Studies of the Liquid-Liquid Partition Systems. IV. The Solvent Extraction Study of Europium(III) Adduct Chelate Complexes with Six Acetylacetone Derivatives and Tributylphosphate

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The enhancement of metal chelate extractions by the addition of a neutral organophilic ligand has attracted the attention of many authors and has very often been called the "synergic effect."

The synergic effect has been found in many metal extraction systems with various chelating acids and neutral ligands; the enhancement of the extraction has been explained by the adduct formation of the metal chelates with the neutral ligand in the organic phases. A short review of this problem is given in Ref. 1.

The synergic enhancement of the metal extraction has been most extensively studied in metal extraction systems with thenoyltrifluoroacetone (TTA) and various organic phosphate esters. Some of the results in the previous work may be summarized briefly as follows: (i) The TTA metal chelate extraction systems show a much larger synergic effect than many other metal chelate extraction systems. (ii) The synergic effect is larger when the neutral adduct-forming ligand is an organic phosphate ester than when it is any other neutral ligand. (iii) The synergic effect is quite different when the central metal ion in the TTA chelate is different. TTA chelates of trivalent lanthanides and actinides or uranyl ions show larger synergic effects than many other metal TTA chelates. (iv) The synergic effect is different in different inert organic solvents. The effect is usually larger when water has a smaller solubility in the solvent.

The mechanism of the synergic enhancement of the metal chelate extraction seems not to be very simple, and even though some discussion has been presented to explain this phenomenon, the details seem not to have been understood completely.

In our laboratory, a systematic study has been carried out to obtain further information on the synergic effect of metal chelates. For the present paper, the authors have studied the differences in the adduct formation of europium(III) chelates with six acetylacetone derivatives and tributylphosphate (TBP) in chloroform. These six β-diketones were chosen in order to determine if the large synergic effect in the metal TTA extraction systems is a character of metal chelates with (a) common β-diketones, (b) β-diketones with a trifluoromethyl group, (c) β-diketones with a large organic group such as a thenoyl group, or (d) β-diketones with both a trifluoromethyl group and a thenoyl group.

Europium(III) was chosen as the central metal ion in the chelate, TBP was chosen as the adduct-forming ligand, and chloroform was chosen as the inert organic solvent. The choices were made in order to make it possible to compare the results with previous results.[1]

Acetylacetone and its five derivatives, benzoylacetone, trifluoroacetylacetone, benzoyltrifluoroacetone, froyltrifluoroacetone and thenoyltrifluoroacetone, were chosen as the chelating acids.

The chemical properties of these β-diketones and the previous work on the metal extraction with these β-diketones were summarized by Morrison and Freiser,[2] Poskanzer and Foreman,[3] and Stary.[4] In the present study, the aqueous phase was always 0.1 M sodium perchlorate solutions with a small amount of a buffer. The influence of the concentration of the electrolytes in the aqueous phase on the synergic enhancement will be reported in another paper of this series.

Experimental

Reagents.—The europium 152+154 tracer was obtained from the Oak Ridge National Laboratory as europium chloride in a dilute hydrochloric acid solution. It was diluted with 0.1 M perchloric acid and used as the stock solution. The six β-diketones were obtained from the Dojin Yakukagaku Co. The other reagents were of reagent grade. Sodium perchlorate was prepared from perchloric acid and sodium carbonate. It was recrystallized two times from water. Tributylphosphate was washed with 0.1 M perchloric acid, water and 0.1 M sodium hydroxide respectively, and then several times with water until the washed solution gave a neutral color on an indicator paper. Chloroform was washed three times with water to remove the alcohol which had been added as the stabilizer.

Procedures.—All of the procedures were carried out in a thermostatted room at 25±0.5°C. The tracer solution, the buffer solution and 0.1 M sodium perchlorate solution were placed in stoppered glass tubes, and then chloroform solutions of the chelating acid and TBP were added to the tubes. The aqueous phase was buffered with sulfanilate, acetate, or triethanolamine. The initial concentration of the buffer was 0.01 M. The initial volumes of the organic and the aqueous phases were 5.0 ml., and the volume of the glass tubes was about 20 ml. All of the solutions were left standing overnight before use. The two phases in the tubes were agitated by a mechanical rotator at 20 r. p. m. for about two hours and centrifuged. Two-milliliter portions were pipetted from both phases and transferred into small test tubes. The γ-radioactivity of the solutions was measured with a well-type (NaI) scintillation counter. A small portion of the aqueous phase was transferred into a small vessel, and the hydrogen ion concentration was determined potentiometrically using a 0.010 M $HClO_4$+ 0.090 M $NaClO_4$ solution as the standard ($-\log[H^+]=2.00$).

The net distribution ratio of europium(III) was calculated as follows:

$$D=\frac{\gamma\text{-count-rate per 2 ml. of org. phase}}{\gamma\text{-count-rate per 2 ml. of aq. phase}} \qquad (1)$$

Statistical Treatment

In the present paper, the subscript "org" denotes a species in the organic phase, while the absence of a subscript denotes a species in the aqueous phase. The suffix "0" denotes the distribution ratio or the extraction constant when no adduct is formed in the organic phase.

Metal Extraction with a Chelating Acid.—The extraction of a trivalent metal ion M^{3+} with an organophilic chelating acid, HA, can be described as follows:

$$M^{3+}+3HA(\mathrm{org})\rightleftarrows MA_3(\mathrm{org})+3H^+ \qquad (2)$$

$$K_0=([MA_3]_{\mathrm{org}}/[M^{3+}])[H^+]^3[HA]^{-3}_{\mathrm{org}} \qquad (3)$$

The net distribution ratio obtained by Eq. 1 is generally described as:

$$D=[M(III)]_{\mathrm{org,\,total}}/[M(III)]_{\mathrm{total}} \qquad (4)$$

From the organic phase, a small amount of the chelating acid is distributed into the aqueous phase, and the metal ion in the aqueous phase may form chelate complexes, MA^{2+}, $MA_2{}^+$,$\cdots$ The total metal ion content in the aqueous phase is generally described as:

$$[M(III)]_{\mathrm{total}}=[M^{3+}]+[MA^{2+}]+[MA_2{}^+]+\cdots \qquad (5)$$

and Eq. 4 is described as:

$$D_0=[MA_3]_{\mathrm{org}}/([M^{3+}]+[MA^{2+}]+[MA_2{}^+]+\cdots) \qquad (6)$$

When the aqueous chelate complexes are negligible, the distribution ratio is :

$$D_0=[MA_3]_{\mathrm{org}}/[M^{3+}] \qquad (7)$$

Then the extraction constant in Eq. 3 is expressed as:

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[1] T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1727 (1964). Three more papers on this subject are to be published in the same journal.

[2] G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Sons Inc., New York (1957).

[3] A. M. Poskanzer and B. M. Foreman, Jr., *J. Inorg. Nucl. Chem.*, **16**, 323 (1961).

[4] J. Stary, "The Solvent Extraction of Metal Chelates," Pergamon Press, Oxford (1964).

$$K_0=D_0[\mathrm{H}^+]^3[\mathrm{HA}]^{-3}_{\mathrm{org}} \tag{8}$$

or:

$$D_0=K_0[\mathrm{HA}]^3_{\mathrm{org}}[\mathrm{H}^+]^{-3} \tag{9}$$

Thus when aqueous complexes are negligible, Eq. 8 or 9 describes the distribution equilibrium of the metal ion.

The aqueous chelate complexes in Eq. 6 can be treated as follows. When the distribution constant and the dissociation constant of a chelating acid are defined as:

$$K_D=[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}] \tag{10}$$

$$K_a=[\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \tag{11}$$

then the following equation can be introduced:

$$[\mathrm{A}^-]=(K_a/K_D)\times([\mathrm{HA}]_{\mathrm{org}}/[\mathrm{H}^+]) \tag{12}$$

When the stability constants of the aqueous chelates are defined as:

$$\beta_{\mathrm{aq},n}=[\mathrm{MA}_n{}^{3-n}]/[\mathrm{M}^{3+}][\mathrm{A}^-]^n \tag{13}$$

then the following equation is introduced on the basis of Eqs. 6, 12 and 13:

$$D_0=[\mathrm{MA}_3]_{\mathrm{org}}[\mathrm{M}^{3+}]^{-1}\times$$

$$\{1+\sum_1^n\beta_{\mathrm{aq},n}(K_a/K_D)^n([\mathrm{HA}]_{\mathrm{org}}/[\mathrm{H}^+])^n\}^{-1} \tag{14}$$

From Eqs. 7 and 9, Eq. 14 can be written as:

$$D_0=K_0[\mathrm{HA}]^3_{\mathrm{org}}[\mathrm{H}^+]^{-3}\times$$

$$\{1+\sum_1^n\beta_{\mathrm{aq},n}(K_a/K_D)^n([\mathrm{HA}]_{\mathrm{org}}/[\mathrm{H}^+])^n\}^{-1} \tag{15}$$

When we can assume that

$$[\mathrm{HA}]_{\mathrm{org}}-([\mathrm{HA}]+[\mathrm{A}^-])\cong[\mathrm{HA}]_{\mathrm{org}}$$

we can use the initial concentration of the chelating acid in Eqs. 14 and 15 instead of the concentration at the equilibrium.

The Adduct Formation of a Metal Chelate with a Neutral ligand.—When a metal chelate complex, MA_3, in the organic phase forms adduct complexes with an organophilic neutral ligand, L, the equilibrium is described as:

$$\mathrm{MA}_3(\mathrm{org})+n\,\mathrm{L}(\mathrm{org})\rightleftarrows\mathrm{MA}_3\mathrm{L}_n(\mathrm{org}) \tag{16}$$

$$\beta_n=[\mathrm{MA}_3\mathrm{L}_n]_{\mathrm{org}}/[\mathrm{MA}_3]_{\mathrm{org}}[\mathrm{L}]^n_{\mathrm{org}} \tag{17}$$

The distribution ratio in Eq. 4 is then:

$$D=([\mathrm{MA}_3]_{\mathrm{org}}+[\mathrm{MA}_3\mathrm{L}]_{\mathrm{org}}+[\mathrm{MA}_3\mathrm{L}_2]_{\mathrm{org}}+\cdots)/$$

$$([\mathrm{M}^{3+}]+[\mathrm{MA}^{2+}]+\cdots) \tag{18}$$

From Eqs. 17 and 18 we can introduce:

$$D=[\mathrm{MA}_3]_{\mathrm{org}}(1+\sum_1^n\beta_n[\mathrm{L}]^n_{\mathrm{org}})/$$

$$([\mathrm{M}^{3+}]+[\mathrm{MA}^{2+}]+\cdots) \tag{19}$$

then from Eqs. 6 and 19 we can introduce:

$$D/D_0=1+\sum_1^n\beta_n[\mathrm{L}]^n_{\mathrm{org}} \tag{20}$$

Here the D_0 is the distribution ratio of the metal ion when no adduct is formed in the system.

When we can assume that there is no chelate formation in the aqueous phase, we can define the extraction constant, K, when the concentration of the neutral ligand is $[\mathrm{L}]_{\mathrm{org}}$ as:

$$K=D[\mathrm{H}^+]^3[\mathrm{HA}]^{-3}_{\mathrm{org}} \tag{21}$$

$$=\{1+\sum_1^n\beta_n[\mathrm{L}]^n_{\mathrm{org}})[\mathrm{MA}_3]_{\mathrm{org}}/[\mathrm{M}^{3+}]\}\times$$

$$[\mathrm{H}^+]^3[\mathrm{HA}]^{-3}_{\mathrm{org}} \tag{22}$$

We can then obtain the following equation from the extraction constant, K_0, in Eq. 8:

$$K/K_0=1+\sum_1^n\beta_n[\mathrm{L}]^n_{\mathrm{org}} \tag{23}$$

Graphical Expression

Metal Extraction with a Chelating Acid.—When no complexes are formed in the aqueous phase, Eq. 9 is valid and the D_0 vs. $-\log[\mathrm{H}^+]$ plot ($[\mathrm{HA}]_{\mathrm{org}}$ is constant) is a straight line with a slope of $+3$. The plot of $\log D_0[\mathrm{H}^+]^3[\mathrm{HA}]^{-3}_{\mathrm{org}}$ vs. $\log[\mathrm{HA}]_{\mathrm{org}}$ or vs. $\log[\mathrm{H}^+]^{-1}$ should be a straight line parallel to the abscissa.

On the other hand, when chelate complexes are formed in the aqueous phase, Eq. 6 or 15 is valid and the plot deviates downward from the straight line with a slope of $+3$. The plot of $\log D[\mathrm{H}^+]^3\cdot[\mathrm{HA}]^{-3}_{\mathrm{org}}$ vs. $\log[\mathrm{H}^+]^{-1}$ or vs. $\log[\mathrm{HA}]_{\mathrm{org}}$ deviates downward from the straight line parallel to the abscissa, as we can see from Eq. 15.

Adduct Chelate Complex Formation in the Organic Phase.—When adduct chelate complexes with an organophilic neutral ligand are formed, Eqs. 18 and 19 are valid. The increase in the extraction with the increase in the ligand concentration can be expressed by Eq. 20.

When the formation of chelate complexes in the aqueous phase is negligible, Eq. 23 can also be used.

The formation constants of the adduct complexes, $\beta_1,\beta_2,\cdots$ can be determined graphically by a curve-fitting method.[1,5,6] It may be possible to describe the problem generally, but in the present study the description will be limited to the $\mathrm{MA}_3\mathrm{L}$- and the $\mathrm{MA}_3\mathrm{L}_2$-type complexes because we have encountered only these two complexes in the present study.

(i) When only the $\mathrm{MA}_3\mathrm{L}$ complex exists in the porganic hase, Eq. 20 can be described as:

$$\log D/D_0=\log(1+\beta_1[\mathrm{L}]_{\mathrm{org}}) \tag{24}$$

When a parameter

$$v=\beta_1[\mathrm{L}]_{\mathrm{org}}$$

is introduced, Eq. 24 can be described as:

$$\log D/D_0=\log(1+v) \tag{25}$$

This plot can be fitted with a standard curve:

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[5] D. Dyrssen and L. G. Sillén, *Acta Chem. Scand.*, **7**, 663 (1953).

[6] L. G. Sillén, ibid., **10**, 186 (1956).

$$\begin{aligned} Y &= \log(1+v) \\ X &= \log\, v \end{aligned} \tag{26}$$

Equation 24 has two asymptotes:

$$[\mathrm{L}]_{\mathrm{org}} \to \infty \qquad Y = \log\beta_1 + \log[\mathrm{L}]_{\mathrm{org}} \tag{27}$$

$$[\mathrm{L}]_{\mathrm{org}} \to 0 \qquad Y = 0 \tag{27'}$$

From the intersect of these two asymptotes, $Y=0$ and $X=\log x_1$, the β_1 can be determined as:

$$\log \beta_1 = -\log x_1$$

(ii) When both the MA_3L and the MA_3L_2 complexes are formed in the organic phase, Eq. 20 is described as:

$$\log D/D_0 = \log(1+\beta_1[\mathrm{L}]_{\mathrm{org}} + \beta_2[\mathrm{L}]^2{}_{\mathrm{org}}) \tag{28}$$

When we introduce two parameters:

$$v = \beta_2{}^{1/2}[\mathrm{L}]_{\mathrm{org}}$$

and

$$p = \beta_1\beta_2{}^{1/2}$$

Equation 28 can be described as:

$$\log D/D_0 = \log(1+pv+v^2) \tag{29}$$

and Eq. 28 can be fitted with a family of standard curves:

$$\begin{aligned} Y &= \log(1+pv+v^2) \\ X &= \log\, v \end{aligned} \tag{30}$$

Equation 28 has two asymptotes:

$$[\mathrm{L}]_{\mathrm{org}} \to \infty \qquad Y = \log\beta_2 + 2\log[\mathrm{L}]_{\mathrm{org}} \tag{31}$$

$$[\mathrm{L}]_{\mathrm{org}} \to 0 \qquad Y = 0 \tag{31'}$$

When the intersects of these two asymptotes is $Y=0$ and $X=\log x_2$, the β_2 can be determined as:

$$\log \beta_2 = -2\log x_2$$

Figure 1 gives the standard curves obtained by Eq. 30 when the p values are 0, 1, 2, 3, 5, 10, 20, and 50 respectively.

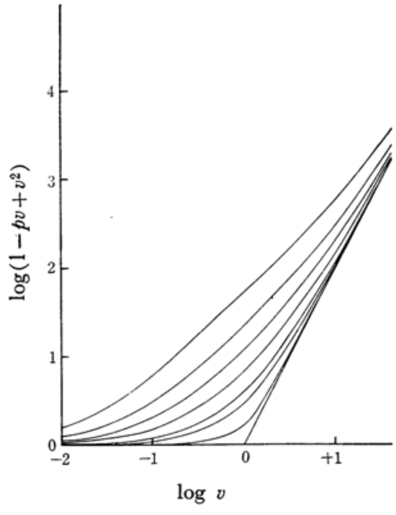


Fig. 1. Standard curves used for the graphical determination of the formation constants of the adducts, $Y=\log(1+pv+v^2)$, $X=\log v$. Each of the curves corresponds to the value of p, 50, 20, 10, 5, 3, 2, 1 and 0 respectively.

When the plot in Eq. 28 is fitted with one of the standard curves, the β_1 can be obtained from the p and from the β_2 as:

$$\beta_1 = p\beta_2{}^{1/2}$$

Results

Figure 2 gives the plot of $\log D$ vs. $\log\,[\mathrm{H}^+]^{-1}$ when the organic phase contained 0.1 M (initial) of the chelating acids.

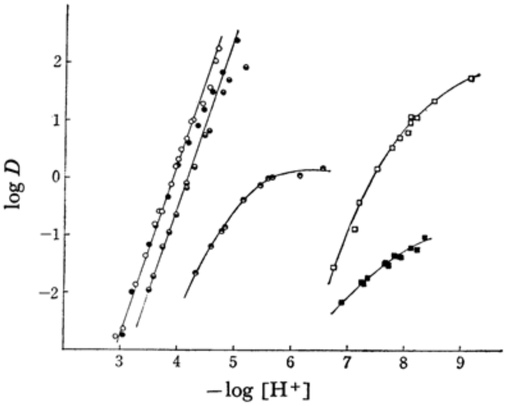


Fig. 2. The hydrogen ion concentration dependence of the distribution of europium(III). Aqueous phase: 0.1 M $NaClO_4$; Organic phase: Chloroform with 0.1 M of acetylacetone(■), benzoylacetone(□), trifluoroacetylacetone(◓), benzoyltrifluoroacetone(◒), froyltrifluoroacetone(●) and thenoyltrifluoroacetone(○).

Figures 3 to 8 give the plot of $\log D/D_0$ vs. $\log\,[\mathrm{TBP}]_{\mathrm{org}}$ when the chelating acid was acetylacetone (AA), benzoylacetone (BZA), trifluoroacetylacetone (TAA), froyltrifluoroacetone (FTA), or thenoyltrifluoroacetone (TTA) respectively.

The extraction constants of europium(III) with

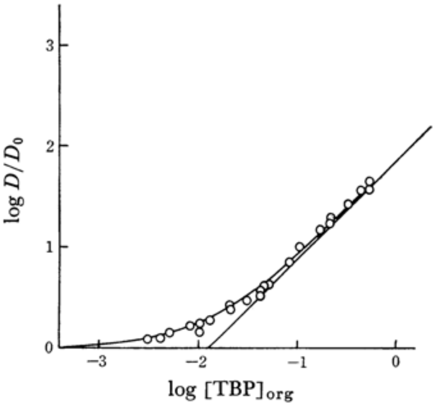


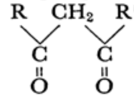
Fig. 3. 0.1 M acetylacetone - TBP system. The curve fitted is $Y=\log(1+v)$, $X=\log v$. The intersect of the two asymptotes is $(-1.90, 0)$.

TABLE I. EQUILIBRIUM CONSTANTS OF EUROPIUM(III) EXTRACTION WITH SIX ACETYLACETONE DERIVATIVES AND THE ADDUCT FORMATION OF THE METAL CHELATES WITH TRIBUTYLPHOSPHATE (TBP)

	AA	BZA	TAA	BFA	FTA	TTA[8]
R-[1]	CH_3-	CH_3-	CF_3-	CF_3-	CF_3-	CF_3-
R′-[1]	CH_3-	benzoyl	CH_3-	benzoyl	froyl	thenoyl
pH of 50% extraction	—[5]	7.5	5.8	4.2	3.9	3.8
log K_0[2]	—[6]	ca. −19[6]	—[6]	−9.47	−8.73	−8.68
log β_1[3]	1.90	1.60	3.32	3.64	3.50	3.34
log β_2[4]	—[7]	—[7]	4.64	5.28	5.00	5.28

Organic phase: 0.1 M of chelating ligand in $CHCl_3$. Aqueous phase: 0.1 M $NaClO_4$.

1) R and R′ indicate the functional group in the β-diketone as indicated in the figure.



2) $K_0=[MA_3]_{org}[H^+]^3/[M^{3+}][HA]^3_{org}$

3) $\beta_1=[MA_3L]_{org}/[MA_3]_{org}[L]_{org}$

4) $\beta_2=[MA_3L_2]_{org}/[MA_3]_{org}[L]^2_{org}$ HA: a chelating ligand L: TBP

5) The extraction is always less than 10% over the entire pH range.

6) Metal chelate complexes are also formed in the aqueous phase and the K_0 cannot be determined definitely.

7) No evidence of the second adduct EuA_3L_2 is observed.

8) The concentration of TTA is 0.05 M for the experiments of the adduct formation.

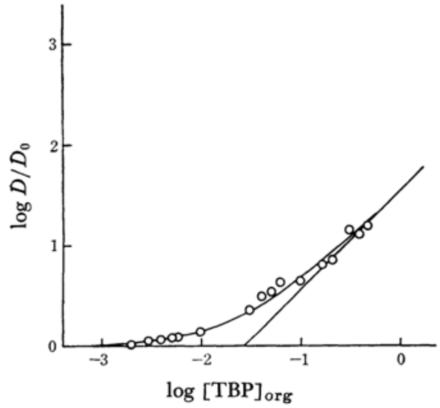


Fig. 4. 0.1 M benzoylacetone - TBP system. The curve fitted is $Y=\log(1+v)$, $X=\log v$. The intersect of the two asymptotes is (−1.60, 0).

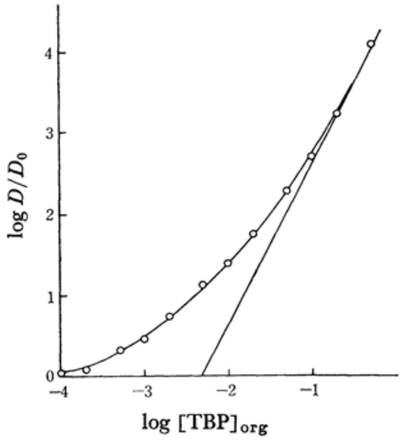


Fig. 5. 0.1 M trifluoroacetylacetone - TBP system. The curve fitted is $Y=\log(1+10v+v^2)$, $X=\log v$. The intersect of the two asymptotes is (−2.32, 0).

these chelating acids were calculated from the distribution data. The formation constants of the TBP adducts were obtained by the curve-fitting method.

The constants thus determined are given in Table I.

Discussion

The six β-diketones in the present study can be described as:

In this discussion, the β-diketones will be classified into two groups and will be called the CH_3-group β-diketones and the CF_3-group β-diketones.

	β-Diketone	R	R′
CH_3-group	Acetylacetone (AA)	CH_3-	CH_3-
	Benzoylacetone (BZA)	CH_3-	Benzoyl
CF_3-group	Trifluoroacetylacetone (TAA)	CF_3-	CH_3-
	Benzoyltrifluoroacetone (BFA)	CF_3-	Benzoyl
	Froyltrifluoroacetone (FTA)	CF_3-	Froyl
	Thenoyltrifluoroacetone (TTA)	CF_3-	Thenoyl

A β-diketone exists in the keto form and in the enol form. A metal ion is extracted into the organic

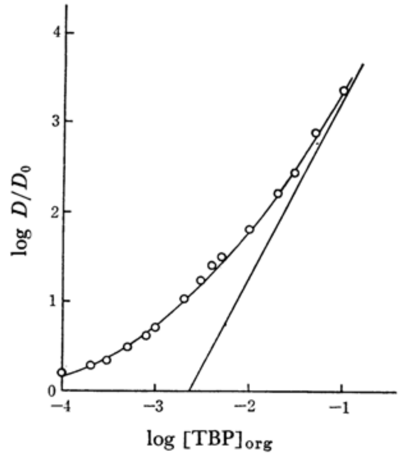


Fig. 6. 0.1 M benzoyltrifluoroacetone-TBP system. The curve fitted is $Y=\log(1+10v+v^2)$, $X=\log v$. The intersect of the two asymptotes is (−2.64, 0).

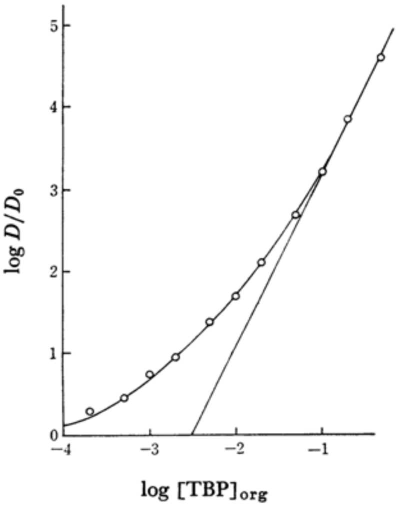


Fig. 7. 0.1 M froyltrifluoroacetone-TBP system. The curve fitted is $Y=\log(1+10v+v^2)$, $X=\log v$. The intersect of the two asymptotes is (−2.50, 0).

phase as a metal chelate with only the enol-form ligand.

Adduct chelate complexes are sometimes also formed with the undissociated chelating acid, HA, as:

$$MA_3(org) + n\,HA(org) \rightleftarrows MA_3(HA)_n(org)$$

However, the formation of adducts of this type may be negligible when the concentration of the chelating acid is 0.1 M in chloroform (cf. Ref. 1, Paper III).

Metal Extraction with Chelating Acids.—The pH of 50% extraction increases in the following order:

$$TTA \cong FTA < BFA < TAA < BZA < (AA)$$

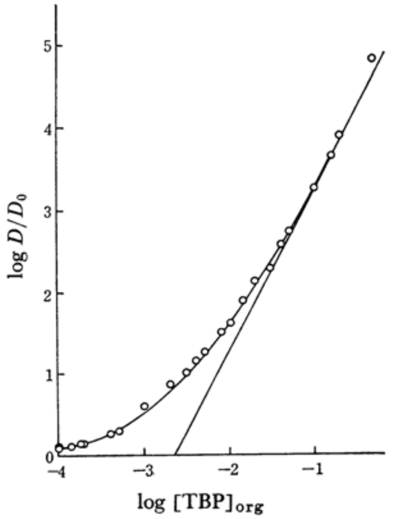


Fig. 8. 0.1 M thenoyltrifluoroacetone-TBP system. The curve fitted is $Y=\log(1+5v+v^2)$, $X=\log v$. The intersect of the two asymptotes is (−2.64, 0).

Acetylacetone showed the least extraction of europium(III). With it the extraction was always less than 10%. The low extraction of trivalent lanthanide ions with this reagent has been reported by several authors.[7]

Benzoylacetone extracts europium(III) much better than acetylacetone, but the pH of 50% extraction is higher than that of the CF_3-group β-diketones. This agrees with previous observations.[8]

The extraction with thenoyltrifluoroacetone seems to agree with the results of the previous work.[1-4,9]

Most of the plots in Fig. 2 deviate from the straight line with a slope of +3. The deviation may be explained as resulting from the formation of aqueous complexes, as is shown in Eq. 15.

In the figure we can see that the deviation is larger in the order:

$$AA > TAA > BZA > FTA > BFA > TTA$$

In Eq. 15 we can see that the formation of aqueous complexes at a certain $[HA]_{org}/[H^+]$ is larger when the stability constants, $\beta_{aq,n}$, are larger and/or the K_a/K_D ratio is larger.

Tables II and III summarize some data of the distribution constants and the dissociation constants of these β-diketones in the literature. In the tables we can see that the dissociation constants of the protons of acetylacetone and benzoylacetone are

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[7] W. B. Brown, J. F. Steinbach and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **13**, 119 (1960); J. Stary and E. Hladky, *Anal. Chim. Acta*, **28**, 227 (1963); J. Rydberg, *Arkiv för Kemi*, **9**, 95 (1955).

[8] I. P. Jefimov and V. M. Peshkova, *Vestnik Moskov. Univ., Ser. Khim.*, **17**, No. 3, 62 (1962); J. Stary, *Zhur. Neorg. Khim.*, **4**, 2412 (1959); J. Stary, *Coll, Czech. Chem. Comm.*, **25**, 86 (1960).

[9] T. Sekine and D. Dyrssen, *Talanta*, **11**, 867 (1964).

TABLE II. DISTRIBUTION CONSTANTS OF β-DIKETONES BETWEEN THE ORGANIC AND THE AQUEOUS PHASE[4)]

$K_D = [HA]_{org}/[HA]$

	$\log K_a$	Solvent	Remarks	Ref.
Acetylacetone	1.37	$CHCl_3$	25°C $\mu=0.1$	11
	0.54	C_6H_6	25°C $\mu=1.0$	12
Benzoylacetone	3.44	$CHCl_3$	25°C $\mu=0.1$	13
	2.79	C_6H_6	25°C $\mu=1.0$	14
Trifluoroacetylacetone	0.18	C_6H_6	2 M $HClO_4$	15
Froyltrifluoroacetone	0.87	C_6H_6	2 M $HClO_4$	15
Thenoyltrifluoroacetone	1.84	$CHCl_3$	25°C $\mu=0.1$	1
	2.12	C_6H_6	25°C $\mu=1.0$	16

TABLE III. DISSOCIATION CONSTANTS OF β-DIKETONES AS AN ACID[4)]

$K_a = [H^+][A^-]/[HA]$

	$-\log K_a$	Remarks	Ref.
Acetylacetone	8.82	25°C $\mu=0.1$	11
	8.76	25°C $\mu=0.1$	12
Benzoylacetone	8.74	20°C $\mu=1.0$	17
	8.24	25°C $\mu=1.0$	14
	8.96	25°C $\mu=1.0$	13
Trifluoroacetylacetone	6.3	25°C	18
Benzoyltrifluoroacetone	6.3	25°C	18
Thenoyltrifluoroacetone	6.23	25°C $\mu=0.1$	19

nearly the same, but that the distribution constant of acetylacetone is much smaller than that of benzoylacetone (this can easily be understood in terms of the higher organophilic tendency of the larger organic group). We can also see in the tables that the dissociation constants of the CF_3-group β-diketones are nearly the same, but that the distribution constant of trifluoroacetylacetone is much lower than those of the others. This shows that the K_a/K_D value of acetylacetone or trifluoroacetylacetone is larger than that of their homologues; we can thus understand why these two β-diketones form much more aqueous chelate complexes and show a lower ability of metal extraction.*

From these results, we may assume that the K_0 values (cf. Eq. 3) for the metal extraction with these two β-diketones are not very far from those of their homologues, even though the apparent metal extraction is quite different.

Adduct Formation of the Metal Chelates with TBP.—The formation constants of the adduct chelate complexes in Table I may be summarized as follows:

1) The formation constants of the first adducts of the metal chelates with the CH_3-group β-diketones are much lower than those of the metal chelates with the CF_3-group β-diketones.

2) The metal chelates with the CH_3-group β-diketones do not form the second adduct, $MA_3\cdot(TBP)_2$, but the metal chelates with the CF_3-group β-diketones form the second adducts.

3) There is no large difference in the formation constants between the adducts of the acetylacetone chelate and those of the benzoylacetone chelate. There is also no large difference in the formation constants among the adducts of the four metal chelates with the CF_3-group β-diketones.

Thus the substitution of a methyl group in a metal chelate with a trifluoromethyl group changes the stability of the metal chelates, as we can see in Fig. 2; this substitution should change the interaction between the central metal ion and the ligands.

When the interaction between the metal ion and the chelating ligand is changed, the residual coordination power of the metal ion which makes the adduct formation possible may be changed. However, as the mechanism of the adduct formation in a synergic extraction system has not yet been clarified, further information on the structrue of the complexes seems to be necessary before this problem can be discussed in more detail.

Conclusion

From the results of this study, we may conclude the following for the extraction of europium(III) in 0.1 M sodium perchlorate with the six β-diketones in chloroform and the adduct formation of these chelates in the organic phase with tributylphosphate:

1) The substitution of a methyl group in acetylacetone or trifluoroacetone with a benzoyl, froyl or thenoyl group increases the possibility of metal extraction, because the substitution increases the organophilic tendency of the molecules and prevents the formation of metal chelates in the aqueous phase. However, the substitution does not seem to change the metal extraction equilibrium,

$$M^{3+} + 3\,HA(org) \rightleftarrows MA_3(org) + 3\,H^+,$$

very much.

2) The β-diketones with one trifluoromethyl group extract the metal ion from aqueous solutions at a lower pH than those without a trifluoromethyl group.

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* In the synergic extraction systems, the deviation caused by the formation of aqueous complexes becomes smaller. The details of this have been discussed in another paper.[10)]

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3) The substitution of one methyl group in acetylacetone or benzoylacetone with one trifluoromethyl group increases the ability of metal chelates with these β-diketones to form adduct complexes with TBP in chloroform.

4) The substitution of one methyl group in acetylacetone chelate or that in trifluoroacetylacetone chelate with one benzoyl, froyl or thenoyl group does not change the adduct formation with TBP very much.

5) The high stability of TBP adducts observed in the metal TTA chelates seems to be similar to that in the TBP adducts of metal chelates with β-diketones which have a trifluoromethyl group.

Summary

The extraction of europium(III) in 0.1 M sodium perchlorate with acetylacetone, benzoylacetone, trifluoroacetylacetone, benzoyltrifluoroacetone, froyltrifluoroacetone and thenoyltrifluoroacetone in chloroform and the adduct formation of these metal chelates with tributylphosphate have been studied at 25°C.

It has been concluded that: (i) The β-diketones which have one trifluoromethyl group extract europium(III) better than those which have no trifluoromethyl group. The difference in the metal extraction with acetylacetone or trifluoroacetylacetone and the metal extraction with the homologues of these β-diketones seems to be mainly due to the aqueous chelate complex formation. (ii) A metal chelate with a β-diketone which has a trifluoromethyl group is a much better acceptor of tributylphosphate to form adduct complexes than a metal chelate with a β-diketone which has no trifluoromethyl group. (iii) The ability of the acetylacetone chelate or the trifluoroacetylacetone chelate to form an adduct is not very much changed by the replacement of the methyl group with a benzoyl, froyl, or thenoyl group.

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