Studies of the Liquid-Liquid Partition Systems. VIII. Stabilities and Extractabilities of Copper(II) and Zinc(II) Complexes with Acetylacetone, Trifluoroacetylacetone, and Hexafluoroacetylacetone in Aqueous Sodium Perchlorate Solution-Carbon Tetrachloride Systems

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The distribution of copper(II) and zinc(II) chelates with three β-diketones, acetylacetone (AA), trifluoroacetylacetone (TFA), and hexafluoroacetylacetone (HFA) between carbon tetrachloride and aqueous sodium perchlorate solutions at 0.1M, 1M, and 3M has been determined at 25°C as a function of the concentration of the dissociated chelate anions. The stability constants for the metal chelates in the aqueous phase and the two phase-distribution constants for the uncharged complexes have been determined by a graphic analysis of the distribution data. The distribution was also measured when the carbon tetrachloride phase was added with tributylphosphate (TBP) or trioctylphosphine oxide (TOPO) and the adduct-formation constants of the uncharged chelate with these ligands have been determined by a graphic analysis of the increase in the distribution ratio as a function of the ligand concentration. The results are as follows: (i) Copper(II) forms first and second complexes with these chelating ligands in the aqueous phase, whereas zinc(II) forms the third complex (except with HFA) besides the first and the second ones; the complexes are more stable in the ligand order of AA>TFA>HFA. (ii) The stability constants of the copper(II) complexes are much higher than those of the corresponding zinc(II) complexes. (iii) The distribution constant of the uncharged copper(II) complex is higher than that of the corresponding zinc(II) complex. (iv) No remarkable relation has been found among the distribution constants of the chelating acid and those of the uncharged metal chelates. (v) The adducts of the metal chelates are more stable in the ligand order of HFA>TFA>AA. The zinc(II) complex forms more stable adducts than does the corresponding copper(II) complex, and TOPO forms more stable adducts than does TBP. (vi) Changes in the concentration of the background salt alter the stability constants of the metal chelates and the distribution constants of the uncharged chelate (salting-out); the effects are, however, very complicated. On the basis of these results, the distribution constants of the uncharged chelates were discussed from the standpoint of the interactions of the central metal ions in the complexes with the water molecules, and a qualitative relationship between these interactions and the stabilities of the adduct chelate complexes was pointed out.

The solvent extraction of metal ions with various weakly acidic chelating reagents has been studied by many authors from the standpoint of the chemical equilibria involved in the extraction processes. The distribution ratios of the metal ions in these systems have been determined as a function of the concentration of the extractants, and the statistical treatments of the distribution data are now very well established.

As will later be discussed in detail, the distribution ratio in metal-chelate extraction systems is represented by the successive complex formations in the aqueous phase and the distribution of the uncharged complex among them.

The stability constants of metal complexes with various chelating anions are an important chemical characteristic of the complexes, and they have been studied by many coordination chemists. However, the two-phase distribution behavior of the uncharged complex is rather a special problem of solvent-extraction chemistry, and, as it is difficult to determine the distribution constant of the uncharged complex in many systems directly, not very much has been established.

In this investigation, the present authors have studied the extraction of copper(II) and zinc(II) mainly from this standpoint. Three β-diketones, acetylacetone (AA), trifluoroacetylacetone (TFA), and hexafluoroacetylacetone (HFA) have been used as the extractants. They were chosen because we desired to know how the distribution behavior of chelate complexes is changed by the substitution of the trifluoromethyl group for the methyl group in acetylacetone; they were also chosen because of the practical reason that the distribution constants are not too high to make an accurate measurement.

Sodium perchlorate solutions were used as the aqueous phase. The concentration of this salt was adjusted at 0.1M, 1.0M, or 3.0M in order to observe the effect of this "*inert*" salt on the stability and the extractability of the metal complexes. In some experiments, the carbon tetrachloride phase was added with tributylphosphate (TBP) or triocytlphosphine oxide (TOPO) in order to determine the enhancements of the distribution due to the adduct-chelate formation and in order to determine the equilibrium constants of the complexes more accurately. The equilibrium constants were determined by a curve-fitting method, on the basis of these data, and some discussion was made of the extractability from the standpoint of the interactions of the metal complexes in the aqueous phase.

Experimental

Reagents. A radioactive tracer, copper-64, and zinc-65 were used in order to determine the distribution ratio of the metal ions. The three β-diketones were obtained from Dojindo & Co. The TBP was obtained from the Tokyo Kasei Co. It was washed perchloric acid, water, and an aqueous sodium hydroxide solution, and then several times with water. The TOPO was obtained from Dojindo & Co.

Standard sodium hydroxide solutions were prepared from a 50% sodium hydroxide solution and decarbonated water. It was standardized to potassium acid phthalate. The sodium perchlorate was prepared from sodium carbonate and perchloric acid. It was recrystallized three times from water. The other reagents were of an analytical grade and were used without further purification.

A certain amount of a β-diketone was dissolved in carbon tetrachloride. The concentration was determined by a two-phase titration; a 5 m*l* portion of the organic solution was pipetted and transferred into a flask containing a certain amount of water, after which the solution was titrated with a standard sodium hydroxide solution by using a suitable indicator (phenolphthalein or azoblue). The concentration of the TBP or TOPO solution was calculated from the weight of the reagent dissolved. The water-saturated TBP was regarded as $TBP \cdot H_2O$. The concentration of the sodium perchlorate stock solution was calculated from the weight of the residue left after a certain amount of the stock solution had been evaporated in an air-bath at 120°C.

Procedures. All of the experiments were carried out in a thermostatted room at 25 ± 0.3°C. An aqueous solution initially containing sodium perchlorate, sodium hydroxide, and 1.0×10^{-5} M copper ions labeled by copper-64 or 1.2×10^{-6} M zinc ions labeled by zinc-65 and carbon tetrachloride containing one of the extractants was placed in the tube. In the highest $-\log[H^+]$ region, the chelating acid distributed into buffered the aqueous phase, and no other buffering reagent was added. In the lower region, however, acetate was used for the experiments with copper(II) and an acetate or acid carbonate buffer was used for the experiments with zinc(II). The initial concentration of the buffer was 0.01 M in the aqueous phase, and practically no difference in the distribution ratio was observed when the buffer concentration was changed to a half: it was thus concluded that the effect of the buffer was negligible. The initial volume of the two phases was always 5 m*l*.

The two phases in the tubes were settled on a rotating framework, agitated mechanically for one hour, and centrifuged. A 2-m*l* portion was pipetted from each phase, and the portions were transferred into small test tubes. The γ-radioactivities of the samples were measured with a scintillation counter, and the distribution ratio was calculated as;

$$D = \frac{\gamma\text{-count-rate per m}l\text{ of the org. phase}}{\gamma\text{-count-rate per m}l\text{ of the aq. phase}}$$

Some portion was also pipetted from the aqueous phase and transferred into a small glass vessel. The hydrogen-ion concentration in the stoichiometric scale was determined by potentiometry using solutions containing 1.00×10^{-2} M perchloric acid and 0.09 M, 0.99 M, or 2.99 M sodium perchlorate as the standard of $-\log[H^+] = 2.00$ in a 0.1 M, 1 M, or 3 M constant ionic medium.

Statistical

When a weak acid, HA, is distributed between an organic and an aqueous phase, the distritution constant is described as:

$$HA \rightleftarrows HA_{(org)}$$

$$K_D = \frac{[HA]_{org}}{[HA]} \qquad (1)$$

The acid dissociation of HA in the aqueous phase is described as:

$$HA \rightleftarrows H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2)$$

If the volumes of the two phases are the same, the initial concentration of the acid in one phase (in the present study, it was the organic phase), C_{HA}, is described, on the basis of the concentrations after the equilibrium is established, as:

$$C_{HA} = [HA]_{org} + [HA] + [A^-] \qquad (3)$$

By introducing Eqs. (1) and (2) into Eq. (3), we obtain:

$$C_{HA} = [A^-]\left(\frac{K_D+1}{K_a}[H^+]+1\right) \qquad (4)$$

Equation (4) shows that the aqueous concentration of the anion from the acid in a liquid-liquid distribution system can be calculated from the initial acid concentration, from the hydrogen-ion concentration at the equilibrium, and from the distribution constant and the dissociation constant of the acid.

The complex formation of a divalent metal ion, M^{2+}, with a ligand anion, A^-, is described as follows:

$$M^{2+} + nA^- \rightleftarrows MA_n^{2-n}$$

$$\beta_n = \frac{[MA_n^{2-n}]}{[M^{2+}][A^-]^n} \qquad (5)$$

Among these complexes, the uncharged one, MA_2, could be extracted into a non-polar organic solvent. The distribution constant of this metal complex is described as:

$$MA_2 \rightleftarrows MA_{2(org)}$$

$$K_{DM} = \frac{[MA_2]_{org}}{[MA_2]} \qquad (6)$$

When the organic phase contains only the MA_2 species, and when the aqueous phase contains a series of metal complexes, the distribution ratio is described as follows:

$$D = \frac{[MA_2]_{org}}{[M^{2+}]+[MA^+]+[MA_2]+[MA_3^-]+\cdots} \qquad (7)$$

By introducing Eqs. (5) and (6), Eq. (7) can be rewritten as:

$$D = \frac{K_{DM}\beta_2[A^-]^2}{1+\beta_1[A^-]+\beta_2[A^-]^2+\beta_3[A^-]^3+\cdots} \qquad (8)$$

When the complex, MA_2, in the organic phase undergoes further complex formation with a neutral organophilic ligand, L, the equilibrium is described as:

$$MA_{2(org)} + nL_{(org)} \rightleftarrows MA_2L_{n(org)}$$

$$\beta_{n(org)} = \frac{[MA_2L_n]_{org}}{[MA_2]_{org}[L]^n_{org}} \qquad (9)$$

When this type of adduct formation occurs in the organic phase, the distribution ratio can be described as follows:

$$D = \frac{K_{DM}\beta_2[A^-]^2(1+\beta_{1(org)}[L]_{org}+\beta_{2(org)}[L]^2_{org}+\cdots)}{1+\beta_1[A^-]+\beta_2[A^-]^2+\beta_3[A^-]^3+\cdots} \qquad (10)$$

If the distribution ratio under a certain $[A^-]$ and $[L]_{org}$ is denoted by D, and when that under the identical $[A^-]$, but in the absence of L, is denoted by D_0, the following can be obtained from Eqs. (8) and (10):

$$D/D_0 = 1 + \beta_{1(org)}[L]_{org} + \beta_{2(org)}[L]^2_{org} + \cdots \qquad (11)$$

When the distribution constant, K_{DM}, into a non-polar solvent is very small, it is very difficult to determine the stability constants of the metal complexes in the aqueous phase from the extraction data by using Eq. (8). However, if a certain amount of an adduct-forming ligand is added to the organic phase, the distribution ratio is increased. When the concentration of the adduct-forming ligand is kept constant throughout a series of experiments, the value in the parentheses in Eq. (10) is always constant. In such a case, the $K_{DM}(1+\sum\beta_{n(org)}[L_1]^n{}_{org})$ value, where $[L_1]_{org}$ is the concentration of the adduct-forming ligand, can be used instead of the K_{DM} value, in Eq. (8) and the stability constants can be determined from these data.

In many papers, the extraction equilibrium of M^{2+} with a chelating extractant is described as:

$$M^{2+} + 2HA_{(org)} \rightleftarrows MA_{2(org)} + 2H^+$$

$$K_{ex} = \frac{[MA_2]_{org}[H^+]^2}{[M^{2+}][HA]^2{}_{org}} \tag{12}$$

When the distribution ratio can be described as:

$$D = \frac{[MA_2]_{org}}{[M^{2+}]} \tag{13}$$

$$= K_{ex}[HA]^2{}_{org}[H^+]^{-2} \tag{14}$$

Thus, when no aqueous chelate complex is formed, the distribution ratio is proportional to the square of the concentration of the chelating extractant in the organic phase or is inversely proportional to the square of the hydrogen ion concentration in the aqueous phase. However, when the distribution ratio is given by Eq. (7), it can be described as:

$$D = \frac{K_{ex}[HA]^2{}_{org}[H^+]^{-2}}{1+\beta_1[A^-]+\beta_2[A^-]^2+\beta_3[A^-]^3+\cdots} \tag{15}$$

as $K_{DM}\beta_2[A^-]^2 = K_{ex}([HA]_{org}/[H^+])^2$;

$$K_{ex} = K_{DM}\beta_2 K_a{}^2 K_D{}^{-2} \tag{16}$$

The equilibrium constants in the above equations may be determined from the following graphic method.[1,2)]

When the distribution ratio given by Eq. (8) is plotted as log D *vs.* log$[A^-]$:

$$Y = \log K_{DM}\beta_2 - \log([A^-]^{-2}+\beta_1[A^-]^{-1}+\beta_2+\beta_3[A^-]+\cdots) \tag{17}$$

If the complexes higher than the MA_2 are negligible, Eq. (17) can be rewritten as:

$$Y = \log K_{DM} - \log(\beta_2{}^{-1}[A^-]^{-2}+\beta_1\beta_2{}^{-1}[A^-]^{-1}+1) \tag{17'}$$

The plot should have the following two asymptotes:

$$\lim_{[A^-]\to 0} Y = \log K_{DM}\beta_2 + 2\log[A^-] \tag{18–1}$$

$$\lim_{[A^-]\to\infty} Y = \log K_{DM} \tag{18–2}$$

The plot in Eq. (17′) could be fitted with the following family of standard curves:

$$Y = \log(1+pv+v^2) \tag{19–1}$$

$$X = \log v \tag{19–2}$$

From the two asymptotes, Eqs. (18-1) and (18-2), the K_{DM} and β_2 values can be obtained, and from the parameter, p, of the best-fit standard curve, β_1 is obtained as:

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

When the aqueous phase also contains the $MA_3{}^-$ complex, the graphic analysis of the data was made as follows. In the lower $[A^-]$ region, the log D *vs.* log$[A^-]$ plot was first fitted with the standard curves in Eqs. (19-1) and (19-2). From this, approximate values of K_{DM}, β_1, and β_2 were determined. Then, by using these constants and an assumed value of β_3, a calculated curve was made and compared with the observed experimental data in the higher $[A^-]$ region. After several trials, the best-fit β_3 was found from the parameter of the best-fit curve.

When a set of constants were thus obtained, the extraction curve was calculated from these constants; it was then compared with the experimental points in order to check whether or not they are reasonable.

When a log D/D_0 *vs.* log $[L]_{org}$ plot, where factors other than $[L]_{org}$ are always kept constant, is made for an adduct-formation system, the data can also be analyzed by the curve-fitting as follows.[3)] If the data are represented by:

$$D/D_0 = 1 + \beta_{1(org)}[L]_{org} \tag{20}$$

that is, if only the first complex is formed, the data could be fitted with the standard curve:

$$Y = \log(1+v) \tag{21–1}$$

$$X = \log v \tag{21–2}$$

When the data are represented by:

$$D/D_0 = 1 + \beta_{1(org)}[L]_{org} + \beta_{2(org)}[L]^2{}_{org} \tag{22}$$

they could be fitted with the standard curves given by Eqs. (19-1) and (19-2). If the asymptote for the log-D/D_0 *vs.* log$[L]_{org}$ plot of the data given by Eq. (20) intersects the X axis at $(X_1, 0)$, the value of log $\beta_{1(org)}$ should be $-X_1$. If the asymptote for the log D/D_0 *vs.* log $[L]_{org}$ plot of the data given by Eq. (22) intersects with the X axis at $(X_2, 0)$, the value of log $\beta_{2(org)}$ should be $-2X$; $\beta_{1(org)}$ can then be obtained from this $\beta_{2(org)}$ and the p of the best-fit standard curve as:

$$p = \beta_{1(org)}\beta_{2(org)}^{-1/2} \tag{23}$$

Results

The results of the measurements were, in general, reproducible. The recovery of the γ-radioactivity from the two phases was always quantitative within the limits of experimental accuracy. The concentration of the chelating anion in the aqueous phase was calculated by using Eq. (4); the dissociation and the distribution constants of these reagents, reported in another paper,[4)] are also given in Table 1 of the present paper.

Figure 1 shows the dependence on the hydrogen-ion concentration of the distribution of copper(II) between carbon tetrachloride and a 1 M sodium perchlorate solution. Figure 2 shows the dependence on the hydrogen-ion concentration of the distribution of zinc(II) between carbon tetrachloride (open symbols) or carbon tetrachloride containing a certain amount of TBP (closed

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[1)] D. Dyrssen and L. G. Sillén, *Acta Chem. Scand.*, **7**, 668 (1953).

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

[3)] T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

[4)] T. Sekine and N. Ihara, This Bulletin, to be published.

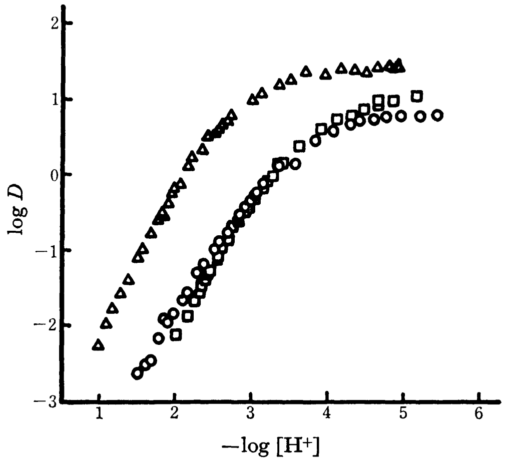

Fig. 1. Extraction of copper(II) complexes with AA(circles), TFA(triangles) and HFA(squares) as a function of the hydrogen ion concentrations.
organic phase: carbon tetrachloride
aqueous phase: 1 M $Na(ClO_4)$

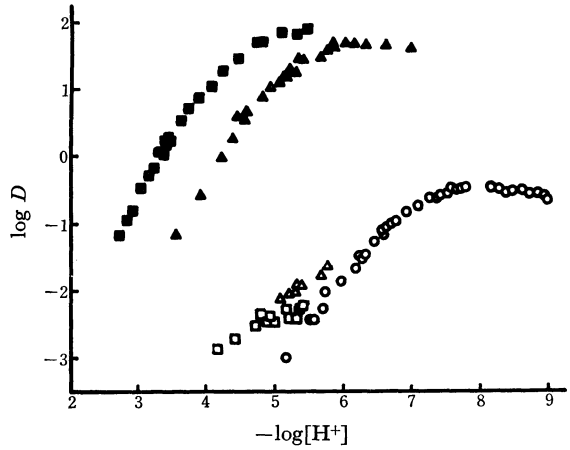

Fig. 2. Extraction of zinc(II) complexes with AA(circles), TFA(triangles) and HFA(squares) as a function of the hydrogen ion concentrations.
organic phase: (open symbols) carbon tetrachloride, (closed symbols) carbon tetrachloride containing 1×10^{-1}M TBP for the TFA or 6×10^{-3}M TBP for the HFA extractions.
aqueous phase: 1 M $Na(ClO_4)$

symbols) and a 1 M sodium perchlorate solution.

As may be seen from Fig. 2, the distribution ratio of zinc(II) in the TFA or HFA extraction is very low in the absence of TBP. However, the distribution ratio is much enhanced by the addition of TBP, and the extraction curves could be determined accurately in these systems. The stability constants of the zinc(II) complexes with TFA and HFA were obtained from these data; they are indicated by the closed symbols in Figs. 2 and 4.

The curves of zinc(II) extraction with TFA and HFA in the absence of TBP in the organic phase are indispensable in determining the distribution constants of the uncharged complexes, K_{DM}, in Eq. (6). Although the distribution ratios were low, the results of the extraction with TFA (open triangles) were reproducible and, as will be shown later, resonable values of K_{DM} and the formation constants of the adducts with TBP

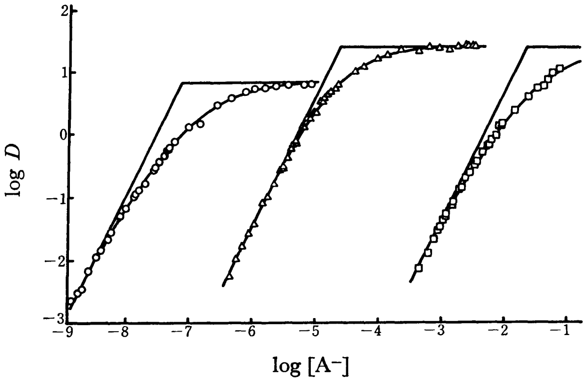

Fig. 3. Extraction of copper(II) complexes with AA(circles), TFA(triangles) and HFA(squares) as a function of the concentrations of the chelate anions.
organic phase: carbon tetrachloride
aqueous phase: 1 M $Na(ClO_4)$
The solid curves are drawn by the equation,
$\log D = \log K_{DM}\beta_2[A^-]^2 - \log(1+\beta_1[A^-]+\beta_2[A^-]^2)$

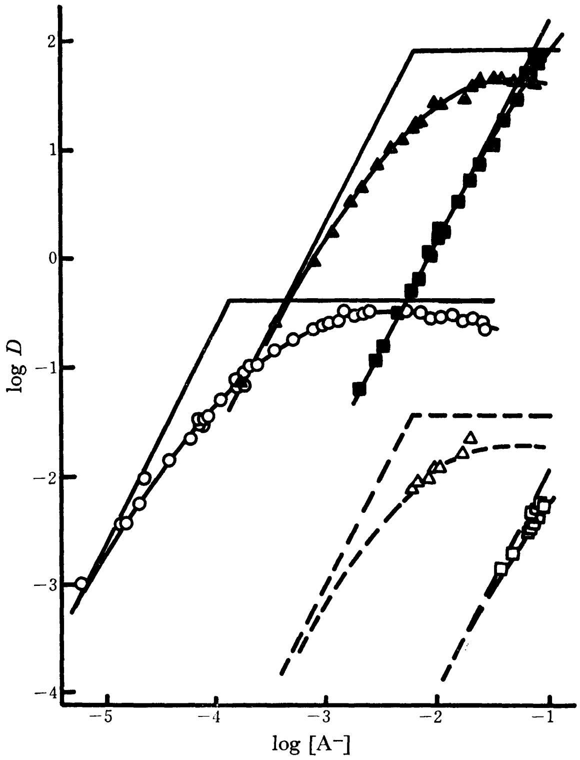

Fig. 4. Extraction of zinc(II) complexes with AA(circles), TFA(triangles) or HFA(squares).
organic phase: (open symbols) carbon tetrachloride, (closed symbols) crabon tetrachloride containing 1×10^{-1}M TBP for the TFA extraction or 6×10^{-3}M TBP for the HFA extractions.
aqueous phase: 1 M $Na(ClO_4)$
The solid curves are drawn by the equation,
$\log D = \log K_{DM}\beta_2 f[A^-]^2 - \log(1+\beta_1[A^-]+\beta_2[A^-]^2 + \beta_3[A^-]^3)$
here, f is the enhancement factor due to the synergism, that is, D/D_0 in Eq. (22). When TBP is absent, f is unity and when 1×10^{-1}M TBP is present in the TFA extractions, f is $10^{3.35}$ and when 6×10^{-3}M TBP is persent in the HFA extractions, f is $10^{4.2}$.

TABLE 1. EQUILIBRIUM CONSTANTS FOR THE β-DIKETONES AND THE METAL β-DIKETONATES AT 25°C
aqueous phase: sodium perchlorate solution
organic phase: carbon tetrachloride

	ionic medium	pK_a[a)]	$\log K_D$[a)]	Cu(II)				Zn(II)				
				$\log \beta_1$	$\log \beta_2$	$\log K_{DM}$	$\log K_{ex}$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log K_{DM}$	$\log K_{ex}$
AA	0.1 M	8.62	0.51	7.74	14.28	0.70	−3.47	4.85	8.22	9.43	−0.65	−10.69
	1 M	8.99	0.40	7.81	14.22	0.83	−3.73	4.58	7.76	9.16	−0.38	−11.40
	3 M	9.75	0.22	8.41	15.42	1.04	−3.52	4.93	8.46	10.26	0.17	−11.35
TFA	0.1 M	6.09	−0.22	5.17	9.38	1.24	−1.12	3.18	5.28	6.14	−1.84	−8.30
	1 M	6.09	−0.19	4.80	9.14	1.40	−1.26	2.72	4.48	5.42	−1.44	−8.76
	3 M	6.52	0.06	5.56	10.04	1.81	−1.31	3.24	5.52	5.68	−1.01	−8.75
HFA	0.1 M	4.42	−1.92	2.52	3.84	0.90	−0.26	1.6	—	—	—[c)]	−4.9
	1 M	4.34	−1.74	2.25	3.20	1.39	−0.61	1.0	—	—	—[c)]	−5.2
	3 M	4.42	−1.40	2.68	4.16	1.76	−0.12	1.1	—	—	—[c)]	−5.0

The literature values for the extraction of copper (II) and zinc (II) in 1 M $NaClO_4$ with AA in benzene are as follows[11)];

	$\log \beta_1$	$\log \beta_2$	$\log K_{DM}$
Cu(II)	8.05(8.22)[b)]	14.75(14.81)[b)]	1.10(1.10)[b)]
Zn(II)	4.63	8.59	−0.19

a) The values of pK_a and $\log K_D$ are taken from another work[4)] in which they are determined by a titration and a spectrophotometry.

b) Experiments at varying acetylacetone concentration.

c) The $\log K_{DM} \times \beta_2$ for the extraction of zinc(II) with HFA are 0.2(0.1 M), 0.0(1 M), and 1.1(3 M).

or TOPO, $\beta_{n(org)}$ in Eq. (9), could be determined for the zinc(II)-TFA chelate. However, the extraction with HFA into carbon tetrachloride containing no TBP is scattered for some unknown reason; only representative data of these extractions are given in Fig. 2 (open squares). Thus, the extraction constant of zinc(II) with HFA, K_{ex} in Eq. (12), in Table 1 and the adduct-formation constants of the HFA chelate, which can be determined only by using the data of the extraction into carbon tetrachloride containing no TBP, may be somewhat erroneous.

In order to analyze these extraction data by using Eq.(8) or Eq.(10), the distribution ratios are plotted against the chelating-anion concentration in the aqueous phase. Figures 3 and 4 show the plot. In Fig. 3, it may be seen that each plot has an asymptote with a slope of +2 and an asymptote with a slope of zero. By the curve-fitting, the constants, β_1, β_2, and K_{DM}, were determined to be as is shown in Table 1. The solid curves in the figures are those calculated by introducing these constants into Eq.(8). The values of K_{ex} defined by Eq.(12) for these extractions were also calculated by using the K_a and K_D values of the chelating acid and Eq.(16).

Figure 4 gives the log D *vs.* log$[A^-]$ plot of the zinc(II) extractions. As the extraction with HFA into carbon tetrachloride is too low to determine the equilibrium constants, the analysis was made by using the plot when the organic phase contains 1×10^{-1}M TBP for the TFA and 6×10^{-3}M TBP for the HFA extractions. As is shown in Eq.(10), the figure of the log D *vs.* log$[A^-]$ plot should be the same even when the organic phase contains a certain amount of the adduct-forming ligand, L (here it is TBP); in this case, $K_{DM}\times(1+\beta_{1(org)}[L_1]_{org}+\beta_{2(org)}[L_1]^2_{org}+\cdots)$, where $[L_1]_{org}$ is the concentration of the adduct-forming ligand, is the apparent distribution constant, which should be used instead of K_{DM} in Eq.(8), as has already been described.

The equilibrium constants for the extraction zinc(II) with AA were obtained by an analysis of the data given by the open circles, whereas those for the extractions with HFA or TFA were obtained by an analysis of the data given by the closed symbols. The distribution constants, K_{DM}, for these extractions were obtained from these apparent distribution constants and the enhancements of the extraction by the TBP, which are given in Fig. 6.

It may be seen from Fig. 4 that the curve for the zinc(II) extraction with HFA is quite close to a straight line with a slope of +2. As can be seen from Eqs. (8) or (10), and (17), the log D *vs.* log$[A^-]$ plot should deviate from a straight line with a slope of +2 when the MA^+ and MA_2 complexes are formed. However, in the $[A^-]$ range studied in this paper ($[A^-]<0.1$M), the range where the MA_2 species is formed in an appreciable amount could not be covered; in other words, the deviation is too small to determine the stability constants for the second complex, β_2, and consequently, it was not possible to devide the $K_{DM}\times\beta_2$ value into the two constants. Thus, only the values for β_1 and $K_{DM}\times\beta_2$, together with K_{ex}, are listed in Table 1 for the zinc(II) complexes with HFA.

As can be seen from Fig. 4, the extraction curve with AA or TFA does not approach an asymptote with a slope of zero, but it decreases somewhat after the maximum. It was assumed to be due to the formation of the third complex, ZnA_3^-; the constants were changed until the best-fit of the calculated curve with the experimental data was obtained. The constants given in Table 1 were thus obtained. The solid curves in Fig. 4 were calculated by the use of these constants.

The above results are for the systems containing 1 M sodium perchlorate solutions as the aqueous phase. In order to ascertain the effect of the concentrations of the coexisting salt on these constants, similar experiments

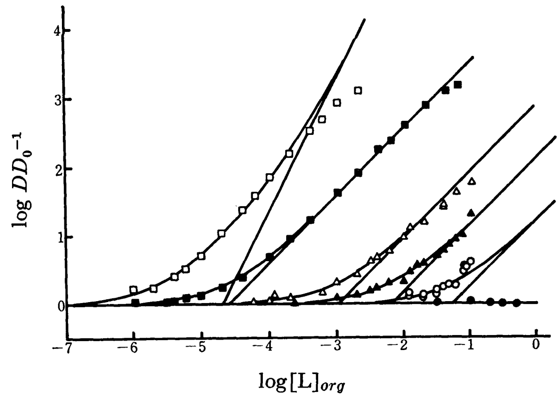

Fig. 5. The enhancement of copper(II) extractions with AA(circles), TFA(triangles) and HFA(squares) by additions of TBP or TOPO.
organic phase: (open symbols) carbon tetrachloride containing TOPO.
(closed symbols) carbon tetrachloride containing TBP.
aqueous phase: 1M $Na(ClO_4)$

Table 2. Adduct formation constants of the metal chelates with TBP and TOPO in CCl_4
aqueous phase: 1.0M $(Na,H)ClO_4$
organic phase: carbon tetrachloride containing 0.1M of HA and various amounts of TBP or TOPO.

	ligand	Cu(II)		Zn(II)	
		$\log\beta_{1(org)}$	$\log\beta_{2(org)}$	$\log\beta_{1(org)}$	$\log\beta_{2(org)}$
$M(AA)_2$	TBP	n.c.[a]	n.c.[a]	n.c.[a]	n.c.[a]
	TOPO	1.28	—	3.07	4.66
$M(TFA)_2$	TBP	2.16	—	4.29	—
	TOPO	2.96	—	6.70	—
$M(HFA)_2$	TBP	4.60	—	5.5[b]	8.5[b]
	TOPO	5.63	9.36	7.0[b]	11.6[b]

$$\beta_{n(org)}=\frac{[MA_2L_n]_{org}}{[MA_2]_{org}[L]^n_{org}}$$

a) n.c. no complex formation ($\beta_{1org}<0.1$)

b) As the distribution ratio of Zn-HFA chelate into carbon tetrachloride, D_0 in Eq.22, could not be determined accurately, these values would be somewhat erroneous.

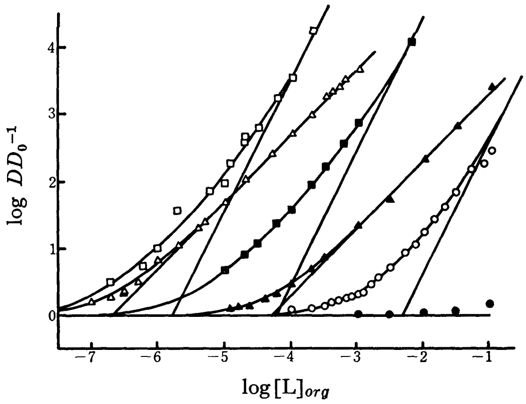

Fig. 6. The enhancement of zinc(II) extractions with AA-(circles), TFA(triangles) and HFA(squares) by addition of TBP or TOPO.
organic phase: (open symbols) carbon tetrachloride containing TOPO.
(closed symbols) carbon tetrachloride containing TBP.
aqueous phase: 1M $Na(ClO_4)$

were also carried out in systems containing 0.1M or 3M sodium perchlorate solutions, while the equilibrium constants were also obtained by a similar graphic analysis. The constants are also given in Table 1.

The enhancements of these extractions by the addition of a neutral organophilic ligand, TBP or TOPO, which are due to the adduct formations (*cf.* Eq. (9)), were determined as a function of the concentration of the neutral ligand. Figure 5 gives the results of the copper(II) extractions, while Fig. 6 gives those of the zinc(II) extractions. In both cases, the addition of TBP did not enhance the extraction with AA. The data were also analyzed by means of curve-fitting; the formation constants of the adduct-chelate complexes were determined to be as is shown in Table 2. The solid curves were calculated by introducing the constants in Table 2 into Eq. (11).

The effect of the background salt on the stability

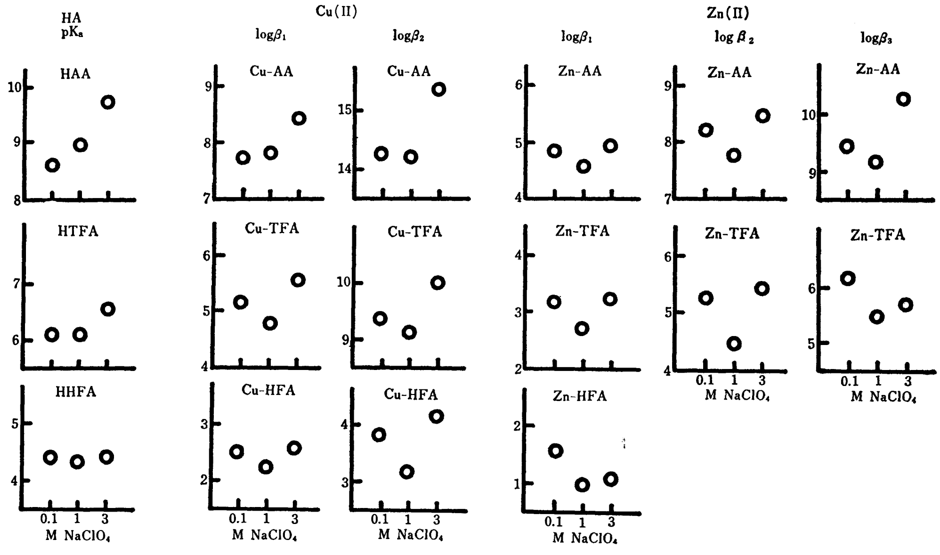

Fig. 7. Effect of the coexisting sodium perchlorate in the aqueous phase on the acid dissociation constant of the chelating agents and the stability constants of the metal chelates. The ordinate gives pK_a or log β_n and the abscissa gives the concentration of sodium perchlorate in the aqueous phase.

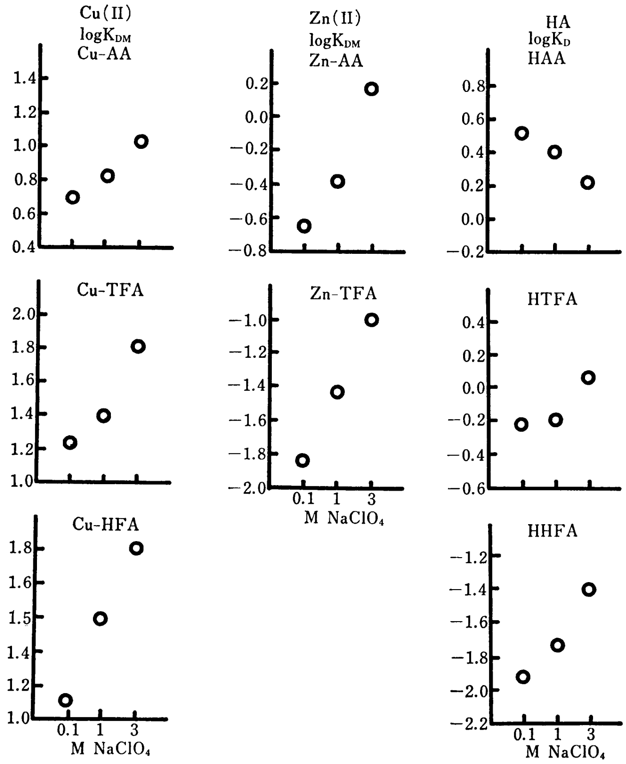

Fig. 8. Effects of the coexisting sodium perchlorate in the aqueous phase on the distribution constant of the reagent (K_D in Eq. (1)) or of the MA_2 chelate complex (K_{DM} in Eq. (6)). The ordinate gives log K_D or log K_{DM} and the abscissa gives the concentration of sodium perchlorate in the aqueous phase.

constants and on the distribution constants is complicated. Figures 7 and 8 summarize these results.

Discussion

As can be seen from Figs. 1 and 2, the −log[H$^+$] range studied in the present paper is from 1 to 5.5 for the copper(II) extraction and from 2.5 to 9 for the zinc(II) extraction; the hydrolyses of these metals in the aqueous phase should be negligible.5,6) Thus, the decrease in the distribution ratio of zinc(II) in the highest −log[H$^+$] region after the maximum can not be due to the hydrolysis, but must be due to the formation of the third complex.

Acetylacetone and its derivatives have been used for the extraction of various metal ions.7) The extraction of copper(II) with AA in benzene,8) in chloroform,9) or in carbon tetrachloride,10) and the extraction of zinc(II) with AA in benzene8) have been reported not to be complete. Recently, Liljenzin, Stary, and Rydberg11) made a very comprehensive study of the AA extraction of these metal ions in a 1.0M sodium perchlorate solution into benzene in the range from 10°C to 40°C. Their results can be compared directly with the present results except for K_{DM} (they used benzene, while the present authors used carbon tetrachloride as the organic phase). These recent data almost completely agree with the present results, although the former are somewhat higher than the latter (the values of K_a and K_D of acetylacetone used for the calculation were not given in Ref. 11). The other two β-diketones, TFA and HFA, have also been used for the extraction of various metal ions,12) but no systematic studies of the extraction equilibria of these metal ions seem to have been made and no constants which can be compared with the present results seem to be available.

The well-known general tendency of the order of the stability constants also appears in the present results shown in Table 1; that is, copper(II) forms more stable complexes than does zinc(II), and the weaker bases which are produced by the substitution of the trifluoromethyl group for methyl groups form less stable complexes.

It can be seen from Table 1 that the highest complexes for copper(II) are the second ones, while those for zinc(II) are the third ones. The four coordination for copper(II) and zinc(II) seem to have been well established; the six coordination for zinc(II) in some cases has been also pointed out. The coordination number of zinc(II) in the third complex with AA or TFA should be six, but it is not possible to confirm the coordination number from only the distribution data.

The effect of the coexisting sodium perchlorate on the stability constants is complicated. However, it can be pointed out, on the basis of Table 1 and Fig. 7, that the stability constants are, in most cases, lowest in the 1M ionic medium and highest in the 3M ionic medium (the exceptions are β_1 for the Cu(II)-AA complex, β_1 for the Zn(II)-HFA complex, and β_3 for the Zn(II)-TFA complex).

Suzuki and his co-workers have made a series of studies of the distribution constant of metal-chelate complexes, MA_m, in liquid-liquid systems.13–21) They

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5) L. G. Sillén and A. E. Martell, "Stability constants," The Chemical Soceity, Spec. Publ. (1964), p. 17.

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12) T. V. Healy, *ibid.*, (1969), p. 257.

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19) N. Suzuki, K. Akiba, T. Kanno, and T. Wakabayashi, *J. Inorg. Nucl. Chem.*, **30**, 2521 (1968).

20) N. Suzuki, K. Akiba, T. Kanno, T. Wakabayashi, and K. Takaizumi, *ibid.*, **30**, 3047 (1968).

21) K. Akiba, N. Suzuki, and T. Kanno, *ibid.*, **42**, 2537 (1969).

have pointed out that the distribution constants of metal-chelate complexes can be well explained by the regular solution theory.[22] They have demonstrated how the distribution constants of a certain metal-chelate into various non-solvating solvents are parallel to that of the chelating acid, HA, for scandium(III) with some β-diketones and zinc(II) chelates with TTA. Furthermore, they have suggested that the distribution of scandium(III)-β-diketonates are satisfactorily explained in the various solvent systems by:

$$\log K_{\mathrm{DM}} = \frac{V_{\mathrm{MA}m}}{V_{\mathrm{HA}}} \log K_{\mathrm{D}} + \text{constant} \tag{24}$$

where V_{HA} and $V_{\mathrm{MA}m}$ denote the molar volume of the chelating reagent and that of the metal chelate complex respectively.[14,17,18,20] This relation was also pointed out for the distribution of Zn(II)-TTA chelates into various solutions.[21]

In the present study, only one organic solvent, carbon tetrachloride, has been used, and so no comparison of the distribution constants into different organic solvents is possible. Thus, only the comparison of the distribution constant of a certain chelating acid, K_{D}, with that of the bis-complex of copper(II) or zinc(II) with the same chelating acid, K_{DM}, may be made. As may be seen from Table 1 and Fig. 8, the distribution constants of the chelating reagents and of the chelate complexes of the two metal ions change in a very complicated manner upon the change in the coexisting salt concentration. The salt effect is parallel neither among three different reagents nor among a certain reagent, HA, and its metal-chelates, CuA_2 and ZnA_2. Actually, the relation given in Eq. (24) is seen only in the extraction of copper(II) in the 1 M ionic medium with AA. Except for this, the relation between K_{D} and K_{DM} is very irregular. Even for the copper(II) extraction with AA, the relation in Eq. (24) is not observed in the extraction from a 0.1 M or 3 M ionic medium. The distribution constants, K_{DM}, of the copper(II) chelates are here higher than that of the chelating reagents, K_{D}, whereas they are much lower in the zinc(II) chelates.

The treatments by the regular solution theory are made on the assumption that there is no special strong interaction between the solute and the solvent molecules. As far as the interactions in the carbon tetrachloride phase are concerned, this assumption can be accepted for all the reagents and metal-chelates. However, in aqueous solutions, it is difficult to assume that the central metal ions in the copper(II) and zinc(II) chelates with a certain ligand have the same interactions with water molecules. It can also be supposed that the interactions of the coexisting salt on the two metal complexes with different central metal ions and the same ligand are somewhat different. As will be considered below, the central copper(II) ion in a chelate complex with a certain ligand should interact with polar molecules weaker than those with which the central zinc(II) ion in the complex with the same ligand interacts. Thus, the zinc(II) complex is retained in the aquoues phase more than is the copper(II) complex.

Until now, not many K_{DM} values in chelate-extraction systems have been reported. Dyrssen has, however, reported the K_{DM} values for a series of divalent metal-chelates with β-isopropyltropolone (IPT) between chloroform and a 0.1 M sodium perchlorate ionic medium.[23] He reported, for example, that the K_{DM} of the copper(II)-IPT chelate ($\log K_{\mathrm{DM}}=4.12$) is much higher than that of the zinc(II)-IPT chelate ($\log K_{\mathrm{DM}}=2.25$), and he described how the K_{DM}^{-1} value presumably shows the affinity of the uncharged chelate for the aqueous phase, that is, the tendency for MA_2 to form a hydrate in the aqueous phase, and how this tendency of hydration reveals a fundamental difference in the remaining coordinating power of the central metal ion in the chelate complex.

It seems that the above hypothesis can be adopted even for the present results. The extraction of copper(II) chelates into carbon tetrachloride is always better than that of zinc(II) chelates; this can be explained in terms of the lower K_{DM} of the latter, which in turn is due to the larger interactions of the central zinc(II) ion with water molecules (hydration) than those of the central copper(II) ion in the complex with the same ligand. This may also be seen in the following discussions.

There have been many studies of the adduct formation of metal-chelates with various organophilic neutral ligands, as has been reviewed by Irving[24] and Healy.[12] A general tendency has been observed in the stabilities of the adduct-chelates in the organic phase—those chelates which are extracted better—(or which are extracted in a lower pH region or in a lower chelating reagent concentration) form less stable adducts than do other metal-chelates with the same ligand, but when the central metal ion is the same but the ligand is different, those extracted better form more stable adducts. At the same time, it has been known that more basic neutral ligands form more stable adduct-chelates.

This tendency can also be observed in the results shown in Table 2; zinc(II) chelates form more stable adducts than do the corresponding copper(II) chelates. The chelates of copper(II) or of zinc(II) form more stable adducts in the ligand order of AA$<$TFA$<$HFA, which is the inverse of the order of the stabilities of the complexes in the aqueous phase, but the same order as the extraction constants, K_{ex}, in Eq. (12).

The stability of an adduct-chelate should be influenced by many factors, and a too simplified consideration of this problem would lead to an erroneous conclusion. However, as far as the results shown in Tables 1 and 2 are concerned, it may be possible to make the following conclusions: (i) the central metal ion retains more ability to accept further coordination with the neutral ligands in the zinc(II) chelate complexes than in the copper(II) complexes, and (ii) the

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[23] D. Dyrssen, *Trans. Royal Inst. Technol. Stockholm, No.* 188 (1962).

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central metal ion among the complexes with the same metal ion retains more ability to accept further coordination with other ligands if the stability of the chelate in the aqueous phase is lower.

When the ability of the central metal ion to accept a further ligand is larger, the stability of the adduct should be larger. At the same time, it would interact with water molecules more strongly; this seems to explain the stability order of the adduct-chelates. The molar volumes of CuA_2 and ZnA_2 would not be very much different from each other, and, as was assumed by Suzuki and his co-workers,[13,14] the solubility parameters of the reagent and of the chelate are practically the same. Thus, the lower K_{DM} value of zinc(II) chelates than that of the copper(II) chelates is probably due to the stronger interactions of the central metal ion in the zinc(II) chelates with water molecules than those in the copper(II) chelates. However, further information seems to be necessary if we are to make a detailed consideration of this problem.

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