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A Solvent-extraction and Spectrophotometric Study of Copper(II) Complexes in Organic Solvents Containing Acetylacetone and Thenoyltrifluoroacetone

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The complex-formation equilibria of copper(II) in chloroform, benzene, or methyl isobutyl ketone (MIBK) containing both acetylacetone (AA) and thenoyltrifluoroacetone (TTA) have been determined by means of a liquid-liquid distribution method and a spectrophotometric method. The extraction constants or the extinction coefficients of the pure complexes were first determined in solutions containing only one of the liquids, and then these constants for the mixed complex and the equilibrium constants among the three complexes in these solvents were determined by the analysis of the results obtained from the experiments in mixed-ligand solutions. From these data, the following conclusions were reached. The constants experimentally obtained are almost identical with those statistically expected. The absorption spectrum of the mixed complex isolated from the absorption of the mixed-ligand system by the statistical analysis is more similar to that of the TTA complex than to that of the AA complex. The results obtained by these two methods are somewhat different from each other.

When the metal ion, the ligand ion, and the solvent molecules are denoted by M^{m+}, L^{l-}, and S respectively, the stepwise equilibria and the stability constants for the "*n*th" uninuclear complex in a solvent can generally be described as;

$$\mathrm{M}_{n-1}^{m-(n-1)l}\mathrm{S}_a + \mathrm{L}^{l-}\mathrm{S}_b \rightleftharpoons \mathrm{ML}_n^{m-nl}\mathrm{S}_c + (a+b-c)\mathrm{S} \tag{1}$$

$$K'_n = \frac{\{\mathrm{ML}_n^{m-nl}\mathrm{S}_c\}\{\mathrm{S}\}^{a+b-c}}{\{\mathrm{ML}_{n-1}^{m-(n-1)l}\mathrm{S}_a\}\{\mathrm{L}^{l-}\mathrm{S}_b\}} \tag{2}$$

The over-all formation equilibria and the stability constants can be described as;

$$\mathrm{M}^{m+}\mathrm{S}_d + n(\mathrm{L}^{l-}\mathrm{S}_b) \rightleftharpoons \mathrm{ML}_n^{m-nl}\mathrm{S}_c + (d+nb-c)\mathrm{S} \tag{3}$$

$$\beta'_n = \frac{\{\mathrm{ML}_n^{m-nl}\mathrm{S}_c\}\{\mathrm{S}\}^{d+nb-c}}{\{\mathrm{M}^{m+}\mathrm{S}_d\}\{\mathrm{L}^{l-}\mathrm{S}_b\}^n} \tag{4}$$

The complex formation can be represented more generally by Eqs. (1) and (2) or (3) and (4). However, as it is not easy to determine the solvation number or the activity of each chemical species, the solvent molecules are eliminated from these equations, assuming that the solvent activity is kept constant, and in many cases the concentration unit is adopted instead of the activity unit, assuming that the changes in the activity coefficients are negligible under the considerations employed. Thus, the stability constants can usually be represented by these two equations:

$$K_n = \frac{[\mathrm{ML}_n^{m-nl}]}{[\mathrm{ML}_{n-1}^{m-(n-1)l}][\mathrm{L}]^{-l}} \tag{5}$$

$$\beta_n = \frac{[\mathrm{ML}_n^{m-nl}]}{[\mathrm{M}^{m+}][\mathrm{L}^{l-}]^n} \tag{6}$$

The constant in Eq. (5) or (6) is a conventional expression for Eq. (2) or (4).

In aqueous solutions, the stability constants in Eqs. (5) and (6) are determined by various experimental methods. In usual organic solvents, however, the dielectric constant is much smaller, and consequently the concentration of any charged species is too small to measure by practical experimental methods; thus, the determination of the stability constants of metal complexes in Eqs. (5) and (6) is not possible. In order to correlate various complex formation equilibria of a metal ion with various ligands in organic solutions, the present author has employed the following equations instead of Eqs. (5) and (6), because the chemical species experimentally determined in usual organic solvents should be uncharged only.

$$\mathrm{MA}_m(org) + n\mathrm{HB}(org) \rightleftharpoons \mathrm{MA}_{m-n}\mathrm{B}_n(org) + n\mathrm{HA}(org) \tag{7}$$

$$K_{m,n} = \frac{[\mathrm{MA}_{m-n}\mathrm{B}_n]_{org}[\mathrm{HA}]^n{}_{org}}{[\mathrm{MA}_m]_{org}[\mathrm{HB}]^n{}_{org}} \tag{8}$$

$$\mathrm{MA}_m(org) + \mathrm{MB}_m(org) \rightleftharpoons \mathrm{MA}_a\mathrm{B}_{(m-a)}(org) + \mathrm{MA}_{(m-a)}\mathrm{B}_a(org) \tag{9}$$

$$K = \frac{[\mathrm{MA}_a\mathrm{B}_{(m-a)}]_{org}[\mathrm{MA}_{(m-a)}\mathrm{B}_a]_{org}}{[\mathrm{MA}_m]_{org}[\mathrm{MB}_m]_{org}} \tag{10}$$

The present paper will describe the complex formation of copper(II) in chloroform, benzene, and methyl isobutyl ketone (MIBK) containing acetylacetone (AA), thenoyltrifluoroacetone (TTA), or a mixture of these two β-diketones. The equilibrium constants given by Eqs. (8) and (10) will be calculated from the solvent extraction data and the spectrophotometric data, and some discussion will be given of this type of stability constants of metal complexes in such organic solvents.

Statistical Treatment

When an organic solvent contains copper(II) and two organophilic chelating acids, HA and HB, and when no formation of polynuclear complex or of adduct complex is assumed, three sorts of copper(II) complexes, CuA_2, CuAB, and CuB_2 may be expected to exist. The equilibria among these three species may be described as follows:

$$CuA_2(org) + HB(org) \rightleftharpoons CuAB(org) + HA(org) \tag{11}$$

$$CuA_2(org) + 2HB(org) \rightleftharpoons CuB_2(org) + 2HA(org) \tag{12}$$

and the equilibrium constants may be defined as:

$$K_{1,1} = \frac{[CuAB]_{org}[HA]_{org}}{[CuA_2]_{org}[HB]_{org}} \tag{13}$$

$$K_{0,2} = \frac{[CuB_2]_{org}[HA]^2_{org}}{[CuA_2]_{org}[HB]^2_{org}} \tag{14}$$

The following equlibrium constant can also be defined:

$$CuA_2(org) + CuB_2(org) \rightleftharpoons 2CuAB(org)$$

$$K = \frac{[CuAB]^2_{org}}{[CuA_2]_{org}[CuB_2]_{org}} \tag{15}$$

Solvent Extraction Method. In an earlier paper, Sekine and Dyrssen[1] have demonstrated that the equilibrium constants in Eqs. (13), (14), and (15) can be determined by a solvent extraction method. When copper(II) ions in aqueous solutions are extracted with HA in the organic phase, the equilibrium constant can be described as;

$$Cu^{2+} + 2HA(org) \rightleftharpoons CuA_2(org) + 2H^+ \tag{16}$$

$$K_{ex_{2,0}} = \frac{[CuA_2]_{org}[H^+]^2}{[Cu^{2+}][HA]^2_{org}} \tag{17}$$

The net distribution ratio of copper(II) can be determined as;

$$D = \frac{[Cu(II)]_{org,total}}{[Cu(II)]_{total}} \tag{18}$$

When only Cu^{2+} species is assumed to exist in the aqueous phase and only the CuA_2 species in the organic phase, Eq. (17) can be described as;

$$K_{ex_{2,0}} = D[H^+]^2[HA]^{-2}_{org} \tag{19}$$

In the same manner, the following can serve to describe the extraction constant for copper(II) with HB:

$$K_{ex_{0,2}} = \frac{[CuB_2]_{org}[H^+]^2}{[Cu^{2+}][HB]^2_{org}} \tag{20}$$

or:

$$K_{ex_{0,2}} = D[H^+]^2[HB]^{-2}_{org} \tag{21}$$

When the organic phase contains both HA and HB, copper(II) may be extracted as CuA_2, CuAB, and CuB_2 species and the extraction constant to the mixed complex may be described as:

$$Cu^{2+} + HA(org) + HB(org) \rightleftharpoons CuAB(org) + 2H^+ \tag{22}$$

$$K_{ex_{1,1}} = \frac{[CuAB]_{org}[H^+]^2}{[Cu^{2+}][HA]_{org}[HB]_{org}} \tag{23}$$

The net distribution ratio in such a system can be described as:

$$D = \frac{[CuA_2]_{org} + [CuAB]_{org} + [CuB_2]_{org}}{[Cu^{2+}]} \tag{24}$$

$$\frac{[CuAB]_{org}}{[Cu^{2+}]} = D - \frac{K_{ex_{2,0}}[HA]^2_{org} + K_{ex_{2,0}}[HB]^2_{org}}{[H^+]^2} \tag{25}$$

By introducing Eq. (25) into Eq. (23), the extraction constant for the mixed complex, $K_{ex_{1,1}}$, can be determined.

From Eqs. (17), (20), and (23), the K constant, the equilibrium constant for the mixed complex in Eq. (15), is obtained as;

$$K = \frac{K^2_{ex_{1,1}}}{K_{ex_{2,0}}K_{ex_{0,2}}} \tag{26}$$

Sekine and Dyrssen[1] reported that the statistical value of K is 4.

Moreover, the constants can be introduced into Eqs. (13) and (14) as;

$$K_{1,1} = K_{ex_{1,1}}/K_{ex_{2,0}} \tag{27}$$

$$K_{0,2} = K_{ex_{0,2}}/K_{ex_{2,0}} \tag{28}$$

Spectrophotometric Method. The equilibrium constants in Eqs. (13) and (14) can also be determined by a spectrophotometric method.

When the molar extinction coefficients of the CuA_2, CuAB, and CuB_2 species at a certain wavelength are ε_{A_2}, ε_{AB}, and ε_{B_2}, the total absorbance of a sample solution may be described as;

$$E = \varepsilon_{A_2}[CuA_2]_{org} + \varepsilon_{AB}[CuAB]_{org} + \varepsilon_{B_2}[CuB_2]_{org} \tag{29}$$

By introducing Eqs. (13) and (14) into Eq. (29), the following equation is obtained:

$$E = [CuA_2]_{org}(\varepsilon_{A_2} + \varepsilon_{AB}K_{1,1}\alpha + \varepsilon_{B_2}K_{0,2}\alpha^2) \tag{30}$$

where α denotes the mixing ratio: $[HB]_{org}/[HA]_{org}$.

The total concentration of copper(II) is written as:

$$\begin{aligned} C &= [CuA_2]_{org} + [CuAB]_{org} + [CuB_2]_{org} \\ &= [CuA_2]_{org}(1 + K_{1,1}\alpha + K_{0,2}\alpha^2) \end{aligned} \tag{31}$$

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1) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 2013 (1964).

From Eqs. (30) and (31), the following equation is obtained:

$$\frac{E}{C} - \varepsilon_{B_2} = \frac{(\varepsilon_{A_2} - \varepsilon_{B_2}) + (\varepsilon_{AB} - \varepsilon_{B_2})K_{1,1}\alpha}{1 + K_{1,1}\alpha + K_{0,2}\alpha^2} \qquad (32)$$

The ε_{A_2} and ε_{B_2} values can be determined by separate experiments. The total copper(II) concentration, C, can be known from the initial concentration, and the total extinction, E, can be determined by spectrophotometry. Moreover, when the concentrations of the chelating acids are much larger than the total copper(II) concentration, we may assume no change in the chelating acid concentrations by the complex formation and may use the initial concentrations instead of those at equilibrium for the calculation of the constants.

In the above case, the unknown terms in Eq. (32) are ε_{AB}, $K_{1,1}$ and $K_{0,2}$ and we can determine these from the total absorbances determined at more than three different α values.

Graphical Treatment of the Spectrophotometric Data. From Eq. (32), the following equation is obtained:

$$\log\left(\frac{E}{C} - \varepsilon_{B_2}\right) = \log\{(\varepsilon_{A_2} - \varepsilon_{B_2}) + K_{1,1}(\varepsilon_{AB} - \varepsilon_{B_2})\} - \log(1 + K_{1,1}\alpha + K_{0,2}\alpha^2) \qquad (33)$$

The values $\log(E/C - \varepsilon_{B_2})$ obtained experimentally at a certain wavelength are plotted against α, while a certain set of the assumed values of $K_{1,1}(\varepsilon_{AB} - \varepsilon_{B_2})$, $K_{1,1}$ and $K_{0,2}$ are introduced to Eq. (33) and the curve thus drawn is fitted with the plot. The trial is repeated until the best-fit curve for the data is found. The constants will be then determined from the parameters of the best-fit curve.

Experimental

Tracer. A pure copper sheet (99.98%) was irradiated with thermal neutrons in the TRIGA-3 reactor at the Atomic Research Institute of St. Paul's University, Kanagawa. The copper sheet was then dissolved in hot concentrated nitric acid. The solution was evaporated gradually on a water bath, and the residue was dissolved in 0.1 M perchloric acid. The solution thus obtained was used as the copper tracer stock solution.

Reagents. All of the reagents used were of a reagent grade. The acetylacetone and thenoyltrifluoroacetone were obtained from Dojindo & Co. When they were dissolved in an organic solvent, the solution was allowed to stand overnight before use. The methyl isobutyl ketone was washed with 0.1 M perchloric acid, water, and a 0.1 M sodium hydroxide solution, and then several times with water. The chloroform was washed three times with water. The other reagents were used without further purification.

Procedures. All of the procedures were carried out in a thermostatted room at 25±0.5°C.

Solvent Extraction Method. The distribution ratio of copper(II) was measured as follows. Stoppered glass tubes (volume, 20 *ml*) were used to equilibrate the two liquid phases. Five milliliters of chloroform, benzene, or MIBK containing 0.1 M TTA or AA or containing both of them at a different mixing ratio, and 5 *ml* of a mixture of 0.1 M perchloric acid and 0.1 M sodium perchlorate containing the copper(II) tracer were placed in the tubes. The initial concentration of copper(II) in the aqueous phase was in the range $1-5\times10^{-5}$ M. The two phases were agitated mechanically for thirty minutes and then centrifuged. A two-milliliter portion was pipetted from each phase. These portions were transferred into small glass tubes for the measurement of the γ-radioactivity with a well-type (NaI) scintillation counter. For the experiments at hydrogen-ion concentrations smaller than 0.01 M, a small portion was also taken from the aqueous phase and transferred into a glass vessel; the hydrogen-ion concentration of this solution was measured potentiometrically by using 0.0100 M $HClO_4$ +0.09 M $NaClO_4$ as the standard of $-\log[H^+]$ 2.00.

The net distribution ratio was calculated as:

$$D = \frac{[\mathrm{Cu(II)}]_{org,total}}{[\mathrm{Cu(II)}]_{total}} = \frac{\gamma\text{-count-rate per } ml \text{ of the org. phase}}{\gamma\text{-count-rate per } ml \text{ of the aq. phase}}$$

Spectrophotometric Method. A certain amount of metallic copper (99.98%) was dissolved in concentrated nitric acid. An excess amount of a dilute sodium hydroxide solution was added to the copper(II) solution, and the copper(II) hydroxide precipitates were collected by decantation and gradually heated in water. The copper(II) oxide thus prepared was finally obtained as a dry powder and was dissolved in an organic solution containing a large excess of TTA or AA to make the stock solution. The sample solutions of copper(II) were prepared from one of the stock solutions or from mixtures of them and were measured by a spectrophotometer (Hitachi-Perkin Elmer type 139) using quartz cells 1 cm thick.

Results

Solvent Extraction Experiments.

Extraction with a Single Chelating Acid. The distribution of copper(II) between 0.1 M (H, Na)ClO_4 and chloroform, benzene, or MIBK containing 0.1 M TTA or AA was determined as a function of $-\log[H^+]$. The $\log D$ *vs.* $-\log[H^+]$ plot in these systems almost falls on a straight line, with a slope of +2 in the region around $-\log[H^+]$ 2.00, but some deviations from the line were observed (especially in the AA system) in the higher $-\log[H^+]$ range. These deviations were assumed to be due to the aqueous chelate formation. Some other experiments showed no adduct formation of these Cu(II) chelates with the extractants in the undissociated form. Thus, it was concluded that when the organic phase contains 0.1 M chelating acid and when the aqueous phase contains the 0.1 M hydrogen ion, the net distribution ratio can be described by the relation: $D = [CuA_2]_{org}/[Cu^{2+}]$. From

TABLE 1. THE EXTRACTION CONSTANTS OF Cu(II) IN 0.1 M (H, Na)ClO_4 with TTA, AA OR MIXTURES OF TTA AND AA IN THREE ORGANIC SOLVENTS

	$CHCl_3$		C_6H_6		MIBK	
	Solv.	Spec.	Solv.	Spec.	Solv.	Spec.
log $K_{ex_{2,0}}$*	−1.23		−0.73		−1.05	
log $K_{ex_{1,1}}$**	−1.95		−2.04		−2.38	
log $K_{ex_{0,2}}$***	−2.98		−3.76		−3.78	
log $K_{1,1}$	−0.72	−0.22	−1.31	−0.80	−1.17	−0.55
log $K_{0,2}$	−1.75	−1.02	−3.04	−2.30	−2.73	−1.59
log $K_{obs.}$	0.31	0.58	0.42	0.70	0.39	0.49
log $K_{ex_{1,1}\,stat.}$	−1.81		−1.95		−2.22	
$\log \frac{K_{ex_{1,1}\,exp.}}{K_{ex_{1,1}\,stat.}}$	−0.14		−0.09		−0.16	

* Extraction constant for $Cu(TTA)_2$ species.
** Extraction constant for Cu(TTA, AA) species.
*** Extraction constant for $Cu(AA)_2$ species.

TABLE 2. EXTRACTION OF Cu(II) WITH MIXTURE OF TTA(HA) AND AA(HB)

Aqueous phase: 0.01 M $HClO_4$+0.09 M $NaClO_4$
Organic phase: $[HA]_{org}+[HB]_{org}=0.10$ M
$[HB]_{org}/[HA]_{org}=\alpha$
$D_{\mathrm{mixed}}=[CuAB]_{org}/[Cu^{2+}]$ (*cf.* Eq. (25))

(a) $CHCl_3$			(b) C_6H_6			(c) MIBK		
α	log D	log D^*_{mixed}	α	log D	log D^*_{mixed}	α	log D	log D^*_{mixed}
1.5	0.107	−0.587	7.3	−0.907	−1.947	7.3	−0.115	−1.831
3.2	−0.182	−0.642	9.0	−1.017	−1.781	9.0	−1.253	−1.950
4.0	−0.288	−0.723	11.5	−1.148	−1.735	11.5	−1.391	−2.015
5.3	−0.382	−0.777	15.7	−1.297	−1.728	15.7	−1.508	−1.929
9.0	−0.563	−0.943	24.0	−1.537	−1.929	24.0	−1.737	−2.161
15.7	−0.710	−1.155	49.0	−1.837	−2.184	49.0	−1.959	−2.381

* From these data, the values of $K_{ex_{1,1}}(=D_{\mathrm{mixed}}[H^+]^2[HA]^{-1}_{org}[HB]^{-1}_{org})$ were calculated and the average values are given in Table 1.

these results, the extraction constants for copper(II) with TTA or AA were calculated to be as given by Eq. (19) or (21) (*cf.* Ref. 2). The extraction constants obtained are given in Table 1.

Extraction with Mixed Chelating Acids. The distribution of copper(II) between 0.1 M (H, Na)ClO_4 and chloroform, benzene, or MIBK containing both TTA(HA) and AA(HB) was also studied. For these experiments, −log[H^+] was always kept at 2.00 and the total concentration of the chelating acids in the organic phase was kept at 0.10 M. The results are given in Table 2. From these results, the extraction constant of the mixed chelate was determined by means of Eqs. (23) and (25). The constants are also given in Table 1.

Spectrophotometric Experiments.

Absorption Spectra of Copper(II)-bis-TTA and Copper(II)-bis-AA Chelates. The absorption spectra of the copper(II)-bis-TTA chelates and of the copper(II)-bis-AA chelates were measured in chloroform, benzene, or MIBK containing 0.1 M of the chelating acid, while the copper concentration was 2×10^{-4} to 8×10^{-4} M. Figure 1 gives the results in chloroform.

As may be seen in Fig. 1, the absorption spectrum of copper(II)-bis-TTA chelates has a pronounced peak at 407 mμ, while that of the copper(II)-bis-AA chelates has one at 332 mμ. From these results, the molar extinction coefficients were determined to be as given in Table 3.

The Absorption of Copper(II) Complexes in Mixed Chelating-acid Systems. The absorption of copper(II) complex was also measured when the organic solvents contained both TTA and AA at various mixing ratios and when the copper concentration was 8×10^{-4} M.

Figure 2 gives the absorption curves obtained when the mixing raio α was 1, 3, 5, 9, 13, and 47, together with the curve obtained when the organic phase contained only TTA or AA.

A graphic method was used to analyze the results in Fig. 2. For example, the data obtained in

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[2] T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1727 (1964).

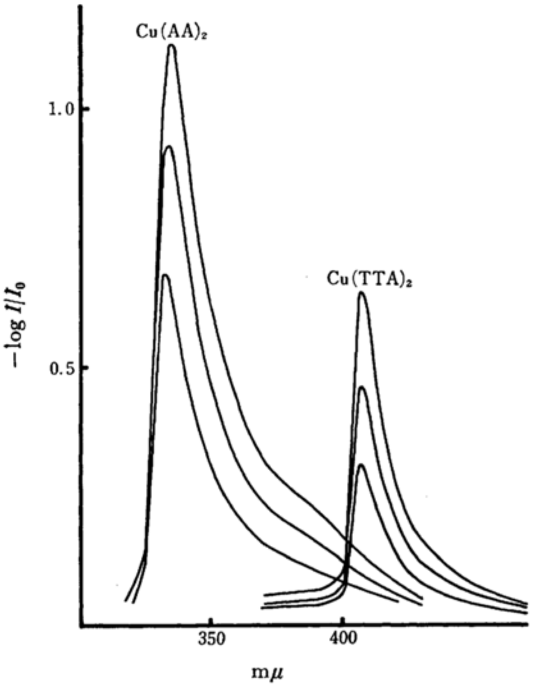


Fig. 1. The absorption spectra of Cu(II)-bis-acetylacetonate and Cu(II)-bis-thenoyltrifluoroacetonate complexes in chloroform. The concentrations of the complexes are 4, 6 and 8×10^{-4} M. The maximum absorptions are at 332 mμ and 407 mμ for AA and TTA, respectively.

TABLE 3. MOLAR EXTINCTION COEFFICIENTS OF Cu(II) CHELATES IN THREE ORGANIC SOLVENTS

Solvent	Chelate	mμ		
		400	410	420
$CHCl_3$	$\varepsilon_{Cu(TTA)_2}$	148	688	353
	$\varepsilon_{Cu(TTA,AA)}$	1121	691	395
	$\varepsilon_{Cu(AA)_2}$	211	150	101
C_6H_6	$\varepsilon_{Cu(TTA)_2}$	108	633	335
	$\varepsilon_{Cu(TTA,AA)}$	829	471	311
	$\varepsilon_{Cu(AA)_2}$	245	177	111
MIBK	$\varepsilon_{Cu(TTA)_2}$	693	512	262
	$\varepsilon_{Cu(TTA,AA)}$	1030	591	341
	$\varepsilon_{Cu(AA)_2}$	218	155	99

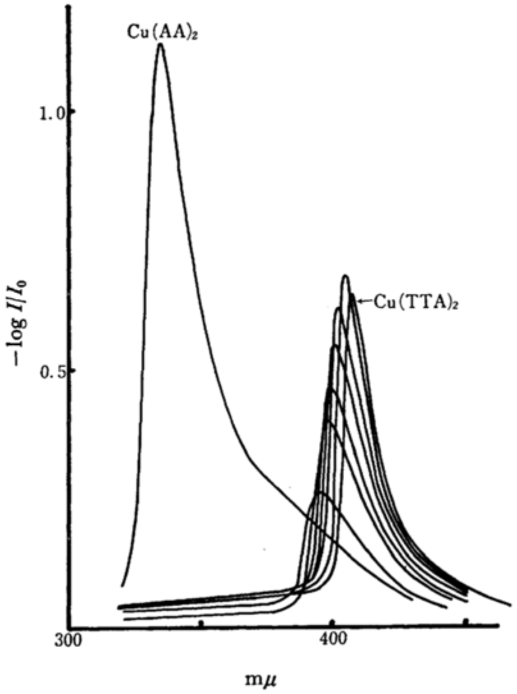


Fig. 2. The absorption spectra of Cu(II) complexes in chloroform containing acetylacetone and thenoyltrifluoroacetone. The mixing ratios, [AA]/[TTA], are 1, 3, 5, 9, 13 and 47.

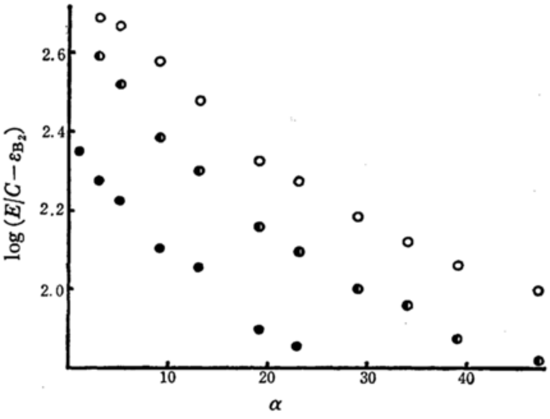


Fig. 3. The change in the absorption at 400 (○), 410 (◐) and 420 (●) mμ by the change of mixing ratio in chloroform expressed by the $\log(E/C-\varepsilon_{B_2})$ vs. α plot.
C: $[Cu(II)]_{total}=8\times10^{-4}$ M
ε_{B_2}: Molar extinction coefficient of copper(II) acetylacetonate $\varepsilon_{400}=211$, $\varepsilon_{410}=150$, $\varepsilon_{420}=101$

the chloroform system were analyzed as follows. The $\log(E/C-\varepsilon_{B_2})$ vs. α plot was made from the absorption data, E, at 400, 410, and 420 mμ, as is shown in Fig. 3, and attempts were made to find the best-fit constants, $K_{1,1}$ and $K_{0,2}$, for these data. Finally, it was found that the "best-fit" was obtained when $K_{1,1}$ and $K_{0,2}$ were 1.2 and 0.20 and when the ε_{AB} values were 1150, 740, and 407 at 400, 410, and 420 mμ respectively. The values of ε_{AB} from 380 mμ to 430 mμ were calculated by introducing these $K_{1,1}$ and $K_{0,2}$ values and the values ε_{A_2} and ε_{B_2} calculated from the data in Fig. 1. The molar extinction coefficients thus calculated are given in Fig. 4 as a function of the wavelengths.

Figure 5 shows the contribution of each chelate species to the total absorption in chloroform, as calculated by Eqs. (13), (14) and (31), when the

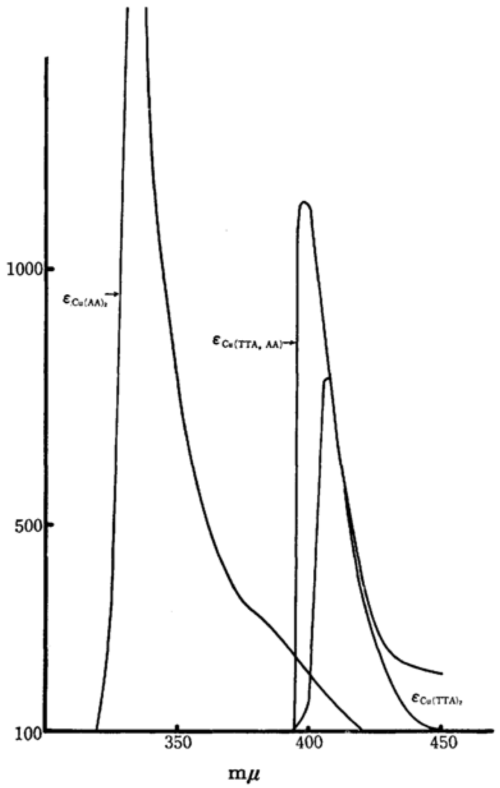


Fig. 4. Molar extinction coefficients of Cu(II) complexes with AA and/or TTA in chloroform. The absorption of Cu(II) complex with TTA and AA is the calculated curve from the data in Fig. 3 (See text).

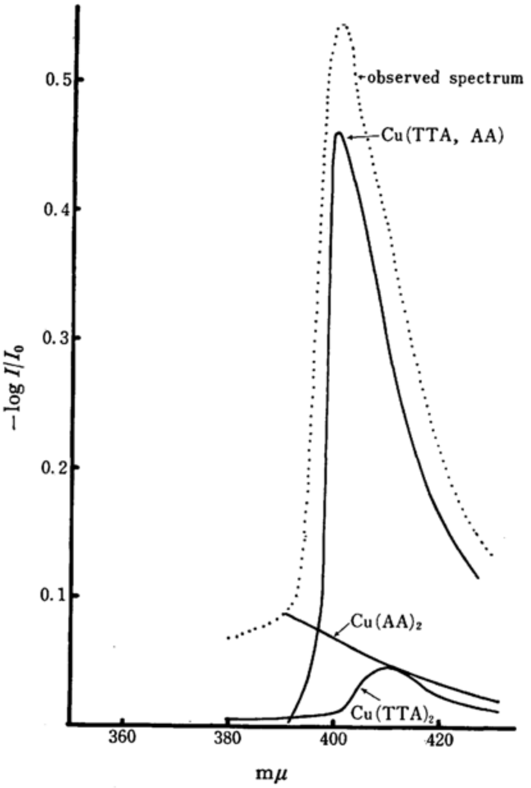


Fig. 5. The contribution of the absorption of the component species to the observed net absorption calculated by Eqs. (33) and (35) using the constants in Table 1.
Solvent; chloroform
The dotted line gives the observed spectrum in the sample solution where $[Cu(II)]_{total}$ is 8×10^{-4} M, $[TTA]_{org}$ is 1.67×10^{-2} M and $[AA]_{org}$ is 8.33×10^{-2} M ($\alpha=5$).
The solid lines show the calculated spectra of $Cu(TTA)_2$ and $Cu(AA)_2$ at this concentration of TTA and AA.

total copper(II) concentration is 8×10^{-4} M and when the the concentrations of TTA and AA are 1.67×10^{-2} and 8.33×10^{-2} M respectively.

The same procedures were carried out on the data obtained in benzene and MIBK. The equilibrium constants, $K_{1,1}$ and $K_{0,2}$, in these systems are also given in Table 1.

By using the $K_{1,1}$ and $K_{0,2}$ constants, in Table 1, which were obtained by both the methods, the percentage distribution of the mixed chelate complex was calculated by the following equation:

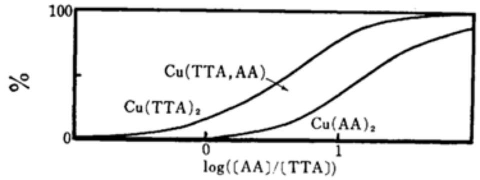
$$\%\text{ distribution of }[CuAB]_{org} = \frac{[CuAB]_{org}\times 100}{[CuA_2]_{org}+[CuAB]_{org}+[CuB_2]_{org}} = \frac{K_{1,1}\alpha\times 100}{1+K_{1,1}\alpha+K_{0,2}\alpha^2} \quad (34)$$

Figure 6 shows the percentage distribution of the three sorts of Cu(II) chelates in chlofoform as a function of the mixing ratio, α. Figure 6-a was calculated from the constants obtained by the solvent extraction, and Fig. 6-b, by spectrophotometry. It may be seen from Fig. 6 that the area of the zone of the mixed complex obtained by the spectrophotometry is larger than that obtained by the solvent extraction. Moreover, the α value at the maximum percentage distribution of the mixed complexes is different ($\alpha=0.88$ by the solvent extraction and 0.51 by the spectrophotometry).

The results thus obtained may be summarized as follows: i) The extraction constant of the copper (II) TTA complex is always larger than that of the copper(II) AA complexes (Table 1).

ii) The extraction constants of the copper(II) TTA-AA mixed complexes experimentally determined are in all cases a little smaller than those statistically calculated, but the differences are not large (the $K_{ex_{1,1}exp.}/K_{ex_{1,1}stat.}$ values are 0.72, 0.81 and 0.69 in chloroform, benzene and MIBK respectively) (Table 1).

iii) The absorption peak of the copper(II)-bis-TTA complex exists over a longer wavelength range than that of the AA complex, and the molar extinction coefficient at the peak of the former is (a)Solvent extraction



(b)Spectrophotometry

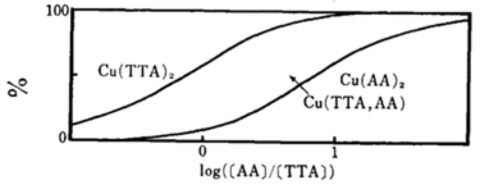


Fig. 6. Percentage distribution of the mixed complexes in chloroform as a function of the mixing-ratio is calculated from the constants in Table 1.

lower than that of the latter (Fig. 1).

iv) The absorption peak of the copper(II) mixed complex with TTA and AA exists over a little shorter wavelength range than that of the Cu(II)-bis-TTA complex, and the molar extinction coefficient of the mixed complex at the peak is a little higher than that of the bis-TTA complex, but much lower than that of the bis-TTA complex (Fig. 4).

v) The values of these constants, $K_{1,1}$, $K_{0,2}$, and K, are different in different organic solvents. The constants obtained by the solvent extraction method are larger in the order: chloroform>MIBK >benzene, while those obtained by the spectrophotometric method are larger in the order: benzene>chloroform>MIBK. Thus, there are some differences in the constants obtained by these two different methods.

Discussion

The extraction constant of copper(II) with AA in benzene has been given as $\log K_{ex}$ -3.76 (present work), -3.93 (Stary and Hladky[3]), and -4.32 (Newman and Klotz[4]), while that with TTA in benzene has been given as $\log K_{ex}$ -0.73 (present work) and -1.32 (Newman and Klotz[4]). It seems to be difficult to ascertain why these extraction constants are so different from each other. However, according to the present results, some part of the copper(II) ions in the aqueous phase are complexed with AA (aqueous chelate formation) under the experimental conditions which Newman and Klotz used in working (0.2 M TTA in benzene and $-\log[H^+]$ 2.20 in 2 M LiCl), and thus the K_{ex} value calculated by using Eq. (19) or (21) is apparently smaller because of the aqueous chelates.[5] Moreover, the presence of chloride ions at such a high concentration may form copper chloride complexes.[6]

The extraction constant of the copper mixed complex with AA and TTA in benzene in the present study is a little smaller than the statistically-calculated values ($K=[CuAB]^2_{org}/[CuA_2]_{org}[CuB_2]_{org}=2.4$, compared with the statistical value, 4), although Newman and Klotz reported that the experimental value is larger than the statistical value ($K=10$). The difference between the present results and the earlier results is not small. One possible explanation for this might be that the use of the underestimated $K_{ex_{0,2}}$ due to the aqueous chelate complex in the earlier work caused an overestimation of the concentration of the mixed chelate in the organic phase.

It was observed by Sekine and Dyrssen[1] that the experimental value of the copper mixed chelate complex with TTA and β-isopropyltropolone (IPT) is more stable than the statistical value and that the stabilization increases with the decrease in the polarity of the solvents (K is 54 for carbon tetrachloride, 30 for chloroform, and 8.9 for MIBK). This order is still retained in the present results, though the mixed complexes are less stable than the statistical values.

The formation of the mixed complex can be apparently observed in the spectrophotometric data in Fig. 2; for example, the absorption peak in the chloroform solution containing 0.05 M TTA and 0.05 M AA (in Fig. 2, it is denoted as the 1 : 1 curve) shifts to a shorter wavelength for the TTA complex and the maximum absorbance increases a little. This can not be explained only in terms of the synthesis of the $Cu(AA)_2$ and $Cu(TTA)_2$ absorption curves.

Figure 7 gives the curve synthesized from the data in Fig. 1 assuming no mixed complex formation. The mixed complex formation can be seen also from Fig. 7, in which the peak of the calculated curve shifts to the shorter wavelength side for the peak of $Cu(TTA)_2$, while the maximum absorbance decreases considerably. This is quite different from the formation observed in Fig. 2. The difference is probably due to the absorption of the mixed complex.

It is remarkable that the maximum extinction of the mixed complex does not appear in midway in the maxima of the extinction of the pure complexes, but appears quite close to that of the $Cu(TTA)_2$ complex. The value of the extinction at the maximum absorption of the mixed complex is also

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[3] J. Stary and E. Hladky, *Anal. Chim. Acta*, **28**, 227 (1963).

[4] L. Newman and P. Klotz, "Solvent Extraction Chemistry," Proceedings of the International Conference, Gothenburg (1966), p. 128.

[5] T. Sekine, M. Sakairi, F. Shimada and Y. Hasegawa, This Bulltin, **38**, 847 (1965).

[6] L. G. Sillen and A. E. Martell, "Stability Constants," The Chemical Society, Spec. Pub. 17, (1964).

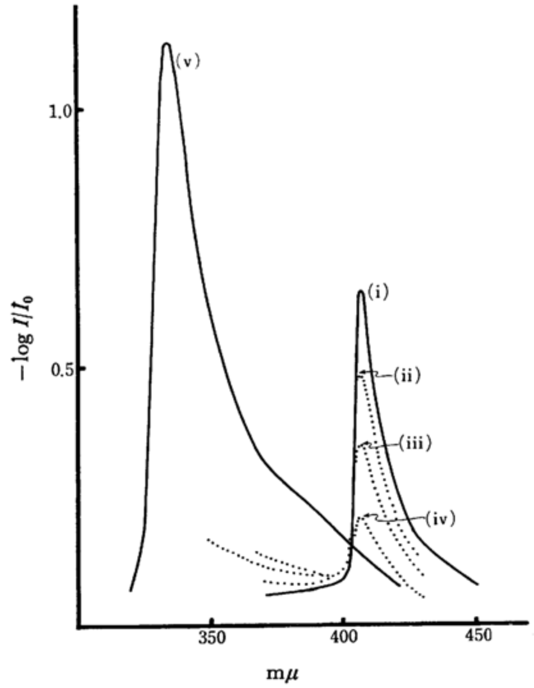

Fig. 7. Calculated absorption curves assuming no mixed complex formation in the system; that is, assuming the existence of only the $Cu(TTA)_2$ and $Cu(AA)_2$ at the following concentrations.
$[Cu(II)]_{org,\ total} = 8\times10^{-4}$ M
i) $[Cu(TTA)_2]_{org} = 8\times10^{-4}$ M
ii) $[Cu(TTA)_2]_{org} = 6\times10^{-4}$ M
$[Cu(AA)_2]_{org} = 2\times10^{-4}$ M
iii) $[Cu(TTA)_2]_{org} = 4\times10^{-4}$ M
$[Cu(AA)_2]_{org} = 4\times10^{-4}$ M
iv) $[Cu(TTA)_2]_{org} = 2\times10^{-4}$ M
$[Cu(AA)_2]_{org} = 6\times10^{-4}$ M
v) $[Cu(AA)_2]_{org} = 8\times10^{-4}$ M

nearer to that of the TTA complex. Further consideration seems to be necessary in order to discuss this resemblance of the extinction of the mixed complex to that of the $Cu(TTA)_2$ complex.

In order to analyze the spectrophotometric data, it was always assumed that the ligands exist in a large excess to copper(II), that, that is, the free-ligand concentration is not changed by the complex formation. This assumption seems to hold even when the mixing ratio is very large or when the initial TTA concentration is very low. For example, in Fig. 3 it may be understood that the analysis can be made even by using the data at $\alpha=40$. Here the total copper concentration is 8×10^{-4} M, while the initial TTA concentration is 2.5×10^{-3} M. However, as may be seen from Fig. 6-b, more than 85% of the copper(II) exists in the CuA_2 form, and thus only about 1.2×10^{-4} M of TTA is complexed with copper(II). The change in the free TTA concentration is only about 5%, which might not cause any significant error in the calculation.

The analysis of the spectrophotometric data is more complicated than that of the solvent extraction data, because in the solvent extraction the unknown constants to be calculated are only $K_{1,1}$ and $K_{0,2}$. As we can see from Eqs. (27) and (28), $K_{0,2}$ can be easily determined from the extraction constants for the pure complexes, $K_{ex2,0}$ and $K_{ex0,2}$, which can themselves be determined by separate experiments. The $K_{ex1,1}$ constant can be calculated from the experimental data in the mixed extractant system by using these $K_{ex2,0}$ and $K_{ex0,2}$ values and Eqs. (25) and (23). Thus, these equilibrium constants can be obtained even from a single value of the distribution data in the mixed chelate system. On the other hand, the unknown constants to be determined in the spectrophotometric study are not only $K_{0,2}$ and $K_{1,1}$, but also the molar extinction coefficients of the mixed complex, ε_{AB}. Thus, we have to determine these three constants simultaneously from a series of absorption data.

As we can see in Table 1 or in Fig. 6, the stabilities of the mixed complex as calculated by the solvent extraction data and by the spectrophotometric data are somewhat different from each other. The essential difference in the experimental conditions is that the organic phase in the spectrophotometry is not saturated with water, while that in the solvent extraction is saturated with water; probably this does not cause any significant difference, although our present information on these systems seems not to be enough for us to discuss whether these differences are due to some unknown factors which cause a systematic deviation in the results of one or both of the methods or whether they are due to an essential difference, one which might arise from the fact that these two methods determined the mixed complex formation from different sides of the phenomenon. Further study seems to be necessary before we can obtain an explanation of this observation.

As was described in the beginning of this paper, the usual stability constants of aqueous complexes defined by Eqs. (5) and (6) are a convenient expression of Eqs. (2) and (4). This means that the stability constants in Eqs. (5) and (6) show the "relative" stability of the metal aquo complex and the metal complexes with L^-, just as Eq. (8) gives the relative stability of the MA_m complex and $MA_{m-n}B_n$ complex. If we take the $Cu(TTA)_2$ complex as the standard of various uncharged complexes in a certain organic phase, we can compare the stabilities of two or more other complexes by using these constants.

When we compare the stability of an aqueous "nth" complex, MA_n^{m-n}, with another "nth" complex, MB_n^{m-n}, we usually use the β_n^A/β_n^B ratio. When we can assume that the hydration numbers of the MA_n^{m-n} and MB_n^{m-n} complexes and those of the A^- and B^- ligands are the same, we see that the ratio of the more generalized stability constants in Eq. (4), β'^A_n/β'^B_n, should be the same as β_n^A/β_n^B.

In the present paper, the relative stability constants for only a pair of ligands, TTA and AA, have been determined. However, if the relative stability constants for another pair of ligands, for example, TTA and a chelating acid HBB, we can compare the stability of the AA complex with the BB complex, as in the follwoing equations:

$$\mathrm{Cu(TTA)_2 + 2HAA \rightleftharpoons Cu(AA)_2 + 2HTTA} \tag{35}$$

$$\mathrm{Cu(TTA)_2 + 2HBB \rightleftharpoons Cu(BB)_2 + 2HTTA} \tag{36}$$

$$K_{0,2}^{\mathrm{TTA-AA}} = \frac{[\mathrm{Cu(AA)_2}]_{org}[\mathrm{HTTA}]^2{}_{org}}{[\mathrm{Cu(TTA)_2}]_{org}[\mathrm{HAA}]^2{}_{org}} \tag{37}$$

$$K_{0,2}^{\mathrm{TTA-BB}} = \frac{[\mathrm{Cu(BB)_2}]_{org}[\mathrm{HTTA}]^2{}_{org}}{[\mathrm{Cu(TTA)_2}]_{org}[\mathrm{HBB}]^2{}_{org}} \tag{38}$$

$$\frac{[\mathrm{Cu(BB)_2}]_{org}[\mathrm{HAA}]^2{}_{org}}{[\mathrm{Cu(AA)_2}]_{org}[\mathrm{HBB}]^2{}_{org}} = \frac{K_{0,2}^{\mathrm{TTA,\,BB}}}{K_{0,2}^{\mathrm{TTA,\,AA}}} \tag{39}$$

This could be compared with the aqueous complexes with AA and BB as follows:

$$\mathrm{Cu^{2+}(H_2O)_{\mathit{a}} + 2AA^-(H_2O)_{\mathit{b}} \rightleftharpoons Cu(AA)_2(H_2O)_{\mathit{c}}} \tag{40}$$

$$\mathrm{Cu^{2+}(H_2O)_{\mathit{a}} + 2BB^-(H_2O)_{\mathit{b}} \rightarrow Cu(BB)_2(H_2O)_{\mathit{c}}} \tag{41}$$

$$(\beta^{\mathrm{AA}})_2' = \frac{[\mathrm{Cu(AA)_2(H_2O)_{\mathit{c}}}]}{[\mathrm{Cu^{2+}(H_2O)_{\mathit{a}}}][\mathrm{AA^-(H_2O)_{\mathit{b}}}]^2} \tag{42}$$

$$(\beta^{\mathrm{BB}})_2' = \frac{[\mathrm{Cu(BB)_2(H_2O)_{\mathit{c}}}]}{[\mathrm{Cu^{2+}(H_2O)_{\mathit{a}}}][\mathrm{BB^-(H_2O)_{\mathit{b}}}]^2} \tag{43}$$

Then we can introduce:

$$\frac{[\mathrm{Cu(BB)_2(H_2O)_2}][\mathrm{AA^-(H_2O)_{\mathit{b}}}]^2}{[\mathrm{Cu(AA)_2(H_2O)_{\mathit{c}}}][\mathrm{BB^-(H_2O)_{\mathit{b}}}]^2} = \frac{(\beta^{\mathrm{BB}})_2'}{(\beta^{\mathrm{AA}})_2'} \tag{44}$$

Equation (44) should be essentially the same as the ratio of the usual stability constants, $\beta_2{}^{\mathrm{BB}}/\beta_2{}^{\mathrm{AA}}$, which is very often used in order to compare the stabilities. The difference between Eqs. (39) and (44) is that the former deals with the acid-form ligands, while the latter deals with the ionic-form ligands. When we can determine the acid-dissociation constants in the organic phase by some experimental methods, we may also calculate the relative stability of the organic complexes in Eq. (44).

As we have seen from the above equation, the "relative" stability constants in Eq. (8) seem to be useful for comparing the stability of complexes of a certain metal with various ligands. As it is not easy to measure ionic species in organic solvents with low dielectric constants, the present expression for the stabilities of various complexes seems to be the most convenient concept for this purpose.

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