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An Investigation of the Stability Constant of the 2,3-Dihydroxybenzoic Acid Complex with Copper(II)

Hikaru HARADA

Department of Chemistry, Faculty of Science, Tohoku University, Sendai

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It has been shown that the stability constants of some metal complexes with tiron (disodium 1,2-dihydroxybenzene-3,5-disulfonate) are larger than those with catechol.[1] This is contrary to what is to be expected from their acid dissociation constants.[2,3]

As this peculiarity seemed to come from the fact that tiron has a negative sulfonic group in the vicinity of the OH group which coordinates to a metal ion, 2,3-dihydroxybenzoic acid (DBA) was used to see whether the COOH group gives any larger stability to the metal-DBA complex. Another problem, however, may rise about this ligand; as DBA is a derivative of salycilic acid with the OH group at the 3 position, there are two possible types of chelation in the complex, namely, the catechol-type and the salycilic acid-type chelate.

Experimental

All the measurenents were carried out by using the same apparatus as was reported previously:[2,4] the reaction vessel and the quartz cell for the measurement of the absorbancy were connected by a Teflon tube. All the reaction solutions were prepared and mixed in a purified nitrogen atmsphere; then the absorbancy and the pH were simultaneously measured. During the measurements, constant-temperature water of 25.0±0.1°C was circulated through the double walls of the reaction vessel. Sodium perchlorate was used to make ionic strength 0.1. The DBA was recrystallized twice from water just before the measurements.

TABLE 1. ACID DISSOCIATION CONSTANTS OF DBA AND RELATED CATECHOL DERIVATIVES

Ligand	pK_{HL}	pK_{H_2L}	pK_{H_3L}
DBA	11.68	9.84	3.10
3,4-Dihydroxybenzoic acid[a]	11.65	8.89	4.61
Tiron[b]	11.96	7.89	
Catechol[a]	12.03	9.32	
3,5-Dinitrocatechol[c]	9.86	3.32	
3-Nitrocatechol[c]	11.48	6.50	

a) H. Harada, *Nippon Kagaku Zasshi*, **90**, 267 (1969).
b) Y. Oka, N. Nakazawa, and H. Harada, *ibid.*, **86**, 1158 (1965).
c) K.S. Math, K.A. Venkatachalam, and M.B. Kabadi, *J. Indian Chem. Soc.*, **36**, 65 (1959).

Results and Discussion

The acid dissociation constants of DBA were obtained by the method previously used with catechol derivatives.[4] The results are shown in Table 1. The larger K_{H_3L} values and the smaller K_{H_2L} value of DBA than the respective values of 4-carboxy catechol may be due to the formation of a hydrogen bond between the OH and COOH groups of DBA through the H atom of the OH group.

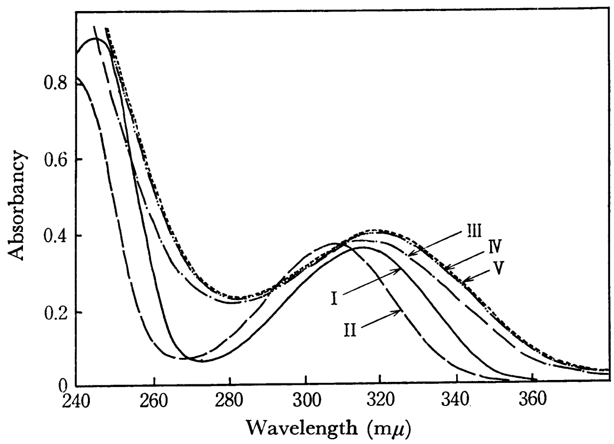

Fig. 1. pH dependence of absorption curve of Cu(II)-DBA system.
pH: I, 2.24 (——)
II, 4.14—4.80 (— —)
III, 5.95 (—·—)
IV, 7.20 (—··—)
V, 7.54 (---------)
concentration:
Cu(ClO$_4$)$_2$, 1.103×10^{-4} mol/*l*
DBA, 1.103×10^{-4} mol/*l*

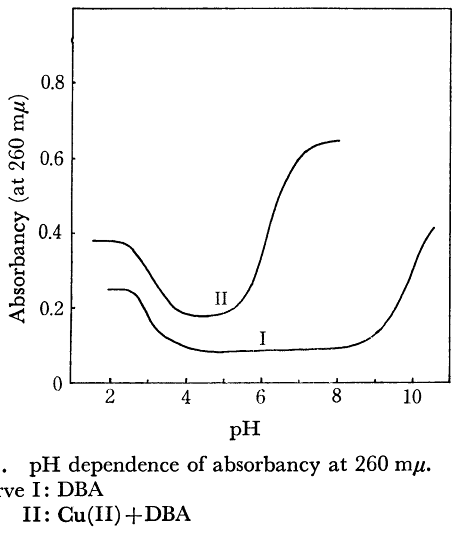

Fig. 2. pH dependence of absorbancy at 260 mμ.
Curve I: DBA
II: Cu(II)+DBA

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[1] H. Harada and Y. Oka, *Nippon Kagaku Zasshi*, **90**, 898 (1969).

[2] Y. Oka and H. Harada, *ibid.*, **88**, 441 (1967).

[3] This problem has also been pointed out in the paper by R. F. Jameson (*J. Inorg. Nucl. Chem.*, **28**, 2667 (1966)), but no explanation is to be found there.

[4] H. Harada, *Nippon Kagaku Zasshi*, **90**, 207 (1969).

The stability constant of the Cu-DBA (1: 1) chelate was obtained in a manner to be described below. The absorption spectra of the solution containing the Cu(II) ion and DBA are shown in Fig. 1. The pH-dependence of absorbancy change at 260 mμ is shown in Fig. 2, together with that of the ligand itself.

As is shown in Fig. 2, the decrease in absorbancy at about pH 3 can be ascribed to the dissociation of the carboxyl group of DBA, as was expected from its pK_{H_3L} value.

On increasing the pH, the absorbancy also increased in the pH range from 5.5 to 6.5; this increase was attributed to the formation of the complex.

Here, it is assumed that the Cu-DBA (1: 1) chelate is formed in the pH 5.5—6.5 range according to the following equation:

$$Cu + H_2L = CuL + 2H \qquad (1)$$

The equilibrium constant of this reaction may be described as:

$$K_1 = \frac{[CuL][H]^2}{[Cu][H_2L]} \qquad (2)$$

When the solution is prepared to make the concentrations of Cu and DBA equal (1.084×10^{-4} mol/*l*) and when its hydrogen ion concentration is varied, the following equation (reported previously[5]) is obtained:

$$A - a\varepsilon_{H_2L} = a(\varepsilon_{CuL}-\varepsilon_{H_2L}) - [H](A-a\varepsilon_{H_2L})^{1/2}\left(\frac{\varepsilon_{CuL}-\varepsilon_{H_2L}}{K_1}\right)^{1/2} \qquad (3)$$

where A is the absorbancy, a is the concentration of the Cu ion and also that of DBA, and ε_{H_2L} and ε_{CuL} are the molar extinction coefficients of DBA and CuL respectively.

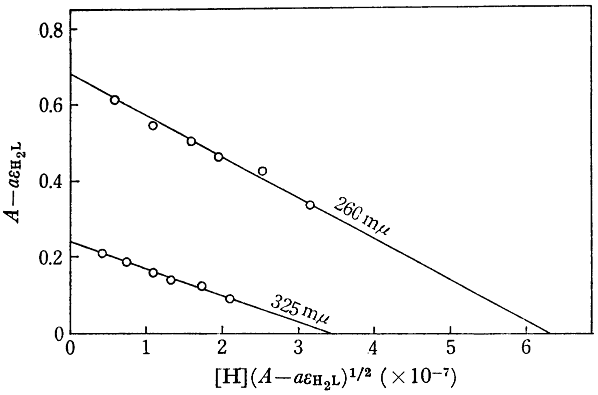

Fig. 3. Relation between $A-a\varepsilon_{H_2L}$ and $[H](A-a\varepsilon_{H_2L})^{1/2}$.
concentration: $Cu(ClO_4)_2$: 1.084×10^{-4} mol/*l*
DBA: 1.084×10^{-4} mol/*l*

If a plot of $[H](A-a\varepsilon_{H_2L})^{1/2}$ on the right-hand side against $A-a\varepsilon_{H_2L}$ on the left-hand side of Eq. (3) is linear, the variation in absorbancy over the pH 5.5—6.5 range can be considered to be due to the formation of the 1: 1 chelate by means of Eq. (1). Figure 3 indicates that the linear relation holds. The division of the intercept of the line by the square of the slop and again by the concentration of Cu(=DBA), a, gave K_1. The value of K_1, thus obtained was divided by the acid dissociation constant of DBA; then the stability constant of the 1: 1 chelate, k_1, was obtained.

Table 2. Stability constants of Cu(II)-complexes with DBA and related catechol derivatives

Ligand	log k_1
DBA	13.24
Salycilic acid[a]	10.64
Catechol[b]	13.50
3,4-dihydroxybenzoic acid[b]	13.15
Tiron[c]	14.43
3,5-Dinitrocatechol[d]	10.45

a) from A. E. Martell and L. G. Sillén, "Stability Constants of Metal Ion Complexes. Section II, Organic Ligands," Chemical Society, London (1964).

b) H. Harada and Y. Oka, *Nippon Kagaku Zasshi*, **90**, 898 (1969).

c) Y. Oka, N. Nakazawa, and H. Harada, *ibid.*, **86**, 1158 (1965).

d) K. S. Math, K. A. Ven Katachalam, and M. B. Kabadi, *J. Indian Chem. Soc.*, **36**, 65 (1959).

As is shown in Table 2, the k_1 value of Cu-DBA is 13.24, which is much nearer to the k_1 value of Cu-catechol (13.50) than to the k_1 value of Cu-salycilic acid (10.64). It can, therefore, be concluded that the DBA in the Cu-complex has a catechol-type-chelation.

When the stability constant of Cu-tiron is compared with that of Cu-DBA, which has a 3-carboxyl group, it can be noticed that Cu-tiron has an appreciably higher value. It seems that the higher stability constant of tiron is not caused by the ordinary substitution effect of the 3-position substituent.

It is supposed that the sulfonic group is more strongly solvated by water than the carboxyl group; hence, the degree of desolvation may also be larger in the sulfonic group when the Cu-chelate is formed. It can perhaps be concluded that the entropy change for the complex formation contributes greatly to the higher stability constant of the Cu-tiron chelate.

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[5] H. Harada, *Nippon Kagaku Zasshi*, **91**, 1064 (1970).