Iron(III) 8-hydroxy quinoline 7-sulfonic Acid Chelate

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With 6 Figures

Abstract

Iron(III) forms in the aqueous medium a green complex with 8-hydroxy quinoline 7-sulfonic acid with maximum absorbence at 610 mμ, stable in the pH range 3—4. The composition of the complex as established by three different methods spectrophotometrically is Fe(III) EHQS (where EHQS is the abreviation used for 8-hydroxy quinoline 7-sulfonic acid). The stability constant calculated by the methods of Banerji and Dey[1]) and the mole-ratio method[2]) was found to be log K = 3.8 $\pm$ 0.05 at 25 °C and the heat of formation was found to be = — 5.24 k.cal/mole at 25 °C.

Introduction

The introduction of 8-hydroxy-quinoline for use as a reagent for the analysis of metal ions by Berg and Hahn[3]) in 1926 has opened a new field in analytical chemistry. A better understanding of the specific activity of the co-ordinating groups in 8-hydroxy quinoline and its analogous will provide a great help in carrying out systematic work towards the improvement and greater applicability of these reagents. By condensation and substitution reactions, certain groups can be introduced into the molecule of this organic compound so as to modify their complex forming properties.

Albert and Magrath[4]) carried out a sensitivity test with 8-hydroxy quinoline 5-sulfonic acid and certain metal ions. It was found that many metal ions did not form a precipitate with this reagent although colour changes were observed in many cases. In these investigations we have prepared 8-hydroxy quinoline 7-sulfonic acid by the method used by Banerji and Srivastava[5]) and Tiao-Hsu Chang[6]).

[1]) S. K. Banerji and A. K. Dey, Z. analyt. Ch. 179, 1, (30) (1961).

[2]) Yoe and Jones, Ind. Eng. Chem.; Anal. Ed. 16, 111 (1944).

[3]) F. L. Hahn, E. angew. Ch. 39, 1198 (1926).

[4]) A. Albert and D. Magrath, Bio-Chem. 41, 534 (1947).

[5]) K. C. Srivastava and Samir K. Banerji, Chem. Age of India 18, 351 (1967).

[6]) Tiao-Hsu Chang et al., J. Chinese Chem. Soc. 11, (3), 125—134 (1964).

BANERJI and SRIVASTAVA [5]) studied the colour reactions of 8-hydroxy quinoline 7-sulfonic acid with different metals and found that iron(III) devolopes a green colour in acidic medium. The complex formation is instantaneous and is very sensitive. As no details are available regarding the nature and composition of the complex formed, an investigation has been made to study the complex spectrophotometrically, using JOB's method of continuous variation [7]), mole-ratio method [8]), and Slope-ratio method [9]).

Experimental

A standard solution of iron was prepared from a sample of ferric chloride (B.D.H.) and the iron content was estimated. 8-hydroxy quinoline 7-sulfonic acid was recrystalised twice from distilled water and a pure sample of the potassium salt was made by adding requisite quantity of KOH (B.D.H.). Absorbence measurements were made by Hilger-Uvispec Spectrophotometer (Model H 700—380) using one cm. effective light path. The cell compartment was fitted with a jacket through which water was circulated from a thermostat to maintain a constant temperature. A thermometer was inserted into the cell compartment and it was allowed to come to temperature equilibrium. It showed a variation of less than 0.1 °C over a period much longer than that needed to make measurements of optical density. Measurements of pH were made with a BECKMAN pH Meter (Model H 2). All the measurements were made at 25 °C. The order of addition of reagent, the effect of time and the optimum conditions were studied and the chelate reported was formed and studied under those optimum conditions.

Results

Nature of the complex formed

Solutions of the reagent and ferric chloride (1×10^{-3} M, 10 ml. each) were taken and pH was adjusted to 4. The complex formed showed a maximum absorbence at 610 mμ. To find out the nature of the complex VOSHBURG and COOPER method [10]) was adopted. Mixtures containing various proportion of ferric chloride and EHQS (1:1, 1:2, 1:3, 1:4) were prepared and absorbence measurements at various wave lengths were taken in the visible range of spectrum. The result has been graphically represented in Fig. 1. It will be evident there from that the λ max. of each mixture is found to be in the spectral region of 610 mμ. It is clear therefore that only one complex is formed under the conditions of study. The absorbence of the ligand does not show any maxima in the visible region of spectrum as may also be seen in Fig. 1.

[7]) P. JOB, C. R. hebd. Seances Acad. Sci. **80**, 928 (1925); Ann. Chimie (X) **9**, 113 (1928); (XI) **6**, 97 (1936).

[8]) YOE and JONES, Ind. Eng. Chem. Anal. Ed. **16**, 111 (1944).

[9]) HARVEY and MANNING, J. Amer. chem. Soc. **72**, 4488 (1950); **74**, 4744 (1952).

[10]) VOSHBURG and COOPER, J. Amer. chem. Soc. **63**, 437 (1941).

Effect of pH on the complex

Solutions containing the same concentration of ferric chloride and the reagent were prepared at different pH and the absorbence at various wave lengths were taken. The complex showed λ max. at 610 mμ in the pH range 2—5, and it gave a constant optical density in the pH range 3—4.5, (Fig. 2). Hence a pH of 4 was selected for subsequent studies.
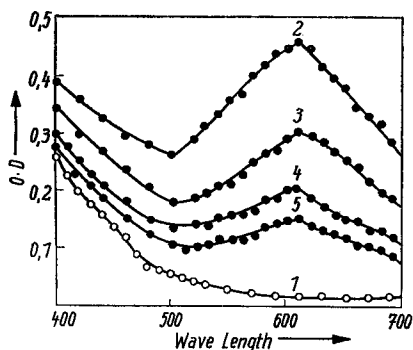

Fig. 1. Absorption spectra studies of mixtures of ferric chloride and 8-hydroxy quinoline 7-sulfonic acid. Curve 1: reagent 1×10^{-3} M. Curve 2: c $= 1 \times 10^{-3}$ M, p $= 1$. Curve 3: c $= 5 \times 10^{-4}$ M, p $= 2$. Curve 4: c $= 3.3 \times 10^{-4}$ M, p $= 3$. Curve 5: c $= 2.5 \times 10^{-4}$ M, p $= 4$
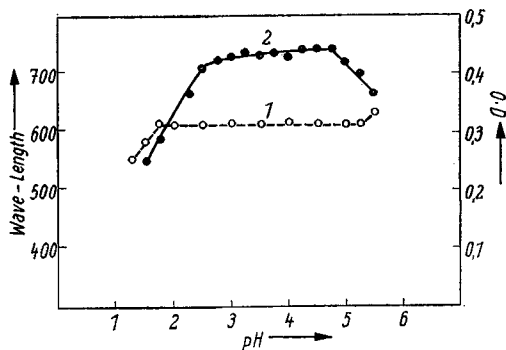
Fig. 2. Effect of pH on the Chelate. Curve 1: Effect of pH on absorption maxima. Curve 2: Effect of pH on optical density at 610 mμ

Effect of temperature

Mixtures containing equimolar solutions of the reagent and metal ion were taken and heated on a water bath at 80 °C, cooled to room temperature and the absorbence were measured. It was found that there was no difference in absorption of the sample and that prepared at room temperature.

Composition of the complex

As has been said before, the composition was studied by three different methods.

Job's method

Job's method of continuous variation[7]) has been adopted for determining the composition of the coloured complex formed. The absorbence of the mixture, metal ion and the chelating agent were measured at two dif-

ferent wave lengths of 585 mμ and 610 mμ, using both equimolar and non-equimolar solutions, adjusting the pH to 4. Some cf the representative results have been shown in Fig. 3 and 4.
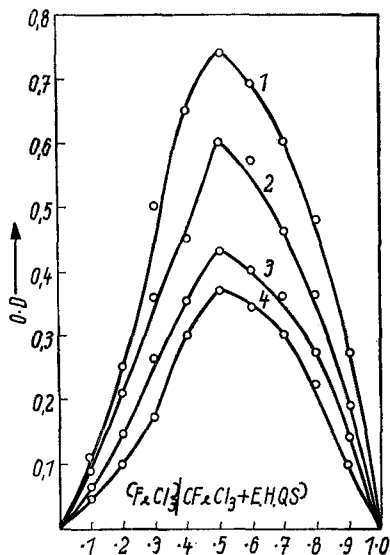

Fig. 3. Determination of composition by Job's Method using equimolar solutions. Curve 1: $c = 2 \times 10^{-3}$ M, $p = 1$. Curve 2: $c = 1.42 \times 10^{-3}$ M, $p = 1$. Curve 3: $c = 1.11 \times 10^{-3}$ M, $p = 1$. Curve 4: $c = 0.91 \times 10^{-3}$ M, $p = 1$
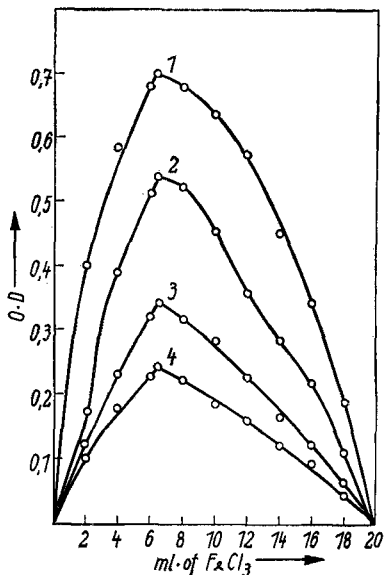
Fig. 4. Job's Method using non-equimolar solutions. Curve 1: $c = 4 \times 10^{-3}$ M, $p = 2$. Curve 2: $c = 2.84 \times 10^{-3}$ M, $p = 2$. Curve 3: $c = 2.22 \times 10^{-3}$ M, $p = 2$. Curve 4: $c = 1.82 \times 10^{-3}$ M, $p = 2$

Mole-ratio method

In the determination of the composition by mole-ratio method[8]) a series of solutions were prepared from 1×10^{-3} M of the reagent and equimolar solutions of the metal ion in such a way that the mole-ratio of the reagent to metal was from 1:0.2 to 1:5. The results obtained have been plotted in Fig. 5. As will be seen from the same, a break occurs at the ratio reagent:metal $= 1:1$, indicating that the composition of the complex is 1:1.

Slope ratio method

In the determination by slope ratio method[9]) the concentration of the variable component was varied from 1×10^{-5} to 1×10^{-3} M in presence of

an excess concentration $(2 \times 10^{-3}\,\text{M})$ of the constant component. The pH of the solutions were adjusted to 4 as required from the pH studies. Fig. 6 shows the absorbence measurements at two different wave lengths of 585 and 610 mμ, plotted against the concentration of the variable component. The slope of the two straight lines provide iron:reagent ratio as 1:1.
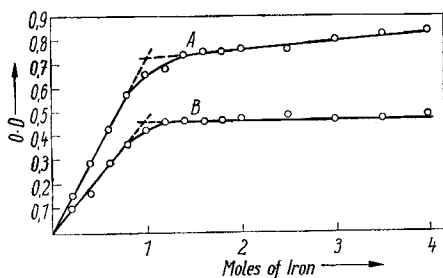

Fig. 5. Mole-ratio Method at 610 mμ. Final concentration of (E.H.Q.S.). Curve A: 2×10^{-3} M.   Curve B: 1×10^{-3} M
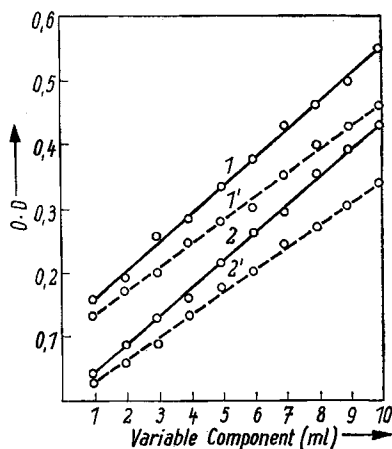
Fig. 6. Slope-ratio Method. 10 ml excess component$(2 \times 10^{-3}\,\text{M}) + vml(1 \times 10^{-3}\,\text{M})$ variable component $+$ (10-V) ml H$_2$O. Curve 1—2: Metal varying.Curve 1'—2': E.H.Q.S. varying. Solid lines refer to 610 mμ. Broken lines refer to 585 mμ

For the purpose of the determination of the stability of the complex, calculation has been made of the formation constant from the optical density data, by the method used by Banerji and Dey[1]) and by the mole-ratio method[8]). The results obtained are given in Table 1. The value of

Table 1
Stability Constant of Iron(III) 8-hydroxy quinoline 7-sulfonate. At pH 4 and temperature 25 °C

Method	Set No.	log K	Mean log K
Method of Banerji and Dey	1	3.8007	
	2	3.8235	
	3	3.7938	
	4	3.8129	
			3.80 ± 0.05
Mole-ratio Method	1	3.7782	
	2	3.8222	

log K in the system iron-8 hydroxy quinoline 7 sulfonic acid chelate works out to be 3.80 ± 0.05 at 25 °C. The free energy of formation of the chelate investigated here is -5.24 k.cal/mole at 25 °C.

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