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Potentiometric Study of Copper(II) Complexes with β-Diketone in Micellar Solution Using a Copper(II) Ion-Selective Electrode

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Synopsis. The distribution of copper(II) complexes with thenoyltrifluoroacetone, pivaloyltrifluoroacetone and 3-phenyl-2,4-pentanedione between micellar and bulk phases in aqueous solution containing nonionic surfactant was investigated by potentiometry with a copper(II) ion-selective electrode. The apparent equilibrium constants for the copper(II) complexes in micellar solution were determined.

The spectrophotometric method using β-diketone in aqueous solution containing nonionic surfactant is usefull for the determination of metal ions.[1–6] The method is based on solubilizing metal complexes to aqueous solution containing nonionic surfactant and it is simple and rapid method compared with solvent extraction-spectrophotometric determination of metal ions.[7–10]

On the other hand, ion-selective electrodes have been used for complex formation studies in aqueous solutions.[11–14] The solid membrane ion-selective electrode could be employed effectively for study of complex formation in micellar solution, too.

In the present paper, the distribution behavior of copper(II) complexes with thenoyltrifluoroacetone (abbreviated as TTA), pivaloyltrifluoroacetone (PTA) and 3-phenyl-2,4-pentanedione(3-phenylacetylacetone, PAA) in aqueous solutions containing trideca (oxyethylene) dodecyl ether, $CH_3(CH_2)_{11}$-O-(CH_2-CH_2-O)$_{13}$-H (Emulgen 120) were investigated by potentiometry with a copper(II) ion-selective electrode and the apparent equilibrium constants for the systems were obtained.

Experimental

Materials. A standard solution of copper(II) was prepared by dissolving reagent grade copper(II) chloride to dilute hydrochloric acid. The concentration of copper(II) ion was determined by EDTA titration. A 1×10^{-2} M (1 M=1 mol dm^{-3}) chelating agent (TTA, PTA, or PAA) solution was prepared by dissolving a known amount of the reagent (Dojin Co., Ltd.) in 5 W/V% Emulgen 120 (Kao-Atlas Co., Ltd.), which was purified with ion-exchange resin (Bio Rad; AG501-X8(D), analytical grade mixed bed resin). All other chemicals used were of an analytical reagent grade.

Copper membrane disks were supplied by Denki Kagaku Keiki Co., Ltd. The preparation of a copper(II) ion-selective electrode was described in previous paper.[15]

Procedure. Direct potentiometry in the solution containing copper(II) ion and 0.5% Emulgen 120 was perfomed by usual method.

Known amounts of copper(II) and a chelating agent containing 0.5% Emulgen 120 were placed in a titration vessel. Dilute hydrochloric acid solution was added to the above solution. After equilibrium was reached, the value of pH was measured and the potential of copper(II) ion-selective electrode was measured to determine the concentration of free copper(II) ion in the system. Each system was allowed to attain equilibrium (±0.1 mV). All measurements were carried out in a 0.1 M sodium perchlorate at 25±0.1 °C.

Results and Discussion

It was recognized by a spectrophotometric method that most of TTA or PTA exists outside the micelle, i.e. in the bulk phase.[4–6] PAA is also anticipated to be exist outside the micelle. On the other hand, metal-β-diketone complex could not be dissolved in an aqueous solution at the low concentration of nonionic surfactant.

The complex CuL_n (HL; TTA, PTA, and PAA) is presummed to be formed by the following equilibrium.

$$Cu^{2+}_{(b)} + nHL_{(b)} = CuL_{n(m)} + nH^{+}_{(b)} \tag{1}$$

the subscripts (b) and (m) refering to mutually equilibrated bulk and micellar phases, respectively.

The equilibrium constant, *K*, and distribution ratio, *D*, are defined by

$$K = \frac{[CuL_n]_{(m)}[H^+]^n_{(b)}}{[Cu^{2+}]_{(b)}[HL]^n_{(b)}} \tag{2}$$

$$D = \frac{[CuL_n]_{(m)}}{[Cu^{2+}]_{(b)}} \tag{3}$$

From Eqs. 2 and 3, Eq. 4 was derived

$$\log D = -n\log [H^+]_{(b)} + n\log [HL]_{(b)} + \log K \tag{4}$$

The following relationship for copper(II) concentration can be expected to hold

$$(V_{(b)}+V_{(m)})\sum Cu = V_{(b)}[Cu^{2+}]_{(b)} + V_{(m)}[CuL_n]_{(m)} \tag{5}$$

where $\sum$ Cu is total concentration of copper ion, $V_{(b)}$ and $V_{(m)}$ are volume of bulk and micellar phases, respectively. Then making use of one approximation,

$$V_{(b)} \gg V_{(m)} \tag{6}$$

Eq. 5 will be written in the form

$$V_{(b)}\sum Cu = V_{(b)}[Cu^{2+}]_{(b)} + V_{(m)}[CuL_n]_{(m)} \tag{7}$$

Combination of Eqs. 3 and 7 results in the Eq. 8

$$D = \frac{\sum Cu-[Cu^{2+}]_{(b)}}{[Cu^{2+}]_{(b)}}\cdot\frac{V_{(b)}}{V_{(m)}} \tag{8}$$

$$= D_{app}\cdot\frac{V_{(b)}}{V_{(m)}} \tag{9}$$

Apparent distribution ratio, D_{app} is determined by potentiometry with a copper(II) ion-selective electrode for each system. Thus, $\log D_{\mathrm{app}}$ is expressed by

$$\log D_{\mathrm{app}} = n\mathrm{pH} + n\log\,[\mathrm{LH}]_{(\mathrm{b})} + \log K_{\mathrm{app}} \tag{10}$$

where $K_{\mathrm{app}}=K \times V_{(\mathrm{m})}/V_{(\mathrm{b})}$. The value of n is obtained as follows

$$\frac{\mathrm{d}\log D_{\mathrm{app}}}{\mathrm{dpH}} = n \tag{11}$$

The concentration of free copper(II) in the bulk, $[\mathrm{Cu}^{2+}]_{(\mathrm{b})}$, were obtained from the measurement of free ion concentration with a Cu(II) ion-selective electrode and the value of D_{app} were calculated.

Figure 1 shows the calibration curves for copper(II) ions in 0.5% Emulgen 120 solutions at the different pH. The copper(II) ion selective electrode responds very well to copper(II) concentration of 10^{-6} M. Nernstian response was observed in each 0.5% Emulgen 120 solution.

The determination of free copper(II) ion concentration was made in the solution containing copper(II) and β-diketone in 0.5% Emulgen 120. The values of D_{app} at each system of TTA, PTA, and PAA were calculated from the experimental data.

Figure 2 shows the variation of $\log D_{\mathrm{app}}$ as a function of pH at 15 and 25 °C. These plots are found to be linear and each value of $\log D_{\mathrm{app}}/\mathrm{dpH}$ was nearly equal to two. These show that the formation of $[\mathrm{Cu(tta)_2}]$, $[\mathrm{Cu(pta)_2}]$, and $[\mathrm{Cu(paa)_2}]$ complexes occur in micellar solution. The results are in agreement with the previous results by spectrophotometric method.[2] The facts described above indicate that the equilibrium (Eq. 1) is set up between bulk and micellar phases. But, it appears to necessary to explain also the equilibrium by dependence of $\log D_{\mathrm{app}}$ on the concentration of the β-diketone. It will be a subject for further study.

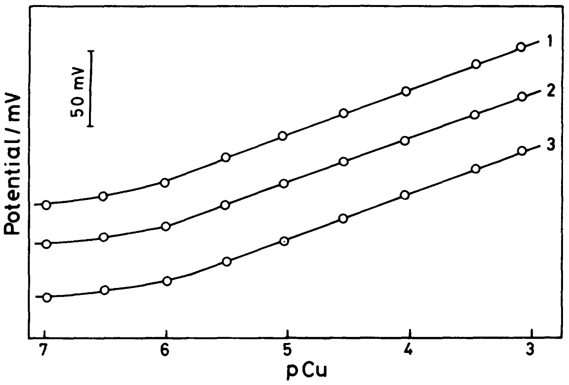

Fig. 1. Calibration curves for copper(II) ions in 0.5% Emulgen 120 solutions at the different pH.
(1): pH=4.00, (2): pH=4.50, (3): pH=5.00.

The apparent equilibrium constants were calculated from the data for Fig. 2 by Eq. 10. The results are summarized in Table 1. The orders of apparent equilibrium constants are $[\mathrm{Cu(tta)_2}] > [\mathrm{Cu(pta)_2}] > [\mathrm{Cu(paa)_2}]$.

These data indicate that the formation reaction of $[\mathrm{Cu(tta)_2}]$ is endothermic and those of $[\mathrm{Cu(pta)_2}]$ and $[\mathrm{Cu(paa)_2}]$ are exothermic. But the dependence of the equilibrium constant on the temperature is small. The distribution behavior of the complexes in micellar solutions will be cleared by further study.

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Table 1. The Equilibrium Constants for the Complex Formation of Cu(β-diketone)$_2$

β-Diketone	$\frac{t}{°\mathrm{C}}$	$\frac{\mathrm{d}\log D_{\mathrm{app}}}{\mathrm{dpH}}$	$\log K_{\mathrm{app}}$
TTA	15	2.0	−1.50±0.02
	25	2.1	−1.27±0.01
PTA	15	2.1	−2.34±0.02
	25	2.0	−2.41±0.01
PAA	15	1.9	−3.00±0.01
	25	2.0	−3.38±0.03

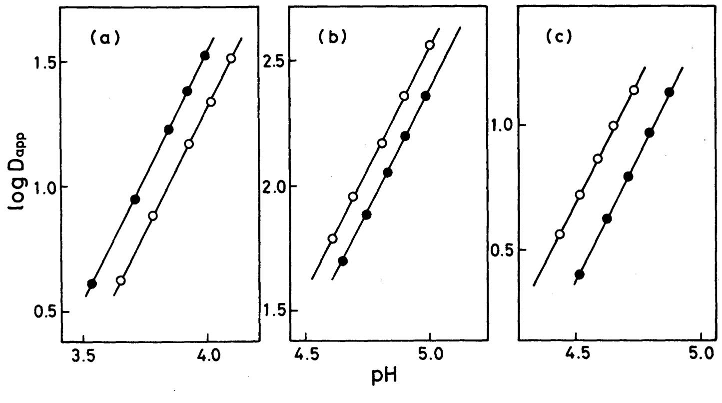

Fig. 2. Variation of $\log D_{\mathrm{app}}$ as a function of pH at 15 °C (○) and 25 °C (●).
(a): Cu(II)–TTA system, (b): Cu(II)–PTA system, (c): Cu(II)–PAA system.

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