[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF THE UNIVERSITY OF OSLO]

Inner Complex Salts of the 8-Hydroxyquinoline-5-sulfonic Acid

BY JACOB MOLLAND

When a solution of ferric sulfate is added to an aqueous solution of 8-hydroxyquinoline-5-sulfonic acid, the mixture is colored a deep green. If increasing amounts of copper sulfate are added to this mixture, the color gradually fades. If copper sulfate is added to a solution of the pure 8-hydroxyquinoline-5-sulfonic acid, no appreciable change of color occurs. The color reaction of iron has a considerable interest for analytical chemistry, as will be shown in papers which are to be published in the near future. The reaction is due to the formation of an inner complex iron salt, and the fading caused by the addition of copper must be explained by the formation of an equilibrium between the green iron salt and a colorless copper salt. The scope of this paper is to study the composition of these salts by means of a spectrophotometric investigation.

Supposing that the color reaction of iron is due to the formation of z molecules of an inner complex salt from x molecules of the 8-hydroxyquinoline-5-sulfonic acid and y ferric ions, the reaction can be represented by the equation

$$x\text{R} + y\text{Fe}^{+++} = z\text{RFe} + s\text{H}^+$$

R denoting the 8-hydroxyquinoline-5-sulfonic acid and RFe the iron compound. Analogously the formation of the copper compound, RCu, can be represented by the equation

$$\xi\text{R} + \eta\text{Cu}^{++} = \zeta\text{RCu} + \sigma\text{H}^+$$

If the initial hydrogen-ion concentration is sufficiently large, the alteration caused by the reaction may be neglected, and the equilibrium condition for an aqueous solution of the 8-hydroxyquinoline-5-sulfonic acid containing iron and copper will be

$$\frac{[\text{Fe}^{+++}]^{y\xi}\,[\text{RCu}]^{x\zeta}}{[\text{Cu}^{++}]^{x\eta}\,[\text{RFe}]^{z\xi}} = \text{const.} \qquad (1)$$

Let the initial concentrations be $[\text{R}]_0 = a$, $[\text{Fe}^{+++}]_0 = b$, $[\text{Cu}^{++}]_0 = c$, $[\text{RFe}]_0 = 0$, $[\text{RCu}]_0 = 0$. In order to simplify the calculation, the concentrations of iron and copper are also kept so large that they may be considered as constant during the reaction. After establishment of the equilibrium, the concentration of the complex iron salt is measured by means of an extinction estimation. Let the observed Bunsen–Roscoe extinction coefficient be d. Further, let the extinction coefficient D be observed when a great excess of iron is added to a solution of the pure 8-hydroxyquinoline-5-sulfonic acid of the concentration A. In this case the 8-hydroxyquinoline-5-sulfonic acid is practically completely transformed to the complex iron salt, giving a concentration Az/x. The salt concentration corresponding to the extinction coefficient, d, is then $[\text{RFe}] = dzA/xD$.

On account of the great excess of iron and of copper, the concentration of the 8-hydroxyquinoline-5-sulfonic acid is vanishing. The amount of the acid which is not used for the formation of the iron salt, is used for the formation of the copper salt. This amount is

$$a - \frac{x}{z}\cdot[\text{RFe}] = a - \frac{A}{D}d$$

and the quantity of the copper salt formed is

$$[\text{RCu}] = \frac{\zeta}{\xi}\left(a - \frac{A}{D}d\right)$$

Finally, the concentrations of iron and of copper will remain practically constant, $[\text{Fe}^{+++}] = b$ and $[\text{Cu}^{++}] = c$. Introducing these values into equation (1), we obtain

$$\frac{b^{y\xi}\left(a - \frac{A}{D}d\right)^{x\zeta}}{c^{x\eta}d^{z\xi}} = \text{const.} \qquad (2)$$

The ratio x/y can be determined by the following experiment. The maximum concentration of the iron compound obtainable from a concentration p of the 8-hydroxyquinoline-5-sulfonic acid will be pz/x. This concentration can be obtained approximately if a great excess of iron is used. Let the extinction coefficient in this case be d_p. Further, the maximum concentration of the iron salt obtainable from a concentration q of iron will be qz/y, and this concentration is approximately reached if a great excess of 8-hydroxyquinoline-5-sulfonic acid is used. Let the extinction coefficient in this case be d_q. If now the same iron compound is formed in both cases, the molecular extinction coefficient ϵ must be the same in the two experiments, and we obtain the equation

$$\epsilon = \frac{d_p}{\frac{z}{x}p} = \frac{d_q}{\frac{z}{y}q}$$

giving $x/y = pd_q/qd_p$. An experiment gave the figures $p = 3.10^{-5}$, $q = 2.10^{-5}$, $d_p = 0.314$, $d_q = 0.630$. Substituting these figures, we obtain $x/y = 3.01$. The simplest formula giving this result is $(C_9H_6O_4NS)_3Fe$. If we accept this formula, we obtain $x = 3$, $y = 1$, $z = 1$.

If b and c are kept large and constant, and the extinction coefficient is measured for different values of a, equation (2) then can be written in the form

$$\left(a - \frac{A}{D}d\right)^{3\zeta/\xi} \Big/ d = \text{const.} \quad (3)$$

allowing the determination of the ratio ζ/ξ. Let the extinction coefficient d_m correspond to the concentration a_m and d_n correspond to a_n. Then ζ/ξ is determined by the equation

$$\frac{\zeta}{\xi} = \frac{1}{3}\,\frac{\log d_m - \log d_n}{\log\left(a_m - \frac{A}{D}d_m\right) - \log\left(a_n - \frac{A}{D}d_n\right)} \quad (4)$$

In order to determine ζ/ξ by means of equation (4), an experiment was carried out with a series of solutions containing 0.003 g. molecule of ferric sulfate, 0.01 g. molecule of copper sulfate, and increasing amounts from 0.00002 to 0.00014 g. molecule of 8-hydroxyquinoline-5-sulfonic acid per liter. The constant A/D for the wave length in question was determined to 0.0000685 by means of the observations given in Table I. The results are seen in Table I. These data should be combined two by two in equation (4). Generally q numbers can be combined in couples in $^1/_2q(q - 1)$ different ways. In the present case with $q = 9$ we get 36 possible combinations. A mathematical investigation[1] will, however, show that a great part of these combinations will give a poor determination of ζ/ξ, as the mean square error of the extinction estimation in some cases will be greatly magnified by insertion into equation (4). Therefore we select ten combinations giving small mean square errors (Table II). The mean value of ζ/ξ is 0.509, showing that one molecule of the copper compound contains two molecules of 8-hydroxyquinoline-5-sulfonic acid.

TABLE I

10^5a	d
2	0.191
3	.300
4	.415
5	.525
6	.662
8	.875
10	1.152
12	1.370
14	1.624

TABLE II

10^5a_m	10^5a_n	ζ/ξ
14	2	0.509
14	3	.506
14	4	.499
14	5	.525
12	2	.494
12	3	.497
12	4	.488
10	2	.537
10	3	.559
8	2	.476

(1) J. Molland, *Avhandl. Norske Videnskaps-Akad. i Oslo. I. Mat.-Naturv. Klasse*, **2** (1936).

If a and b are kept constant, we are now able to write equation (2) in the form

$$\frac{\left(a - \frac{A}{D}d\right)^3}{c^{3\eta/\zeta}d^2} = \text{const.}$$

allowing the determination of η/ζ. Let the extinction coefficients d_m and d_n correspond to the concentrations c_m and c_n. Then

$$\frac{\eta}{\zeta} = \frac{\left(\log\left(a - \frac{A}{D}d_m\right) - \frac{2}{3}\log d_m\right) - \left(\log\left(a - \frac{A}{D}d_n\right) - \frac{2}{3}\log d_n\right)}{\log c_m - \log c_n} \quad (5)$$

An experiment for the determination of η/ζ by means of equation (5) was carried out with a series of solutions containing 0.0025 g. molecule of ferric sulfate, 0.00013 g. molecule of 8-hydroxyquinoline-5-sulfonic acid, and increasing amounts of copper sulfate, from 0.01 to 0.1 g. molecule per liter. The extinction coefficients seen in Table III were observed (corrected for the extinction of the ferric sulfate and the copper sulfate). For the wave length used, A/D was determined to 0.0000786 by means of the data of Table III. Also in this case ten combinations with small mean square errors are collected (Table IV).

TABLE III

$100c$	d
0	1.654
1	1.407
2	1.202
3	1.025
4	0.902
5	.765
6	.681
7	.600
8	.553
9	.502
10	.481

TABLE IV

$100c_m$	$100c_n$	η/ζ
10	1	0.987
10	2	.972
10	3	.937
9	1	1.015
9	2	1.011
9	3	1.030
8	1	1.018
8	2	1.016
7	1	1.039
6	1	1.035
	Mean value	1.006

The copper compound thus contains one atom of copper and two molecules of 8-hydroxyquinoline-5-sulfonic acid.

Summary

The inner complex iron and copper salts of the 8-hydroxyquinoline-5-sulfonic acid were studied by means of extinction measurements, and the composition of the salts is found to correspond to the formulas $(C_9H_6O_4NS)_3Fe$ and $(C_9H_6O_4NS)_2Cu$.

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