complex and thus the value of $K$ may be calculated from the relation

$$K = \frac{(a_1 - x)(b_1 - x)}{x} = \frac{(a_2 - x)(b_2 - x)}{x}$$

where the $a$'s and $b$'s denote initial concentration of uranyl and sulfosalicylate, respectively, and $x$ denotes the concentration of complex formed.

$K$ values calculated by this method are of the same order of magnitude as those obtained by the first method but show greater precision. The average $K$ from several determinations is

$$K = 1.93 \times 10^{-4} \pm 0.08 \times 10^{-4} \text{ (at } 25^\circ\text{)}$$

The free energy of *formation* of the complex may be calculated readily from the relation $\Delta F = RT \ln K = -5060$ cal./mole (where $K$ denotes the *dissociation* constant as determined above).

**Temperature Effect and Heat of Reaction.**—From the data in Table II it may be seen that increased temperature tends to increase complex formation but that the effect is not pronounced. A determination of the dissociation constant at 33.2° gave an average value of $1.48 \times 10^{-4} \pm 0.6 \times 10^{-4}$.

It is apparent that the heat of reaction must be small. It can be calculated readily from standard relations, but since the difference in $K$ values is small the effect of experimental errors becomes very pronounced and can outweigh the temperature effect itself. Such a calculation is then of uncertain validity.

**Structure of Complex.**—None of the experiments using Job's method in the region of *p*H 4.6 indicate other than a 1:1 mole ratio in the complex. Since the color fades rapidly as the *p*H changes, there is no evidence for formation of more than one colored complex under the conditions of these experiments.

No attempt should be made to express a structural formula for this complex until more evidence is available, in particular concerning the presence or absence of hydrogen or hydroxide ions.

It may be noted, however, that the low free energy of formation indicates a weak association effect rather than a strong covalent bond. Extraction tests with various organic solvents such as benzene and carbon tetrachloride were unsuccessful, giving no positive evidence for the presence of any neutral, covalent grouping. The 1:1 ratio, the *p*H region in which the maximum effect occurs, and the rapid formation—without appreciable "aging" effect—indicate association of ions such as $UO_2^{++}$ and $^-O_3SC_6H_3OHCOO^-$. This would give an apparent charge of zero, but a "zwitterion" type of structure is possible. The *p*H effect and the apparently high reactivity of the complex with either increase or decrease in *p*H are suggestive of such a structure.

The authors wish to express their appreciation to the Pan American Refining Corporation for its generous support of this work by a fellowship grant (to R. T. F.).

## Summary

1. Spectrophotometric data for solutions with concentrations in the region of 0.005 *M* and over a *p*H range of 2 to 10 indicate only one complex formed with uranyl ion and sulfosalicyclic acid. This involves a 1:1 mole ratio of uranyl and sulfosalicyclic acid.

2. The effects of changing *p*H, of temperature, and of acetate ion have been studied.

3. The dissociation constant and free energy of formation of the complex have been calculated.

RECEIVED JUNE 9, 1948

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

# Spectrophotometric Studies on Complex Formation with Sulfosalicylic Acid. III. With Copper(II)

BY STANLEY E. TURNER AND ROBBIN C. ANDERSON

As part of a series of experiments on complex formation by sulfosalicylic acid with various metal ions in solution[1] a study of its reaction with copper (II) ions has been made.

Spacu and Macarovici[2] reported formation of a deep olive-green complex of composition $[Cu(OC_6H_3CO_2 \cdot SO_3)_2]H_4$ in connection with experiments on copper-cobalt complex sulfosalicylates. Babko[3] has studied the copper-salicylate system and reports a complex of the type CuR from *p*H 3-5 and $CuR_2$ from *p*H 7–9.

## Experimental

The apparatus used was the same as that described previously.[1] Preliminary absorption measurements were made with a General Electric Hardy Recording Spectrophotometer. Data for determination of composition of the complex, temperature effects, etc., were taken with a Beckmann Model DU Spectrophotometer equipped with a thermostat for temperature control in the absorption cells.

*p*H measurements were made with a Beckman model G *p*H meter.

To avoid any interference from iron, Merck Reagent Grade copper sulfate was precipitated and redissolved in ammonium hydroxide. The solution was acidified with nitric acid and evaporated almost to dryness to remove

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(1) Robt. T. Foley and Robbin C. Anderson, THIS JOURNAL, **70**, 1195 (1948).

(2) G. Spacu and G. Gh. Macarovici, *Bull. Soc. Stiintje Cluj*, **8**, 364 (1936); *cf. Chem. Abs.*, **31**, 3810 (1937).

(3) A. K. Babko, *J. Gen. Chem. (U. S. S. R.)*, **17**, 443 (1947), *cf. Chem. Abs.*, **42**, 475 (1948).

ammonium nitrate. The resulting sludge was heated with sulfuric acid to drive off the nitric acid and water. In this manner crystals of copper sulfate with a small amount of residual sulfuric acid were obtained. Solutions were prepared by dissolving this material in distilled water and standardizing electrolytically with a Fisher Scientific Co. Electroanalyzer.

Sulfosalicylic acid and sodium hydroxide were prepared as described earlier.[1]

For comparisons of various mixtures at constant *p*H, the copper(II) sulfate and sulfosalicylic acid were mixed in proportion such as to give the desired final concentration. The mixture was then adjusted to the desired *p*H by adding sodium hydroxide and diluted to final volume with water containing a little sulfuric acid or sodium hydroxide as needed to bring it to the same *p*H.

## Results

**Effect of *p*H.**—Since Babko had reported different complexes in different *p*H ranges with copper(II) and salicylic acid, the effect of *p*H on color of the sulfosalicylate system was first tested. In Fig. 1 are shown three typical transmittance curves taken on the recording spectrophotometer using solutions containing 0.0055 *M* copper(II) sulfate and 0.0075 *M* sulfosalicyclic acid at different *p*H values (5.3 for curve I, 6.8 for II, and 10.9 for III). From a series of such curves at values from *p*H 3.6 to 11.7 it was found that curves for solutions above *p*H 8.5 were of the type of III, with an absorption peak at 660 mμ. Those for solutions of *p*H less than 5.5 were of the type such as I, with maximum absorption at 700 mμ or above. Between *p*H 5.5 and 8.5 there was apparently a transition from type I to III, as illustrated by curve II.

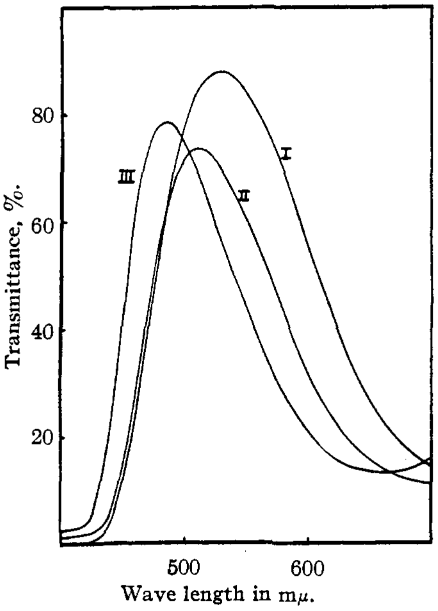

Fig. 1.

This suggested the existence of two different complexes, in this case also. Studies of composition were then made both at *p*H 5 and *p*H 9.

**Complex at *p*H 5.**—The ratio of copper(II) to sulfosalicylic acid in the complex was determined by Job's method of continuous variations.[4] A series of solutions was prepared with varying ratios of copper(II) and sulfosalicyclic acid, but with the total molarity of the two constant at 0.038 *M* and with the *p*H constant at 5. The difference ($\bar{D}$) between the observed optical density of each solution and that which would be given by the original reagents if no association occurred (in this case that of copper(II) since sulfosalicyclic acid is colorless) is plotted against the ratio $[Cu^{++}]/[Cu^{++}] + [HO_3SC_6H_3OHCOOH]$. This gives a curve which should rise to a maximum at a point corresponding to the ratio in which the reagents combine to form the complex.

The results are shown in Fig. 2, curves II and III. Curve II is for data taken at a wave length of 700 mμ and curve III at 630 mμ. The curves clearly indicate a complex of composition CuR (where R might be sulfosalicylic acid or one of its ions).

**Complex at *p*H 9.**—A similar determination by the Job method was made at *p*H 9. The result is shown in curve I of Fig. 2 (the total molarity of copper(II) plus sulfosalicylate being 0.038 *M*). The curve indicates that in this *p*H region the complex is of the type $CuR_2$.

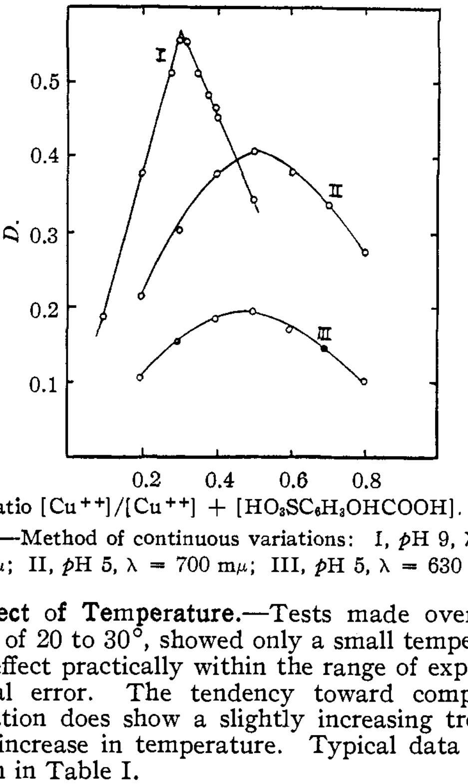

Fig. 2.—Method of continuous variations: I, *p*H 9, λ = 660 mμ; II, *p*H 5, λ = 700 mμ; III, *p*H 5, λ = 630 mμ.

**Effect of Temperature.**—Tests made over a range of 20 to 30°, showed only a small temperature effect practically within the range of experimental error. The tendency toward complex formation does show a slightly increasing trend with increase in temperature. Typical data are shown in Table I.

**Dissociation Constants.**—To determine the dissociation constant of the complex at *p*H 5 a mixture containing 0.019 *M* copper(II) and 0.019 *M* sulfosalicylate (corresponding to the

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(4) P. Job, *Ann. chim.*, **11**, 97 (1936); *cf.* Vosburgh and Cooper, THIS JOURNAL, **63**, 436 (1941).

TABLE I

TEMPERATURE EFFECT, ($[Cu^{II}] = 0.019 = [HO_3SC_6H_3OHCOOH]$, $pH = 5$)

| Temp., °C. | Optical density 630 | Optical density 700 |
|---|---|---|
| 22 | 0.235 | 0.492 |
| 25 | .236 | .493 |
| 27 | .239 | .496 |
| 30 | .241 | .495 |

peak of curves II and III, Fig. 2) was diluted in successive stages—adding sodium sulfate as needed to keep the ionic strength constant. From this dilution curve and the data of Fig. 2 a series of pairs of solutions could be selected, having equal optical density (and thus essentially equal concentrations of complex) but different concentrations of reagents. From the equation

$$K = \frac{[Cu_1^{II} - X][R_1 - X]}{X} = \frac{[Cu_2^{II} - X][R_2 - X]}{X}$$

$X$ and $K$ could then be calculated since the values for $Cu^{II}$ and $R$ were known.

As a first approximation the effect of $Cu^{++}$ on the optical density was neglected, but, by using the value of $K$ so obtained, correction could be made for the optical density of unreacted $Cu^{++}$ and better values for $K$ determined. Results are shown in Table II for data at 630 mμ and 25°. A similar determination at 700 mμ gave a value in agreement with that at 630 mμ, but the variations are larger since much higher corrections have to be applied for absorption by copper(II) ions.

TABLE II

DISSOCIATION CONSTANT

| Total [$Cu^{++}$ | Total [R] | $K$ |
|---|---|---|
| 0.0076 | 0.0304 | $1.7 \times 10^{-3}$ |
| .0114 | .0266 | 2.3 |
| .0152 | .0228 | 2.0 |
| | | Mean value = $2 \times 10^{-3}$ |

$K$ can also be determined by assuming that, in solutions containing large excess of sulfosalicyclic acid, association is complete. A value for the extinction coefficient can then be calculated and used to determine dissociation in other solutions. This method gives $K$ values showing wider variation than the data of Table II, but the average value is $1.8 \times 10^{-3}$—in agreement with the result above.

The approximate extinction coefficients as determined by this method were 16 at 630 mμ and 33 at 700 mμ.

The dissociation constant for the $CuR_2$ type complex cannot be determined so well because the data are not sufficiently accurate to permit correction for effects of precipitation, dissociation to the CuR type complex, and similar factors. However, the sharp peak at the maximum of curve I, Fig. 2 indicates that dissociation is small. Assumption that dissociation is negligible in the presence of fairly large excess of sulfosalicyclic acid (for example where the ratio $[Cu^{++}]/[Cu^{++}] + [R]$ is 0.1) should be reasonably well justified.

From the observed optical densities of such solutions, a value of 53 was obtained for the approximate extinction coefficient of the complex at 660 mμ. Using this extinction coefficient, the concentrations of complex in other solutions and the dissociation constant were determined. An average value of $8 \times 10^{-7}$ for $K$ at 25° was obtained. It should be noted that the results show some "drift," the $K$ value increasing somewhat as the proportion of sulfosalicyclic acid decreases. Such an effect must be expected since no correction could be made for the presence of the 1:1 complex.

From the dissociation constants above, one may calculate the free energies of formation: $\Delta F = RT \ln K$. This gives a value of −3700 cal./mole for the free energy of formation of the complex of type CuR and approximately −8000 cal./mole for the type $CuR_2$.

**Structure of the Complex.**—The close resemblance in reactions of copper(II) with salicylic and sulfosalicylic acids indicates that linkage occurs with the carboxyl and/or phenolic groups. Since at $pH$ 5 the carboxyl group is largely dissociated, the 1:1 complex is probably a combination of $Cu^{++}$ and $^{-}O_3SC_6H_3OHCOO^{-}$ ions. At $pH$ values in the region of 9, it seems likely that the phenolic group is also involved—the linkage with two carboxyl and two phenolic groups being in accord with the normal coördination number of 4 for the copper.

The authors wish to acknowledge the coöperation and assistance of Mr. L. L. Antes, Bureau of Engineering Research, in making the measurements with the recording spectrophotometer. This research was supported by a grant from the University of Texas Research Institute.

## Summary

Spectrophotometric measurements indicate copper(II) ions and sulfosalicylate ions react in a 1:1 ratio in the $pH$ range 3–5.5 and a 1:2 ratio at $pH$ values above 8.5, with mixtures of the two forming in the intermediate ranges.

Temperature changes within ordinary ranges were found to have little effect on the complexes.

Dissociation constants and approximate extinction coefficients for the two complexes have been determined.

RECEIVED AUGUST 30, 1948