Investigation of Copper(II) Chelate with Chromotropic Acid

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Copper(II)-chelate with chromotropic acid was investigated by potentiometric titration. The measurements have been carried out at 25.0±0.1°C and $\mu=0.10$ (with KNO_3). The acid dissociation constant of chromotropic acid, the formation constant of the 1 : 1 chelate (the molar ratio of ligand to copper(II) ion) and the hydrolysis constant of this chelate were determined.

Experimental

Reagents. Chromotropic acid disodium salt (1,8-dihydroxynaphthalene-3,6-disulfonic acid disodium salt) was supplied by Dojindo Co., Ltd., and was used without further purification. The concentration of the acid was determined by potentiometric titration with standard potassium hydroxide solution. Analytical grade cupric nitrate was used. The solution of Copper(II) ion was standardized by chelatometric titration.

Potentiometric Measurements. The same apparatus and procedures as in a preceding paper1) were used for the potentiometric titrations.

Results and Discussion

The corrected potentiometric titration curves of chromotropic acid with and without copper(II) ion are shown in Fig. 1. Two sulfonic acid groups in chromotropic acid are completely dissociated even at a very low $-\log[H^+]$ range. The third dissociation constant pK_{H_2L} is 5.30±0.1. Schwarzenbach *et al.*,2) Zollinger *et al.*3) and Tôei *et al.*4) have reported that pK_{H_2L} is 5.36, 5.53 and 5.44, respectively, at ≃20°C. The fourth dissociation is very weak because of the hydrogen bridge between two naphtholic hydroxyl groups and thus the fourth dissociation constant, pK_{HL}, can not be determined by usual potentiometric titration. Therefore, $pK_{HL}=15.6$, which was reported by Schwarzenbach *et al.*,2) was used for the calculation of the formation constant and the hydrolysis constant of the copper(II) chelate. When the concentration of chromotropic acid is 1.0×10^{-3} M, the concentration of copper(II) ion should be less than 1.0×10^{-3} M, otherwise, copper hydroxide precipitates above $-\log[H^+]$ 7.

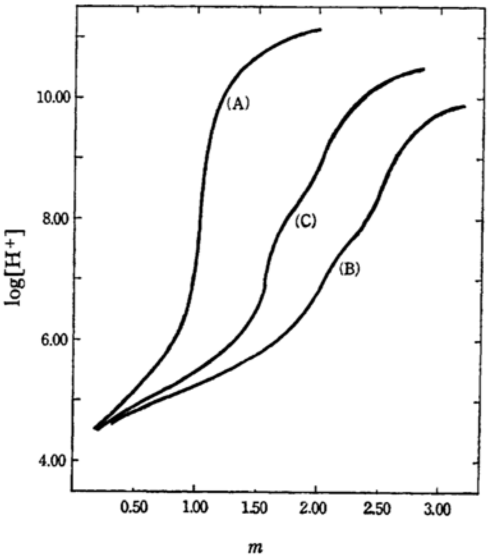

Fig. 1. Potentiometric titration curves with and without cupric ion. (A) Chromotropic acid alone; (B) and (C) are the curves of 1 : 1 and 2 : 1 (the ratio of ligand to cupric ion). m=moles of base added per mole of ligand. $T_L=1\times10^{-3}$ M

The formation constant of the copper(II)-chelate was calculated through the following equations:

$$H_2L^{2-} \rightleftharpoons H^+ + HL^{3-}$$

$$K_{H_2L^{2-}} = \frac{[H^+]\cdot[HL^{3-}]}{[H_2L^{2-}]} \tag{1}$$

$$HL^{3-} \rightleftharpoons H^+ + L^{4-}$$

$$K_{HL^{3-}} = \frac{[H^+]\cdot[L^{4-}]}{[HL^{3-}]} \tag{2}$$

$$Cu^{2+} + L^{4-} \rightleftharpoons CuL^{2-}$$

$$K_{CuL} = \frac{[CuL^{2-}]}{[Cu^{2+}]\cdot[L^{4-}]} \tag{3}$$

From the relationships among the electroneutrality, the total copper(II) concentration and the total ligand concentration, Eq. (4) is derived:

$$K_{CuL}=\frac{\begin{pmatrix} T_{OH}+[H^+]-[OH^-]-T_L \\ -[L^{4-}]+[H_2L^{2-}] \end{pmatrix}}{\begin{pmatrix} \{T_{Cu}+T_L+[OH^-]-T_{OH} \\ -[H^+]+[L^{4-}]-[H_2L^{2-}]\}[L^{4-}] \end{pmatrix}} \tag{4}$$

T_L, T_{Cu} and T_{OH} represent the total concentration of the ligand, copper and potassium hydroxide

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1) S. Nakashima, H. Miyata and K. Tôei, This Bulletin, **40**, 870 (1967).

2) L. Heller and G. Schwarzenbach, *Helv. Chim. Acta*, **34**, 1876 (1951).

3) H. Zollinger and W. Buchler, *ibid.*, **34**, 591 (1951).

4) M. Sakaguchi, A. Mizote, H. Miyata and K. Tôei, This Bulletin, **36**, 886 (1963).

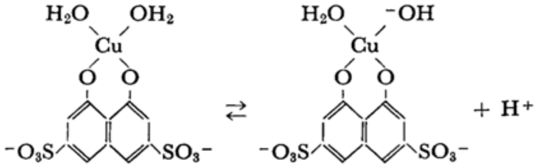
added, respectively. Data obtained from B and C in Fig. 1 were employed in this calculation, and the results obtained are identical up to $-\log[H^+]=7.0$ for both titrations (Table 1).

The titration curves also indicate that 1 : 1 (ligand to metal ion) chelate is predominant in the low $-\log[H^+]$ region. Jantti[5] has considered species of copper(II)-L and copper(II)-HL, and has evaluated the equilibrium constants of these complexes (Table 1). However, Eq. (4) was fairly well satisfied by the data up to $-\log[H^+]=7.0$, and the existence of the copper(II) chromotropate chelate was verified, but copper(II)-HL was not observed in this experiment. The existence of the 2 : 1 chelate (copper(II)-L_2) could not be determined from the calculations and titration curves.

The second inflection on the titration curves, which is striking in the 2 : 1 titration, indicated more complicated reactions, such as hydrolysis, olation of the chelate or precipitation of $Cu(OH)_2$. As described above, the equations were not satisfied above $-\log[H^+]$ 7.5 at all, and the formation of $Cu(OH)_2$ and $Cu_2(OH)_2^{2+}$ did not improve the situation. Then, assuming that the hydrolysis of the chelate occurs according to the following equation

$$CuL^{2-}(H_2O)_2 \rightleftharpoons CuL(OH)(H_2O)^{3-} + H^+,$$

the authors tried to determine the hydrolysis constant.



$$K_{CuL(OH)} = \frac{[CuL(OH)^{3-}]\cdot[H^+]}{[CuL^{2-}]} \tag{5}$$

From the relationship concerning electroneutrality, the total copper(II) content and the amount of hydroxide, Eq. (6) is derived.

$$K_{CuL(OH)} = \frac{\left(\begin{array}{c}\{T_{OH}-2T_L+[H^+]-[OH^-]\\ +2[H_2L^{2-}]+[HL^{3-}]\}[H^+]\end{array}\right)}{\left(\begin{array}{c}3T_L-T_{OH}-[H^+]+[OH^-]\\ -3[H_2L^{2-}]-2[HL^{3-}]-[L^{4-}]\end{array}\right)} \tag{6}$$

In this calculation, it is difficult to consider all four equations (1), (2), (3) and (5) at once, so $\log K_{CuL}=13.45$, which was determined at a low $-\log[H^+]$ range, was employed. The result is shown in Table 1. In a high $-\log[H^+]$ range, these equations did not explain the system, for the titration curves are unexpectedly low above $-\log[H^+]$ 9.5. It may be due to the olation of the chelate, the pecipitation of $Cu(OH)_2$ and so on. It is too complicated to study this system quantitatively above $-\log[H^+]$ 9.5.

Jantti[5] studied copper(II) chelate potentiometrically at a low pH range and Rahman[6] investigated the chelate spectrophotometrically; however they treated chromotropic acid as a monobasic acid in their calculations. The results are shown in Table 1 and they are very different from each other, the present authors' result being far apart from their values.

A similar potentiometric titration was carried out for solutions of a 1 : 1 molar ratio of chromotropic acid to other bivalent transition metal ions, such as manganese, cobalt, nickel and zinc. However, depression of the hydrogen ion concentration was not observed in any of these cases. This fact indicates that copper(II) forms the most stable chelate with chromotropic acid among the metals of the Irving-Williams stability series.

TABLE 1

The authors	$\log K_{CuL} = 13.45\pm0.1$	$-\log K_{CuL(OH)} = 8.3$
O. Jantti[5]	$pK_h{}^{*}=2.68$	$pK_1{}^{**}=7.4$
S. M. F. Rahman[6]	$\log K=5.54$	

* $H_2L^{2-} + Cu^{2+} = CuHL^- + H^+$

$$K_h=\frac{[CuHL^-]\cdot[H^+]}{[H_2L^{2-}]\cdot[Cu^{2+}]}$$

** $H_2L^{2-} + Cu^{2+} = CuL^{2-} + 2H^+$

$$K_1=\frac{[CuL^{2-}]\cdot[H^+]^2}{[HL^{3-}]\cdot[Cu^{2+}]}$$

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[5] O. Jantti, *Suomen Kem.*, **30**, B, 136 (1957).

[6] S. M. F. Rahman, *J. Inorg. Nucl. Chem.*, **26**, 385 (1964).