_{org}\right) \\
&= K_{\mathrm{LHA(org)}}[\mathrm{TOPO}]_{org}[\mathrm{HA}]_{org}, \qquad (32)
\end{aligned}
$$

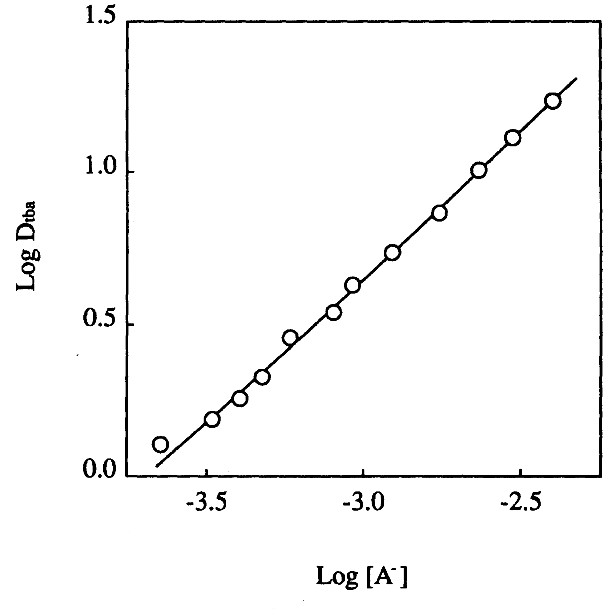

Fig. 2. Distribution ratio of tetrabutylammonium ions as a function of the concentration of the dissociated anion of 1-naphthoic acid. Org. phase: chloroform containing 0.1 mol dm^{-3} 1-naphthoic acid. Aq phase: 0.1 mol dm^{-3} sodium chloride solution containing 1×10^{-3} mol dm^{-3} tetrabutylammonium. The solid line was calculated on the basis of Eq. 24 using the values given in Table 1 and $K_{exXB}=10^{0.1}$.

Table 2. Change in the pH of the Aqueous Phase in Equilibrium with the Organic Phase Containing 1-Naphthoic Acid as a Function of the Concentration of Added TOPO

The unit of concentrations in the table is mol dm^{-3}.

$[\mathrm{TOPO}]_{\mathrm{total}}$	pH	$[\mathrm{HA}]_{\mathrm{org}}$	$[\mathrm{TOPO{\cdot}HA}]_{\mathrm{org}}$	$[\mathrm{TOPO}]_{\mathrm{org}}$	$K_{\mathrm{LHA(org)}}$
0	4.16	2.51×10^{-2}	—	—	—
1×10^{-3}	4.15	2.56×10^{-2}	—	—	—
2×10^{-3}	4.16	2.51×10^{-2}	—	—	—
3×10^{-3}	4.16	2.51×10^{-2}	—	—	—
4×10^{-3}	4.15	2.56×10^{-2}	—	—	—
5×10^{-3}	4.16	2.51×10^{-2}	—	—	—
6×10^{-3}	4.16	2.51×10^{-2}	—	—	—
7×10^{-3}	4.15	2.56×10^{-2}	—	—	—
8×10^{-3}	4.16	2.51×10^{-2}	—	—	—
1×10^{-2}	4.17	2.45×10^{-2}	6.91×10^{-3}	3.09×10^{-3}	$10^{1.96}$
2×10^{-2}	4.19	2.33×10^{-2}	1.44×10^{-2}	5.63×10^{-3}	$10^{2.04}$
3×10^{-2}	4.20	2.27×10^{-2}	1.78×10^{-2}	1.22×10^{-2}	$10^{1.81}$
4×10^{-2}	4.21	2.22×10^{-2}	2.12×10^{-2}	1.88×10^{-2}	$10^{1.71}$
5×10^{-2}	4.23	2.11×10^{-2}	2.74×10^{-2}	2.26×10^{-2}	$10^{1.76}$
6×10^{-2}	4.25	2.01×10^{-2}	3.30×10^{-2}	2.70×10^{-2}	$10^{1.78}$
7×10^{-2}	4.27	1.92×10^{-2}	3.82×10^{-2}	3.18×10^{-2}	$10^{1.80}$
8×10^{-2}	4.30	1.78×10^{-2}	4.51×10^{-2}	3.49×10^{-2}	$10^{1.86}$
1×10^{-1}	4.34	1.62×10^{-2}	5.31×10^{-2}	4.69×10^{-2}	$10^{1.84}$

a) $K_{\mathrm{LHA(org)}}$ av$=10^{1.84}$. b) When $[\mathrm{TOPO}]_{\mathrm{org,initial}}$ is lower than 1×10^{-2} mol dm^{-3}, the change in the pH by the addition of TOPO is too small to make accurate calculation of $[\mathrm{TOPO{\cdot}HA}]_{\mathrm{org}}$.

where $[\mathrm{TOPO}]_{\mathrm{org}} = [\mathrm{TOPO}]_{\mathrm{org,initial}} - [\mathrm{TOPO{\cdot}HA}]_{\mathrm{org}}$. From these the association constant, $K_{\mathrm{LHA(org)}}$ in Eq. 28, was obtained to be $10^{1.8}$.

Extraction of Europium(III) with 1-Naphthoic Acid. The extraction curves of 10^{-5} to 10^{-3} mol dm^{-3} europium(III) (at initial) with 0.1 mol dm^{-3} 1-naphthoic acid (at initial) in the organic phase are given in Fig. 3. As can be seen from Fig. 3, the extraction is better when the initial europium(III) concentration is higher. This indicates the extraction of a polynuclear species, as can be seen from Eq. 10.

From Eqs. 10 and 11, the following equation may be introduced:

$$[\mathrm{Eu(III)}]_{\mathrm{org,total}} = \sum_{n}\sum_{m} nK_{\mathrm{ex}3n,m,0}\left([\mathrm{Eu}^{3+}][\mathrm{A}^-]^3\right)^n [\mathrm{HA}]_{\mathrm{org}}{}^m. \qquad (33)$$

Figure 4 gives a $\log[\mathrm{Eu(III)}]_{\mathrm{org,total}}$ vs. $\log[\mathrm{Eu}^{3+}][\mathrm{A}^-]^3$ plot of the data in Fig. 3. The concentration of $\mathrm{HA}_{(\mathrm{org})}$ in these experiments was approximately kept constant at 2.5×10^{-2} mol dm^{-3}. As can be seen from Fig. 4 and Eq. 33, if $[\mathrm{Eu(III)}]_{\mathrm{org,total}}$ is lower than 5×10^{-6} mol dm^{-3}, the slope of the plot is nearly $+1$ and, thus, the europium(III) in the organic phase is mainly present as the mononuclear species. However, when $[\mathrm{Eu(III)}]_{\mathrm{org,total}}$ is higher than this, the extraction of the dinuclear species should be taken into account. When $[\mathrm{Eu(III)}]_{\mathrm{org,total}}$ is higher than 10^{-4} mol dm^{-3}, the slope of the plot is nearly $+2$; this indicates that the europium(III) in the organic phase is present mainly in the form of the dinuclear species.

In order to determine the number of HA in the extracted species, the distribution ratio of europium(III) was determined when its initial concentration in the aqueous phase was 1×10^{-5}, and 1×10^{-3} mol dm^{-3} as a function of the $[\mathrm{HA}]_{\mathrm{org}}$ when the concentration of A^- was approximately kept constant at 7.4×10^{-3} and at 8.0×10^{-3} mol dm^{-3}, respectively. The results are given in Fig. 5. The values of $[\mathrm{HA}]_{\mathrm{org}}$ were calculated from the $[\mathrm{HA}]_{\mathrm{org,initial}}$ and pH on the basis of Eqs. 3, 4, 5, and 6. As can be seen from Fig. 5, the distribution ratio is dependent on $[\mathrm{HA}]_{\mathrm{org}}$; this should show that the extracted species should contain the acid in the HA form. However, under conditions in which the dinuclear species are extracted, the distribution ratio is dependent not only on $[\mathrm{HA}]_{\mathrm{org}}$, but also on $[\mathrm{Eu}^{3+}]$. When the main extracted species is the dinuclear species, the following equation can be introduced from Eq. 10:

$$D_0/[\mathrm{Eu}^{3+}] = \left(\sum 2K_{\mathrm{ex}6,\mathrm{m},0}[\mathrm{A}^-]^6[\mathrm{HA}]_{\mathrm{org}}{}^m\right) / \sum \beta_p[\mathrm{A}^-]^p. \qquad (34)$$

Figure 6 is a $\log D_0/[\mathrm{Eu}^{3+}]$ vs. $\log[\mathrm{HA}]_{\mathrm{org}}$ plot when the initial europium(III) concentration is 1×10^{-3} mol dm^{-3}. Thus, the most of the extracted species should be in the dinuclear form. In Fig. 6, the limiting slope of the plot is $+2$. As can be seen from Figs. 5 and 6, the number of HA in the mononuclear species and dinuclear species in the highest $[\mathrm{HA}]_{\mathrm{org}}$ region is one and two, respectively.

The data given in Figs. 3, 4, 5, and 6 were calculated

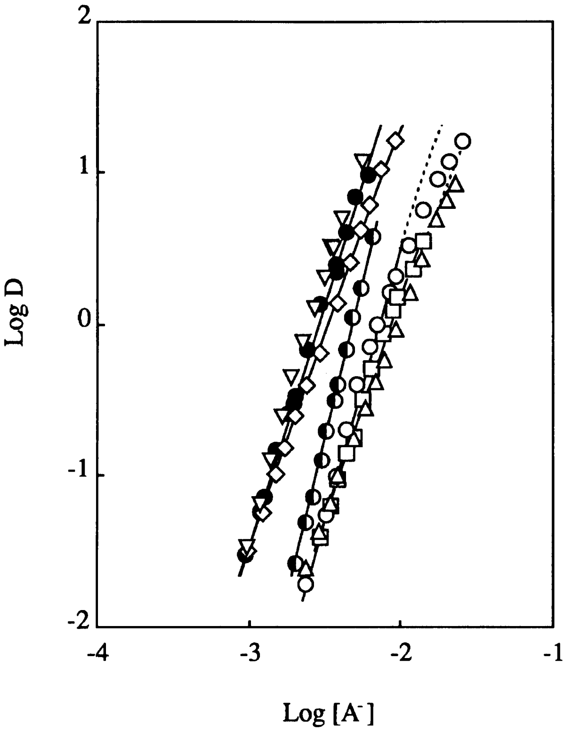

Fig. 3. Distribution ratio of europium(III) as a function of the concentration of the dissociated anion of 1-naphthoic acid in the absence and presence of tba^+ or TOPO. The initial concentration of europium(III) is 1×10^{-5} (△), 3×10^{-5} (□), 1×10^{-4} (○), 1×10^{-3} (◐) mol dm^{-3} in the absence of tba^+ or TOPO, 1×10^{-4} (●), 1×10^{-3} (▽) mol dm^{-3} in the presence of 1×10^{-2} mol dm^{-3} tba^+, and 1×10^{-4} (◇) mol dm^{-3} in the presence of 1×10^{-2} mol dm^{-3} TOPO. The solid lines were calculated on the basis of Eqs. 13, 22, and 27 using the values given in Table 3.

on the basis of Eq. 10 by a successive-approximation approach using a least-squares computer program. It was concluded from these calculations that the data can be explained by the extraction of the EuA_3HA, Eu_2A_6, and $Eu_2A_6(HA)_2$ species. The equilibrium constants for these obtained species are listed in Table 3. The solid lines in Figs. 3, 4, 5, and 6 were calculated on the basis of Eq. 13 using the values given in Table 3. Since they fit the data, it can be concluded that the data are well explained by Eqs. 12 and 13.

Effect of Tetrabutylammonium Ions on the Extraction of Europium(III) with 1-Naphthoic Acid. Although the extraction of europium(III) is greatly enhanced by the addition of tba^+, the distribution ratio is nearly similar, even when the initial europium(III) concentration is one order different but the conditions are otherwise identical, as can be seen from Fig. 3. From this, it can be concluded that only the mononuclear species in the form of $EuA_4^-tba^+$ is mainly extracted under these conditions. Although a small effect of the initial metal concentration is found in Fig. 3, even in the presence of tba^+, especially in the higher $[A^-]$ range, this should not be due to the extraction of polynuclear anionic complexes. This small effect should be due to the extraction of $Eu_2A_6(HA)_2$, which is dependent on the metal concentration. These data were statistically analyzed on the basis of Eq. 22 by a least-squares program; the obtained extraction constant for $EuA_4^-tba^+$, $K_{ex4,0,1}$ in Eq. 15 is listed in Table 3. From these data, the formation constant of the $EuA_4^-tba^+$ species from the EuA_3HA species in the organic phase, $K_{org}{}^*$ in Eq. 16, was also calculated. The obtained value is listed in Table 3.

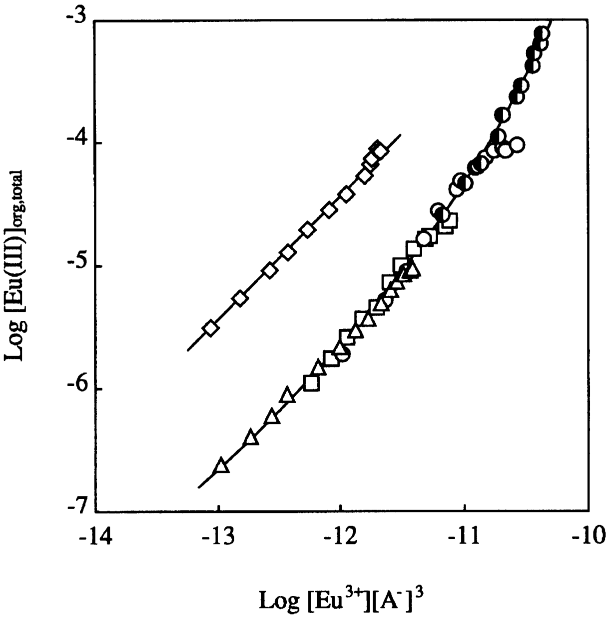

Fig. 4. Relation between $\log[\mathrm{Eu(III)}]_{\mathrm{org,total}}$ and $\log[\mathrm{Eu}^{3+}][\mathrm{A}^-]^3$. The initial concentration of europium(III) is 1×10^{-5} (△), 3×10^{-5} (□), 1×10^{-4} (○), 1×10^{-3} (◐) mol dm^{-3} in the absence of tba^+ or TOPO, and 1×10^{-4} (◇) mol dm^{-3} in the presence of 1×10^{-2} mol dm^{-3} TOPO. The solid lines were calculated on the basis of Eqs. 13 and 27 using the values given in Table 3.

Effect of Trioctylphosphine Oxide on the Extraction of Europium(III) with 1-Naphthoic Acid. As can be seen from Fig. 3, the addition of TOPO enhanced the extraction of europium(III) with 1-naphthoic acid. This enhancement of the extraction can be explained by the extraction of the adducts complexes, $EuA_3(TOPO)_n$. The initial europium(III) concentration of the data given in Fig. 3 was 1×10^{-4} mol dm^{-3}. Although the experiments at higher initial europium(III) concentrations were performed, the results were not reproducible. For example, when the initial concentration was 1×10^{-3} mol dm^{-3}, the recovery of the metal ion was less than 90%. For this reason, these data are not given here. From Eqs. 11 and 27, the following equation is introduced:

Table 3. Equilibrium Constants for the Solvent Extraction of Europium(III) with 1-Naphthoic Acid in Eqs. 8, 9, 11, 15, 16, and 25 in the Absence and Presence of Tetrabutylammonium Ions or Trioctylphosphine Oxide

Org. phase: chloroform containing 1-naphthoic acid. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution.

$\log K_{\mathrm{ex3,1,0}}$	$\log K_{\mathrm{ex6,0,0}}$	$\log K_{\mathrm{ex6,2,0}}$	$\log \beta_1$	$\log K_{\mathrm{ex4,0,1}}$	$\log K_{\mathrm{org}}{}^{*}$	$\log \beta_{(\mathrm{org})1}{}^{*}$	$\log \beta_{(\mathrm{org})2}{}^{*}$
7.9	15.7	20.4	1.9	13.5	2.4	1.8	3.9

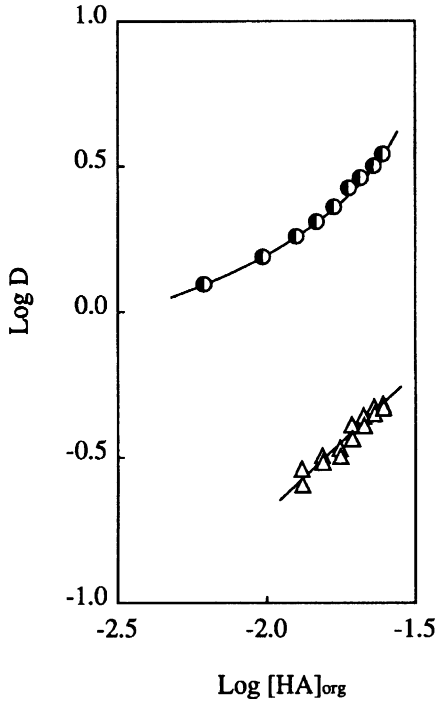

Fig. 5. Distribution ratio of europium(III) as a function of $\log [\mathrm{HA}]_{\mathrm{org}}$ in the absence of tba$^+$ or TOPO. The initial concentration of europium(III) was 1×10^{-5} at $[\mathrm{A}^-]=7.4\times10^{-3}$ (△), 1×10^{-3} at $[\mathrm{A}^-]=8.0\times10^{-3}$ (◐). The solid lines were calculated on the basis of Eq. 13 using the values given in Table 3.

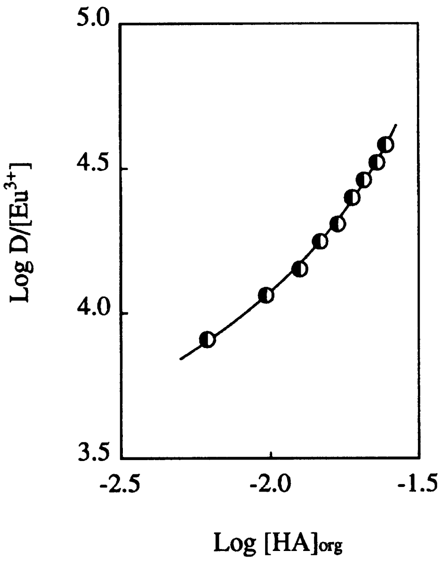

Fig. 6. $\log D/[\mathrm{Eu}^{3+}]$ as a function of $\log [\mathrm{HA}]_{\mathrm{org}}$ in the absence of tba$^+$ or TOPO. The initial concentration of europium(III) was 1×10^{-3} mol dm^{-3}. The solid line was calculated on the basis of Eq. 13 using the values given in Table 3.

$$[\mathrm{Eu(III)}]_{\mathrm{org,total}} = \Big(K_{\mathrm{ex3,1,0}}[\mathrm{HA}]_{\mathrm{org}} + \sum \beta_{(\mathrm{org})n}{}^{*}K_{\mathrm{ex3,1,0}}[\mathrm{A}^-]^3[\mathrm{TOPO}]_{\mathrm{org}}{}^{n}\Big)[\mathrm{Eu}^{3+}][\mathrm{A}^-]^3 + \Big(2K_{\mathrm{ex6,0,0}} + 2K_{\mathrm{ex6,2,0}}[\mathrm{HA}]_{\mathrm{org}}{}^{2}\Big)\Big([\mathrm{Eu}^{3+}][\mathrm{A}^-]^3\Big)^2. \qquad (35)$$

Figure 4 also gives a $\log [\mathrm{Eu(III)}]_{\mathrm{org,total}}$ vs. $\log [\mathrm{Eu}^{3+}][\mathrm{A}^-]^3$ plot of the data in the presence of TOPO in Fig. 3 on the basis of Eq. 35. Under these conditions, $[\mathrm{TOPO}]_{\mathrm{org}}$ and $[\mathrm{HA}]_{\mathrm{org}}$ approximately remain constant at 3.1×10^{-3} and 2.5×10^{-2} mol dm^{-3}, respectively. As can be seen from Fig. 4 the slope of the plot is nearly +1. This should indicate that the adduct complexes are also mononuclear.

In order to calculate the formation constant $\beta_{(\mathrm{org})n}{}^{*}$ in Eq. 25, the distribution ratio was determined as a function of $[\mathrm{TOPO}]_{\mathrm{org}}$ (10^{-4} to 10^{-2} mol dm^{-3} at initial) when the initial concentration of europium(III) and the $[\mathrm{A}^-]$ was kept constant at 1×10^{-5} and 4.8×10^{-3} mol dm^{-3}, respectively. Under these conditions, the extraction of the polynuclear species should be negligible; the concentration of $\mathrm{HA}_{(\mathrm{org})}$ approximately remained constant at 2.5×10^{-2} mol dm^{-3}. Figure 7 gives a $\log D$ vs. $\log [\mathrm{TOPO}]_{\mathrm{org}}$ plot which was calculated on the basis of Eq. 30. A statistical analysis of the data was carried out on the basis of Eq. 27. It was concluded from the analysis that both $\mathrm{EuA_3TOPO}$ and $\mathrm{EuA_3(TOPO)_2}$ were extracted; the values of the formation constants, $\beta_{(\mathrm{org})1}{}^{*}$ and $\beta_{(\mathrm{org})2}{}^{*}$, were calculated by using a least-squares computer program. The obtained values are listed in Table 3. The solid line in Fig. 7 was calculated on the basis of Eq. 27 using the values in Table 3.

Discussion

Like several other metal ions with various carboxylic acid,[12—23] europium(III) is extracted not only as a mononuclear species, but also as a polynuclear species. This makes the equilibrium complicated, and the results of metal extraction very intricate.

As can be seen from Table 2, when the initial 1-naphthoic acid concentration is 0.1 mol dm^{-3} and the $[\mathrm{TOPO}]_{\mathrm{org,initial}}$ is, for example, 5×10^{-2} mol dm^{-3}, about half of the TOPO is combined with 1-naphthoic acid. This causes a decrease in the concentration of HA

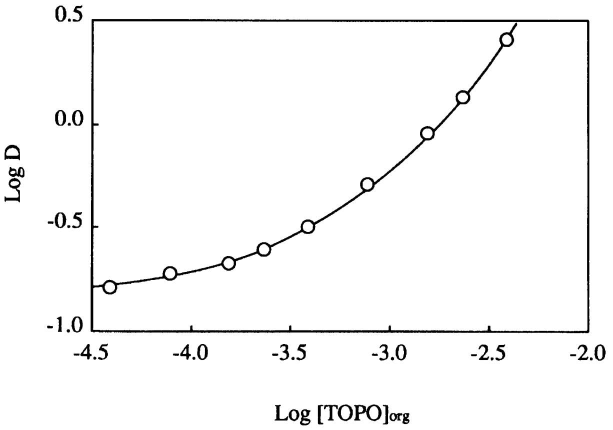

Fig. 7. Distribution ratio of europium(III) as a function of log $[\mathrm{TOPO}]_{\mathrm{org}}$, which was calculated on the basis of Eq. 30. Org. phase: chloroform containing 0.1 mol dm^{-3} 1-naphthoic acid and various amount of TOPO. Aq phase. 0.1 mol dm^{-3} sodium nitrate solution containing 1×10^{-5} mol dm^{-3} europium(III) at $[\mathrm{A}^-]=4.8\times10^{-3}$. The solid line was calculated on the basis of Eq. 27 using the values given in Table 3.

in the organic phase and, thus, a decrease in the extraction of the $\mathrm{EuA_3HA}$ and $\mathrm{Eu_2A_6(HA)_2}$ species, even when the initial sodium hydroxide concentration is kept constant. However, this effect of TOPO on the concentration of $\mathrm{HA_{(org)}}$ is small when the concentration of added TOPO is lower than 1×10^{-2} mol dm^{-3}. This also decreases the free concentration of TOPO in the organic phase. On the other hand, it was reported[24] that the association of TOPO with Htta was negligible in chloroform. This should be favorable for the synergistic enhancement of the europium(III) extraction with Htta, than with 1-naphthoic acid.

It is assumed that the two oxygen atoms of the carboxyl group do not situate so well as to form a stable chelate ring. This is indicated by the fact that the complex in the aqueous phase is much more stable with tta$^-$ ($\beta_1=10^{4.5}$)[3] than with naphthoate ($\beta_1=10^{1.9}$). Thus, the nature of the 1-naphthoate complex may be somewhat different from that of the β-diketonate complexes.

The addition of 1×10^{-2} mol dm^{-3} of TOPO enhanced the 1-naphthoic acid extraction by a factor of 20. The enhancement of the distribution ratio, D/D_0, of the Htta extraction of europium(III) into chloroform by the addition of 1×10^{-2} mol dm^{-3} of TOPO was reported[8] to be 7×10^3, which is more than two-orders larger than that found in the extraction systems with 1-naphthoic acid in the present study. The enhancement of extraction by the addition of 10^{-2} mol dm^{-3} of tba$^+$ is also inferior in the 1-naphthoic acid extraction system than in the Htta extraction system. As has been pointed out, the enhancement due to the addition of tba$^+$ is dependent on the multiplication, $[\mathrm{tba}^+][\mathrm{A}^-]$ or $[\mathrm{tba}^+][\mathrm{tta}^-]$.[1—5] The enhancement of the distribution ratio, D/D_0, of Htta extraction of europium(III) into chloroform when $[\mathrm{tta}^-]$ is 10^{-3} mol dm^{-3} by the addition of 1×10^{-2} mol dm^{-3} of tba$^+$ (at the begining) can be calculated; the enhancement of distribution ratio should be 6×10^4, as was estimated from the previous data.[3] The addition of 1×10^{-2} mol dm^{-3} of tba$^+$ enhanced the 1-naphthoic acid extraction by a factor of 20 when $[\mathrm{A}^-]$ was 10^{-3} mol dm^{-3}. Although the adduct formation or the ternary complex formation in the extraction system with 1-naphthoic acid is caused by an exchange of HA in $\mathrm{EuA_3HA}$ with TOPO or $\mathrm{A^-tba^+}$, that in the extraction system with Htta is achieved only by the addition of TOPO or $\mathrm{tta^-tba^+}$ on the $\mathrm{Eu(tta)_3}$ chelate. Thus, no direct comparison can be made in these two extraction systems. However, it may be assumed that the europium(III) complex with Htta should be a much better acceptor of such donors as TOPO or the extractant anion than the complex with 1-naphthoic acid.

It is mentioned that the extracted anionic europium(III) complex with the tba$^+$ or TOPO adducts is only the mononuclear species under conditions in which mainly the polynuclear species are extracted in the absence of tba$^+$ or TOPO. The two metal ions in the polynuclear species may most probably be combined with carboxylate ions or the HA form acid. This combination of two metal ions in a polynuclear species by the extractant should be interfered if the anionic complex, and an adduct with TOPO would be formed.

As can be seen from the results, the assumption that the extraction of an anionic complex may occur in a liquid–liquid system in which the synergistic effect with a solvating ligand, such as TBP, is found, has been confirmed by extraction with 1-naphthoic acid. However, it has not been successful to explain the reason why the enhancement of metal extraction due to the formation of adducts with a solvating ligand or an anionic complex occurs only in some extraction systems. Further studies are necessary in order to clarify this problem.

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