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The Determination of the Stability Constant of the Copper(II) Chelate of 2-(*o*-Acetylphenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic Acid

Shinichi NAGAMORI* and Haruo MIYATA

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama-shi

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We have synthesized the *o*-substituted phenylazochromotropic acids and investigated the effect of substituents on the metal-chelate stabilization. In a previous paper,[1] we reported that the acid dissociation constant of 2-(*o*-acetylphenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (2-(*o*-acetylphenylazo)chromotropic acid) and the stability constant of its 1:1 chelate with alkaline earth metals could be determined by means of a pH titration method. In the present investigation, the stability constant of the copper(II) chelate was determined spectrophotometrically at 25°C and at an ionic strength of 0.1, with potassium nitrate as the supporting electrolyte. The procedures for the measurements were similar to those described in another previous paper.[2]

The absorption spectra of the reagent and its copper chelate were measured by means of a Hitachi Model EPS-3T recording spectrophotometer; they are shown in Fig. 1. Two sulfonic groups in the reagent are completely dissociated, and the dissociation constant for one of the naphthoic hydroxyl groups was calculated from the absorbance at 566 nm using a Hitachi Model 139 spectrophotometer. The pH measurements were made with a Hitachi-Horiba Model F-5 SS pH meter. The pK_a value is 9.66; Katayama *et al.*[1] have reported that the value is 9.65 by pH titration. The dissociation of another hydroxyl group is very weak because of the strong hydrogen bridge. The reagent thus behaves like a monobasic acid under these experimental conditions. Moreover, the effect of the acetyl group on the pK_a value is unusual, irrespective of its electron-attractive effect. That is, the value of pK_a is higher than 9.19 for the phenylazochromotropic acid.[1]

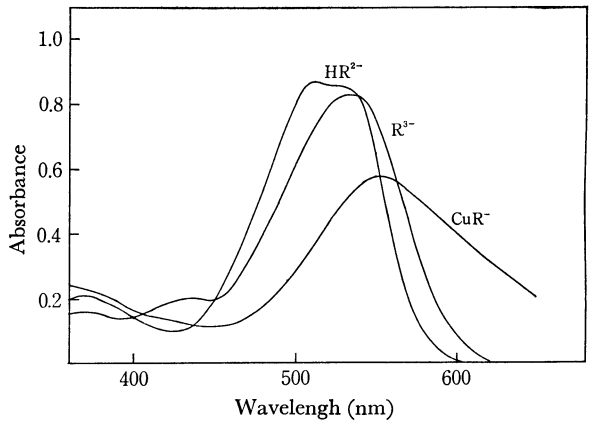

Fig. 1. Absorption spectra of the reagent and its copper chelate.
HR^{2-} at pH 1.0, R^{3-} at pH 12.6, and CuR^{-} at pH 5.57.
ligand concentration, 3.0×10^{-5}M.
copper concentration, 3.0×10^{-3}M.

The chelate formation of this reagent with the copper(II) ion become distinct at a pH of about 5, and the ratio of the reagent to the copper ion, as determined by the continuous-variation method, was 1:1. The stability constant of the copper chelate was calculated

* Present address: Santen Pharmaceutical Co., Ltd., Osaka.

1) T. Katayama, H. Miyata, and K. Tōei, This Bulletin, **44**, 2712 (1971).
2) H. Miyata, *ibid.*, **36**, 385 (1963).

by means of the following equations:

$$HR^{2-} \rightleftarrows H^+ + R^{3-} \quad (1)$$

$$K_a = \frac{[H^+][R^{3-}]}{[HR^{2-}]}$$

$$Cu^{2+} + HR^{2-} \rightleftarrows CuR^- + H^+ \quad (2)$$

$$K' = \frac{[CuR^-]}{[Cu^{2+}][HR^{2-}]} = \frac{[CuR^-]}{(C'_{Cu}-[CuR^-])(C_R-[CuR^-])}$$

$$Cu^{2+} + R^{3-} \rightleftarrows CuR^- \quad (3)$$

$$K = \frac{[CuR^-]}{[Cu^{2+}][R^{3-}]} = \frac{[CuR^-]}{(C'_{Cu}-[CuR^-])\{(K_a/[H^+](C_R-[CuR^-])\}}$$

where

K': the conditional stability constant of the copper chelate

K: the stability constant of the copper chelate

C_R: the total concentration of the reagent, $C_R = [HR^{2-}]+[CuR^-]$

C'_{Cu}[3]: the corrected concentration of copper, $C'_{Cu} = [Cu^{2+}]+[CuR^-]$

$[CuR^-]$: the concentration of the copper chelate.

The calculation procedure has been described in detail in a previous paper.[2] The values of the constants, $\log K'$ and $\log K$, of the copper chelate are listed in Table 1. The plots of the $\log K'$ *vs.* pH are shown in Fig. 2. The slope of this line is equal to 1, showing that the chelate is formed according to Eq. (2). In general, it is considered that the relation between the metal and the reagent is a Lewis-acid-and-base reaction. By comparing the $\log K$ value of the copper chelate with the value of 7.5 of the copper-phenylazochromotropic acid chelate, we can see that the stabilization of the copper chelate with this reagent is possibly due to the increase in the pK_a value of the reagent because of the effect of acetyl group existing in the *ortho* position.

Table 1. Conditional and conventional (first-step) stability constants of the copper(II)-2-(*o*-acetylphenylazo)chromotropic acid chelate at 25°C and at μ=0.1 (KNO_3)

pH	Absorbance at 500 nm	log K'	K	log K
3.68	0.821	2.83	6.51×10^8	
4.05	0.793	3.26	7.35	
4.08	0.791	3.28	7.26	
4.52	0.745	3.65	6.19	
4.54	0.731	3.74	7.17	
4.97	0.658	4.11	6.35	
		average	6.81×10^8	8.8

ligand concentration, 3.0×10^{-5}M.
copper concentration, 6.0×10^{-5}M.
$\varepsilon^{500nm}_{HR^{4-}}=2.80\times10^4$.
$\varepsilon^{500nm}_{CuR^-}=1.01\times10^4$.

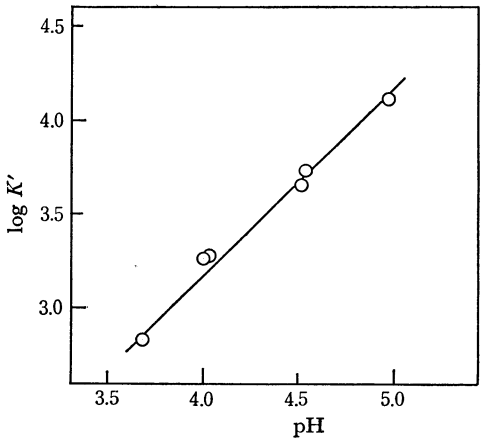

Fig. 2. log K' *vs.* pH.

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3) This value was corrected for the concentration of copper-acetate complex by using an acetate buffer.