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A Spectrophotometric Study of the Complex Formation between Iron(III) and Sulfosalicylic Acid

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A spectrophotometric study of the complex formation between iron(III) and sulfosalicylic acid was carried out over the pH range up to 8; further, an attempt was made to test the applicability of sulfosalicylic acid as a reagent for the spectrophotometric determination of iron(III) in the presence of iron(II). The absorption maxima are found at 510 mμ independently of the pH between 1 to 2.5, while they shift in the direction of shorter wavelength as the pH rises. It was concluded that three complex species, Fe(Su), $Fe(Su)_2{}^{3-}$, and $Fe(Su)_3{}^{6-}$, are formed successively in acid solutions; their stability constants were determined to be:

$$\frac{[Fe(Su)]}{[Fe^{3+}][Su^{3-}]}=1.13\times10^{14} \qquad \frac{[Fe(Su)_2{}^{3-}]}{[Fe^{3+}][Su^{3-}]^2}=2.14\times10^{24} \qquad \frac{[Fe(Su)_3{}^{6-}]}{[Fe^{3+}][Su^{3-}]^3}=1.25\times10^{33}$$

where Su^{3-} denotes the sulfosalicylate anion, $C_6H_3(O^-)(COO^-)(SO_3{}^-)$. If the pH of the solution is adjusted from 3 to 4.5 and if the absorbancy measurements are made at 480 to 490 mμ, sulfosalicylic acid can be used as a reagent for determining iron(III) in the presence of iron(II). The optimum concentration of iron(III) is 2 to 10 p. p. m.; iron(II) does not interfere, even at a concentration of 100 p. p. m.

Sulfosalicylic acid, because it gives characteristic colors with iron(III), has been known as a reagent[1] for the colorimetric determination of iron(III). However, though several investigators have studied this complex-forming reaction, there have been some discrepancies between their results. For instance, Foley and Anderson[2,3] studied this reaction spectrophotometrically; they concluded that a 1 to 1 complex was formed in the pH range up to 8. On the other hand, Banks and Patterson[4] reported in their polarographic investigation that the molar ratio of sulfosalicylic acid to iron(III) in a complex formed in a solution of pH 9 was 3 to 1. Afterwards, Ågren[5] and Vareille[6] demonstrated the formation of more than one complex in their potentiometric and photometric studies.

The present study was undertaken in order to make possible a choice between the above alternative explanations and to test the applicability of sulfosalicylic acid as a reagent for determining spectrophotometrically iron(III) in the presence of iron(II).

Experimental

Reagents.—A standard solution of iron(III) was prepared by dissolving ammonium iron(III) sulfate, $Fe_2(SO_4)_3(NH_4)_2SO_4\cdot24H_2O$, in sulfuric acid. A standard solution of iron(II) was prepared by dissolving ammonium iron(II) sulfate, $FeSO_4(NH_4)_2SO_4\cdot6H_2O$, in sulfuric acid. The final concentration of acid in these solutions was adjusted to about 0.05 N. A solution of sulfosalicylic acid was prepared by dissolving a commercial product, $C_6H_3(OH)(COOH)(SO_3H)\cdot2H_2O$, in distilled water. For the adjustment of the pH, 1 N hydrochloric acid ($pH<2$), a 0.5 M monochloroacetic acid - sodium hydroxide solution (pH 2—3), a 1 M acetic acid - sodium acetate solution (pH 3—6.5), and a 1 M ammonium chloride - ammonium hydroxide solution ($pH>7.5$) were used. All the chemicals used were of the reagent grade.

Apparatus.—The absorption curves were recorded by using a Hitachi EPS-2-type Automatic Pen Recording Spectrophotometer, while a Hitachi EPU-2A-type Spectrophotometer was used for the absorbancy measurements. These spectrophotometers were equipped with absorption cells 10 mm. thick. The pH values were measured with a Horiba M-3-type pH meter equipped with a glass electrode.

Procedures.—An aliquot of a standard solution of iron(III) was taken, and the pH was adjusted to the required value by adding a buffer solution. After an aliquot of a solution of sulfosalicylic acid had been added, the solution was diluted to 100 ml. with distilled water. An absorbancy measurement was made on a part of the resulting solution within 3 hr. after the solution had been prepared, and, if necessary, an absorption curve

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[1] E. B. Sandell, "Colorimetric Determination of Traces of Metal," 3rd. Ed., Interscience Publishers, New York (1959), p. 544.

[2] R. T. Foley and R. C. Anderson, *J. Am. Chem. Soc.*, **70**, 1195 (1948).

[3] R. T. Foley and R. C. Anderson, ibid., **72**, 5609 (1950).

[4] C. V. Banks and J. H. Patterson, ibid., **73**, 3062 (1951).

[5] A. Ågren, *Acta Chem. Scand.*, **8**, 266 (1954); *Chem. Abstr.*, **48**, 11970 (1954).

[6] L. Vareille *Bull. Soc. Chim. France*, **1955**, 870; *Chem. Abstr.*, **49**, 12173 (1955).

covering the range from 400 to 600 mμ was recorded and the pH was measured for the other part.

Preliminary experiments showed that solutions containing both 1.83×10^{-4} M of iron(III) and 7.3×10^{-3} M of sulfosalicylic acid gave the same absorption curves after 3 hr. of standing at room temperature for each pH value: 3.4, 4.5 and 5.2.

Results and Discussion

The Effects of the pH Values on the Absorption Curves.—Figure 1 shows the absorption curves for the solutions which contain 1.83×10^{-4} M of iron(III) and 8×10^{-3} M of sulfosalicylic acid at different pH values. The absorption maxima are found at 510 mμ independently of the pH between 1 to 2.5, while they shift to shorter wavelength as the pH rises. These color variations, from violet through deep red or rose in acid solutions to yellow in alkaline, suggest that more than one complex may be formed in aqueous solutions.

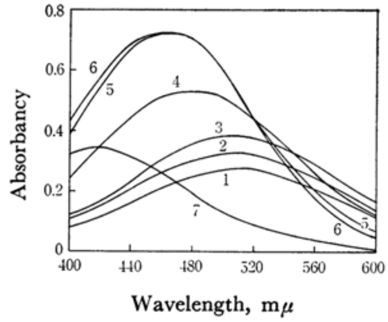

Fig. 1. Absorption curves. Solutions were 1.83 $\times10^{-4}$ M in iron(III) and 8×10^{-3} M in sulfosalicylic acid.
Curve 1, at pH 1.38 in 0.05 M hydrochloric acid: 2, at pH 2.00; 3, at pH 2.49 in 0.05 M of total monochloroacetate: 4, at pH 3.08; 5, at pH 4.40; 6, at pH 5.34 in 0.05 M of total acetate: 7, at pH 7.88 in 0.05 M of total ammonium

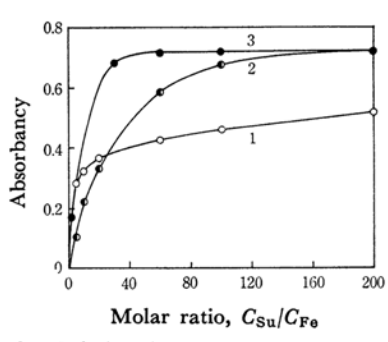

Fig. 2. Relation between absorbancy and C_{Su}/C_{Fe}, keeping C_{Fe} at 1.83×10^{-4} and varying C_{Su} up to 3.66×10^{-2} M in 0.05 M of total acetate.
Curve 1, at pH 3.39 for 480 mμ; 2 at pH 4.46 for 470 mμ; 3, pH 5.20 for 470 mμ

The Effects of the Molar Ratio of Sulfosalicylic Acid to Iron(III).—The relations between the absorbancies and the molar ratios of sulfosalicylic acid to iron(III) in solutions were obtained at different pH values; the results are shown in Fig. 2. In a solution of pH 5.20, a constant absorbancy is obtained with increasing molar ratios of over sixty parts of sufosalicylic acid to one of iron(III), while solutions in the lower pH region do not level off to a constant absorbancy in spite of the presence of more than a hundred moles of sulfosalicylic acid to one mole of iron(III). Judging from this, higher complexes seem to be produced successively with an increasing concentration of sulfosalicylic acid.

The Composition of the Complex.—The compositions of the complexes were determined by applying the continuous variation method.[7] Figure 3 shows the results obtained at different pH values by plotting Y, the difference between the observed absorbancy and that calculated assuming no complex formation, against the ratio of the total concentration of sulfosalicylic acid, C_{Su}, to the sum of the total concentration of iron(III) and that of sulfosalicylic acid, $C_{Fe}+C_{Su}$. The maximum value of Y in curve 1 occurs at a ratio of 0.5, indicating that a 1 to 1 complex is formed here. In curve 2 the maximum value of Y is found at a ratio of 0.6, and in curve 3, at a ratio of 0.75; this suggests that complex species in which the molar ratios of sulfosalicylic acid to iron(III) are 2 to 1 and/or 3 to 1 are formed in addition to the 1 to 1 complex at higher pH values.

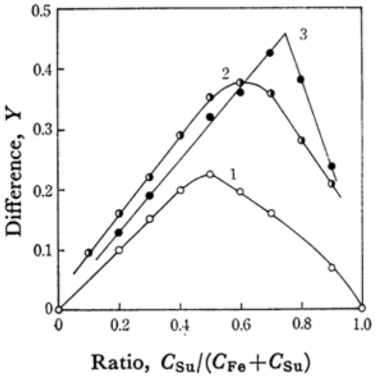

Fig. 3. Relation between Y and $C_{Su}/(C_{Fe}+C_{Su})$ in the application of the continuous variation method. Solutions were 4.57×10^{-4} M in $C_{Fe}+C_{Su}$, and 0.05 M in total monochloroacetate (curve 1) or 0.05 M in total acetate (curves 2 and 3).
Curve 1, at pH 2.20 for 500 mμ; 2, at pH 3.40 for 480 mμ; 3, at pH 4.46 for 470 mμ

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[7] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York (1952), p. 28.

The Stability Constant of the Complex.— From the aforementioned results, the complex-forming reaction between iron(III) and sulfosalicylic acid in an acid solution may be assumed to be represented in general as three successive steps:

$$\mathrm{Fe^{3+}} + \mathrm{Su^{3-}} \rightleftarrows \mathrm{Fe(Su)} \tag{1}$$

$$\mathrm{Fe(Su)} + \mathrm{Su^{3-}} \rightleftarrows \mathrm{Fe(Su)_2{}^{3-}} \tag{2}$$

$$\mathrm{Fe(Su)_2{}^{3-}} + \mathrm{Su^{3-}} \rightleftarrows \mathrm{Fe(Su)_3{}^{6-}} \tag{3}$$

The corresponding equilibrium constants are, then:

$$K_1 = \frac{[\mathrm{Fe(Su)}]}{[\mathrm{Fe^{3+}}][\mathrm{Su^{3-}}]} \tag{4}$$

$$K_2 = \frac{[\mathrm{Fe(Su)_2{}^{3-}}]}{[\mathrm{Fe(Su)}][\mathrm{Su^{3-}}]} \tag{5}$$

$$K_3 = \frac{[\mathrm{Fe(Su)_3{}^{6-}}]}{[\mathrm{Fe(Su)_2{}^{3-}}][\mathrm{Su^{3-}}]} \tag{6}$$

where $\mathrm{Su^{3-}}$ denotes the sulfosalicylate anion, $\mathrm{C_6H_3(O^-)(COO^-)(SO_3{}^-)}$. The absorptions of both iron(III) and sulfosalicylic acid in the solution are so weak that they are negligible compared with the absorption of complexes over the range from 450 to 600 mμ. Therefore, the observed absorbancy, *As*, is expressed in general as:

$$As = \varepsilon_1[\mathrm{Fe(Su)}] + \varepsilon_2[\mathrm{Fe(Su)_2{}^{3-}}] + \varepsilon_3[\mathrm{Fe(Su)_3{}^{6-}}] \tag{7}$$

where ε_1, ε_2 and ε_3 are the molar absorbancy indices of Fe(Su), $\mathrm{Fe(Su)_2{}^{3-}}$ and $\mathrm{Fe(Su)_3{}^{6-}}$ respectively.

If a condition is now selected where only a 1 to 1 complex is formed, $[\mathrm{Fe(Su)_2{}^{3-}}]$ and $[\mathrm{Fe(Su)_3{}^{6-}}]$ become zero and K_1 is expressed as:

$$K_1 = \frac{[\mathrm{Fe(Su)}]\Phi}{\{C_{\mathrm{Fe}} - [\mathrm{Fe(Su)}]\}\{C_{\mathrm{Su}} - [\mathrm{Fe(Su)}]\}} \tag{8}$$

$$= \frac{\varepsilon_1 As \Phi}{(\varepsilon_1 C_{\mathrm{Fe}} - As)(\varepsilon_1 C_{\mathrm{Su}} - As)} \tag{9}$$

where:

$$\Phi = 1 + \frac{[\mathrm{H^+}]}{k_3} + \frac{[\mathrm{H^+}]^2}{k_2 k_3} \tag{10}$$

where k_2 and k_3 are the second and the third acid dissociation constants of sulfosalicylic acid; these values, which were described in the literature,[8] will be used in subsequent calculations. The data at pH 2.20 were applied to Eq. 9, and K_1 and ε_1 were determined by the successive approximation method. As a first approximation, ε_1 for 480 mμ was assumed to be equal to $1.78 \times 10^3\ \mathrm{M^{-1}\,cm^{-1}}$, and the first approximations to K_1 were calculated from Eq. 9. Using the mean of these K_1 values, the second approximations to ε_1 were calculated from the absorbancy. Again using the mean of these values of ε_1, new values of K_1 were obtained from Eq. 9. This procedure was repeated four times. The results of these calculations are summarized in Table I.

Next, K_2 and K_3 can be determined when sulfosalicylic acid is present in a large excess over iron(III). Under these conditions, the concentration of the sulfosalicylic acid combining with iron(III) is negligible in comparison with its total concentration, so C_{Su} is nearly equal to $[\mathrm{Su^{3-}}]\Phi$.

If a condition can be found where the reaction for the complex formation is represented as the two successive steps of reactions 1 and 2, $[\mathrm{Fe(Su)_3{}^{6-}}]$ becomes zero, and from Eqs. 4, 5 and 7 the following relationship is derived;

$$\frac{C_{\mathrm{Fe}}}{As} = \frac{1}{\varepsilon_1} + \frac{F_2}{\varepsilon_2 \beta_2} \tag{11}$$

where:

$$F_2 = \frac{\Phi^2}{C_{\mathrm{Su}}{}^2}\left\{1 + \frac{K_1}{\Phi} C_{\mathrm{Su}} - \frac{\varepsilon_1 K_1 C_{\mathrm{Fe}} C_{\mathrm{Su}}}{As\Phi}\right\} \tag{12}$$

and where β is the overall stability constant of the complex, which is expressed in general as $\beta_n = \Pi K_n$. The plot of C_{Fe}/As against F_2 in Eq. 11 was applied to the data at pH 3.39, which gave a straight line, as is shown in Fig. 4. From the slope and the intercept at $F_2 = 0$, ε_2 and β_2 were then calculated: the results are included in Table II.

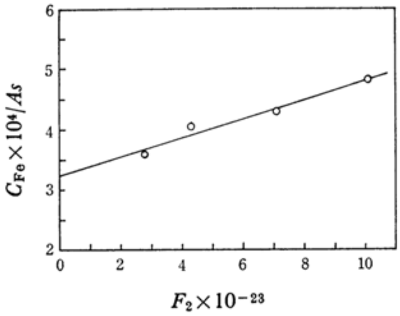

Fig. 4. Plot of C_{Fe}/As vs. F_2 at pH 3.39 for 480 mμ, keeping C_{Fe} at 1.83×10^{-4} M and varying C_{Su} from 3.6×10^{-3} to 3.66×10^{-2} M in 0.05 M of total acetate.

If, finally, a condition is selected where three complex species are formed, from Eqs. 4, 5, 6 and 7 the following equation is derived:

$$\frac{C_{\mathrm{Fe}}}{As} = \frac{1}{\varepsilon_3} + \frac{F_3}{\varepsilon_3 \beta_3} \tag{13}$$

where:

$$F_3 = \frac{\Phi}{C_{\mathrm{Su}}{}^3}\left\{1 + \frac{K_1}{\Phi} C_{\mathrm{Su}} + \frac{\beta_2}{\Phi^2} C^2{}_{\mathrm{Su}}\right\} - \frac{C_{\mathrm{Fe}} C_{\mathrm{Su}}\left(\varepsilon_1 \frac{K_1}{\Phi} + \varepsilon_2 \frac{\beta_2 C_{\mathrm{Su}}}{\Phi^2}\right)}{As} \tag{14}$$

The application of Eq. 13 to the data at pH 5.20

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[8] J. Bierrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants, Part I: Organic Ligands," The Chemical Society, London (1956), p. 56.

TABLE I. DETERMINATION OF ε_1 AND K_1 BY SUCCESSIVE APPROXIMATIONS*

Approximation							Mean
	$C_{Fe}\times10^4$ (M)	1.37	1.83	2.28	2.74	3.20	
	$C_{Su}\times10^4$ (M)	3.20	2.74	2.28	1.83	1.37	
	As (at 480 mμ)	0.158	0.195	0.225	0.195	0.150	
1	$\varepsilon_1\times10^{-3}$	—	—	—	—	—	1.78
	$K_1\times10^{-14}$	1.07	1.24	1.68	1.24	0.93	1.23
2	$\varepsilon_1\times10^{-3}$	1.93	1.77	1.96	1.77	1.83	1.87
	$K_1\times10^{-14}$	0.84	1.07	1.43	1.07	0.81	1.04
3	$\varepsilon_1\times10^{-3}$	1.68	1.89	2.08	1.89	1.60	1.83
	$K_1\times10^{-14}$	1.00	1.14	1.53	1.14	0.85	1.13
4	$\varepsilon_1\times10^{-3}$	1.75	1.84	2.03	1.84	1.67	1.83
	$K_1\times10^{-14}$	1.00	1.14	1.53	1.14	0.85	1.13

* Measurements were made at pH 2.20. Solutions were 0.05 M in total monochloroacetate. $\Phi=1.37\times10^{10}$.

TABLE II. CALCULATION OF K_2 AND K_3

Calculation of K_2 from Fig. 4

pH	Φ $\times10^{-8}$	Intercept $\times10^4$	Slope $\times10^{26}$	ε_2 $\times10^{-3}$	β_2 $\times10^{-24}$	K_2 $\times10^{-10}$
3.39	2.67	3.24	1.53	3.08	2.12	1.88

Calculation of K_3 from Fig. 5

pH	Φ $\times10^{-6}$	Intercept $\times10^4$	Slope $\times10^{34}$	ε_3 $\times10^{-3}$	β_3 $\times10^{-33}$	K_3 $\times10^{-8}$
5.20	3.48	2.73	2.19	3.66	1.25	5.90

TABLE III. THE OVERALL STABILITY CONSTANTS

Method*1	Medium	Temp., °C	$\log K_1$	$\log \beta_2$	$\log \beta_3$	Reference
sp.	0.05 M monochloroacetate or acetate	Room temp. (25—28)	14.05	24.33	33.10	Present
pot.	3 M $NaClO_4$	25	14.42	25.18	32.24	Ågren8)
sp.	*2	18	14.64	25.18	32.12	Vareille8)

*1 The two abbreviations, "sp." and "pot." mean "spectrophotometric" and "potentiometric" respectively.

*2 Ionic strengths is 0.25 M.

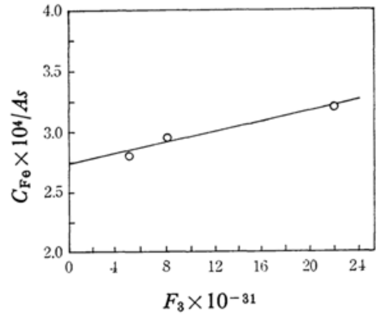

Fig. 5. Plots of C_{Fe}/As vs. for 480 mμ at pH 5.20 keeping C_{Fe} at 1.83×10^{-4} M and varying C_{Su} from 5.5×10^{-3} to 2.95×10^{-2} M in 0.05 M of total acetate.

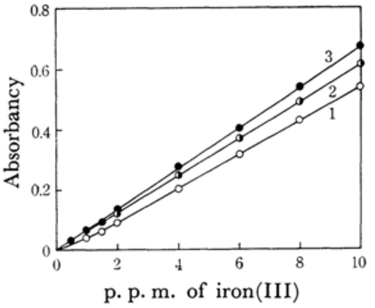

Fig. 6. Calibration curves. Solutions were 0.016 M in sulfosalicylic acid and 0.5 M in total acetate. Curve 1, at pH 3.40 for 480 mμ; 2, at pH 4.50 for 470 mμ; 3, at pH 5.20 for 470 mμ

gave a straight line plot, as is shown in Fig. 5. The results of the calculation of ε_3 and β_3 from the slope and the intercept at $F_3=0$ are included in Table II.

The logarithmic values of the stability constants calculated above are given in Table III, where they are also compared with those determined by Ågren3) and by Vareille6). There are differences in ionic strength, temperature and buffer components between the findings of these investigations. Nevertheless, it may be concluded that the results obtained in these investigations are in reasonable agreement.

The Spectrophotometric Determination of Iron(III) in the Presence of Iron(II).—*Calibration Curves.*—The calibration curves prepared for different pH values with a series of solutions containing up to 10 p.p.m. of iron(III) are shown in Fig. 6. A linear or nearly linear relation has been found between the absorbancy and the concentration of iron(III).

The Effect of Iron(II).—As is shown in Table IV, the determination of iron(III) at pH 3.40 and 4.50 is not interfered with or is given a negative error of only a few percentage points because of the presence of iron(II). At pH 5.20, the sensitivity is greater, but even small quantities of iron(II) produce a large positive error.

TABLE IV. SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH SULFOSALICYLIC ACID IN THE PRESENCE OF IRON(II)*

pH	Fe(II) present p. p. m.	Absorbancy	Fe(III) found p. p. m.	Error %
3.40	10	0.409(480 mμ)	7.8	−3
	50	0.408(480 mμ)	7.7	−4
	100	0.408(480 mμ)	7.7	−4
4.50	10	0.499(470 mμ)	8.1	+1
	50	0.490(470 mμ)	8.0	0
	100	0.490(470 mμ)	8.0	0
5.20	10	0.552(470 mμ)	8.2	+3
	50	0.577(470 mμ)	8.6	+8
	100	0.784(470 mμ)	11.7	+46

* The amount of Fe(III) taken in each case was 8 p. p. m. Solutions were 0.016 M in sulfosalicylic acid and 0.5 M in total acetate.

Summary

A spectrophotometric study of the complex formation between iron(III) and sulfosalicylic acid has been carried out over the pH range up to 8. Three complex species, Fe(Su), $Fe(Su)_2^{3-}$, and $Fe(Su)_3^{6-}$, have been concluded to be formed in acid solutions, and their stability constants have been determined to be:

$$\frac{[Fe(Su)]}{[Fe^{3+}][Su^{3-}]}=1.13\times 10^{13}$$

$$\frac{[Fe(Su)_2^{3-}]}{[Fe^{3+}][Su^{3-}]^2}=2.12\times 10^{24}$$

$$\frac{[Fe(Su)_3^{6-}]}{[Fe^{3+}][Su^{3-}]^3}=1.25\times 10^{33}$$

Also, it has been ascertained that sulfosalicylic acid can be used as a reagent for determining iron(III) in the presence of iron(II) if the spectrophotometric measurements are made in the pH range from 3 to 4.5.

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