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5. Analytical Chemistry by Means of Organic Compounds.(XXIV)

## Studies on the Reaction between Copper and 7-Azo-benzene-8-hydroxy-quinoline-5-sulfonic Acid

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Some oxine derivatives react with many cations, resulting in the formation of inner complex compounds which may be used in the inorganic analytical chemistry. We are conducting a systematic investigation of the reactions of a series of oxine derivatives to many metal ions.

This paper introduces 7-azo-benzene-8-hydroxyquinoline-5-sulfonic acid, from this class of compounds, as a new reagent for the analytical chemistry and the chemistry of complex compounds. We prepared this compound using the reactions represented by the following schema[1].
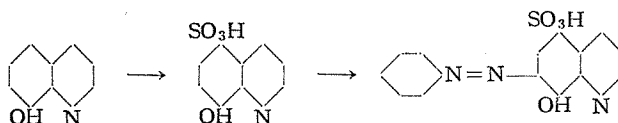
This compound was obtained in the needles of red color. It is slightly soluble in hot alcohol and water, and decomposes at 310°C. In acid solution with pH value below 3, it is deep red. If the solution is made alkaline, the color changes slowly to orange at pH 3~7 and becomes orange yellow at pH 8.

We studied the reaction of this reagent with cupric ion, the effect of the pH on the reaction of the complex formation and the structure of the complex.

EXPERIMENTAL

Instruments.

Spectrophotometric measurements were made with the Beckman Quartz Spectrophotometer, Model DU, using 1 cm. corex glass and silica transmission cells. The Beckman glass electrode pH meter, Model H-2, was used for all pH measurements.

Stock solution of $CuSO_4$ was prepared in a concentration of $10^{-3}M$ using recrystallized $CuSO_4 \cdot 5H_2O$, and that of 7-azo-benzene-8-hydroxyquinoline-5-sulfonic acid

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was prepared in a concentration of $5 \times 10^{-4}M$, dissolving the compound in $0.5M$-acetic acid and ammonium acetate buffer solution. Solutions of other concentration were obtained from these by dilution with distilled water or the buffer solution.

The acetate buffer solution were prepared by mixing the distilled acetic acid and ammonia water so that the concentration of acetic acid and that of ammonium acetate in the resultant solution were both $0.5M$. The pH value of this buffer is 4.7. Solution of other pH were prepared by adding the proper amounts of concd. distilled hydrochloric acid and the solution of sodium hydroxide to the acetate buffer solution.

Studies of the Reaction of Cupric Ion and 7–Azo–benzene– 8–hydroxy–quinoline–5–sulfonic Acid

Fig. 1 shows the absorption of the 7-azobenzene-8-hydroxyquinoline-5-sulfonic-acid, and of the mixture of copper salts and this reagent. Absorptions were determined from 240 to 600 mμ, and in the range of 240 to 280 mμ the extinctiou was so large that the solutions diluted three folds were used. The pH value of both solutions was 4. 7. Curve 1 was two maxima at 317 and 492 mμ, but curve 2 has three maxima at 255, 317 and 375 mμ. From Fig. 1 it is deduced that the soluble complex compound was formed by the addtion of cupric ion to the reagent (mole ratio 1 : 2), for curve 2 differs remarkably from curve 1 in the wave length of the maximum extinction and the value of extinction.
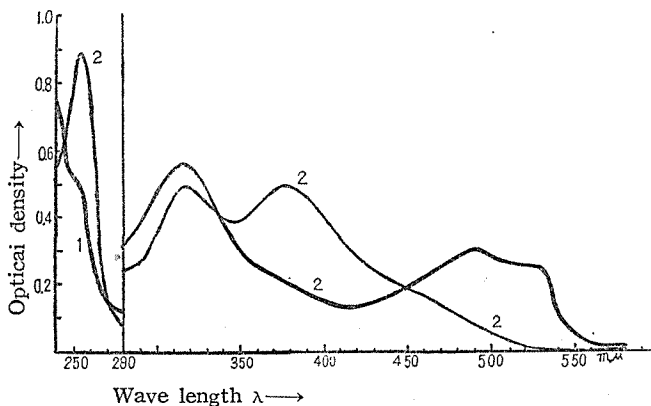

Fig. 1.

Curve 1 : Absorption spectra of $10^{-4}M$ of 7–azobenzene–8–hydroxyquinoline–5–sulfonic acid.

Curve 2 : Absorption spectra of the mixture of cupric ion and the reagent. The concentration is $5 \times 10^{-5}M$ for cupper and $10^{-4}M$ for the reagent.

Masayoshi Iṣhibashi and Yuroku Yamamoto

The Effect of the Hydrogen-ion Concentration on the
Reaction of the Complex Formation

The effect of pH value on the reaction was studied. The absorption of the reagent itself and that of the mixture of cupric ion and the reagent were measured at various pH's. Fig. 2 shows the absorption curves of the reagent. It is observed that in acid solution the absorption curve has two maxima of extinction at 500 and 530 mμ, and in the solution with pH value below 3 the peak at longer wave lengths is higher than that of shorter wave lengths, but with the increase of pH value it decreases and in alkaline solution it has only one maximum at 475 mμ. Both maxima shift to the shorter wave length with the increase of pH.

Fig. 3 shows the absorption of the mixture of the reagent and cupric ion at verious pH's (mole ratio 2 : 1). From Fig. 1 it has been concluded that the evidence
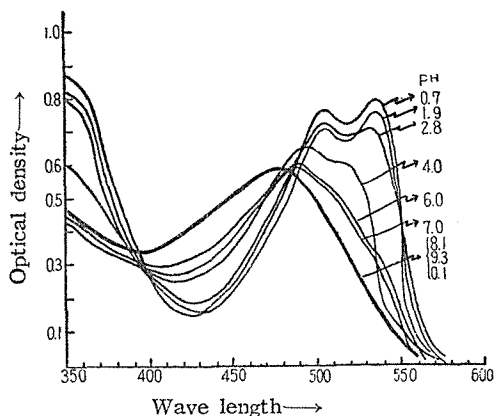

Fig. 2. Absorption spectra of 1.5×10⁻⁴M of the reagent at various pH's.
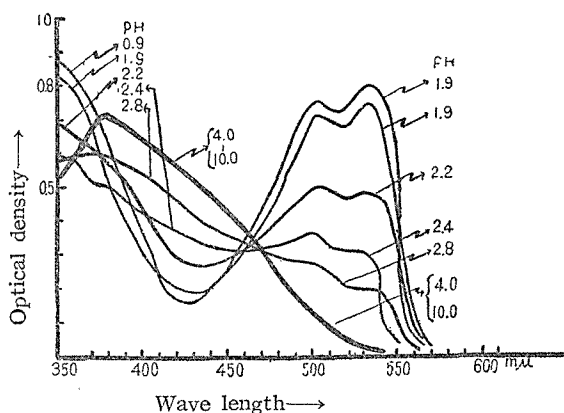

Fig. 3. Absorption spectra of the mixture of cupric ion and the reagent (mole ratio 1 : 2). The concentration is the same as in Fig. 2.

of the complex formation is the appearance of the maximun at wave length of 375 mμ. When Fig. 2 and 3 are compared, the maximum at 375 mμ begins to appear in the mixture of pH 2.2 and its optical density rises sharply with a slight increase of pH, and in the solutions of pH higher than 4.0 it becomes constant. Also, it is observed that the complex is not formed in the mixture of pH below 1.9, because the curves in Fig. 3 show almost the same figures as in Fig. 2. So, it is concluded that the complex begins to be formed in the mixture with pH 2.2 and the reaction is compiete at pH 4.0. It may be said that the complex is very stable.

Studies on the Constitute of the Complex. (Methods of Continuous Variations)

Using the continuous variation methods as modified by Vosburgh and Cooper[2], the cooper complex solutions of cupric sulfate of $10^{-4}M$ and the solution of the reagent of $10^{-4}M$ were prepared, in the buffer of pH 4.7, varying proportions so that the total solute concentration was the same in each solution. The optical density of the resulting solution was measured at the wave lengths of 492, 385, 260 and 255 mμ, where the difference in absorption of the reagent and copper complex was greatest. For the range of ultra violet, more diluted solutions were used. Then, the optical density of the reagent itself in the same concentration as the above solutions was measured at the same wave lengths. The absorption of cupric sulfate was not taken into consideration, because its optical density was negligibly small in such concentrations. The difference between the optical density of the solution of mixture and that of the reagent itself, *i.e.*, Vosburgh's Y, is plotted in Fig. 4 At 492 mμ Y shows minimum, and at the other wave lengths, Y takes maximum. From the position of the maximum and minimum, mole ratio of the constituents in complex formed is 2 moles of the reagent to one mole of cupric ion. So, the structure of this com-
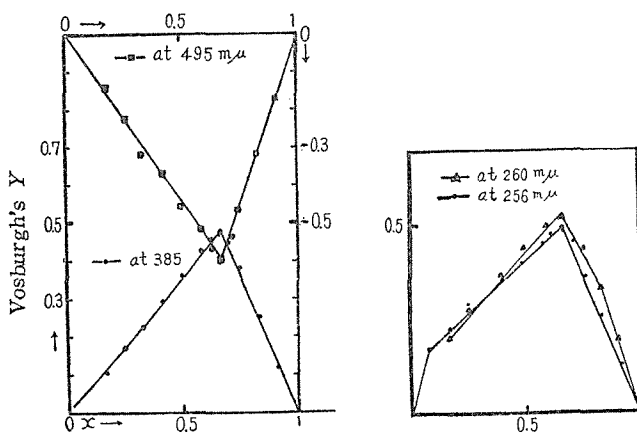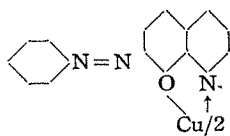

Fig. 4. Continuous variation study of the complex.
Mole ratio of reagent/complex
x, volume fraction of the reagent added to $(1-x)$ equimolar Cu++ solution.

plex must be the same as copper-oxine complex :

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(2) Warren C.Vosburgh and Gerald R.Cooper : *J. Am. Chem. Soc.*, **63,** 437 (1941).