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

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A spectrophotometric study of the complex formation between iron(III) and salicylic acid was carried out over the pH range up to 6; further, an attempt was made to test the applicability of salicylic acid as a reagent for the spectrophotometric determination of iron(III) in the presence of iron(II). The absorption maxima of the mixture of iron(III) and salicylic acid are found at 530 mμ independently of the pH between 0.7 to 2.5, while they shift to shorter wavelength when the pH rises above 3. The isosbestic point occurs at 550 mμ between pH values from 3 to 6. It was concluded that three complex species, $Fe(Sa)^+$, $Fe(Sa)_2^-$, and $Fe(Sa)_3^{3-}$, are formed successively in acid solutions; their stability constants were determined to be:

$$\frac{[Fe(Sa)^+]}{[Fe^{3+}][Sa^{2-}]}=2.25\times10^{15} \qquad \frac{[Fe(Sa)_2^-]}{[Fe^{3+}][Sa^{2-}]^2}=1.57\times10^{27} \qquad \frac{[Fe(Sa)_3^{3-}]}{[Fe^{3+}][Sa^{2-}]^3}=1.86\times10^{36}$$

where Sa^{2-} denotes the salicylate anion, $C_6H_4(O^-)(COO^-)$. If the pH of the solution is adjusted from 2 to 3 and if absorbancy measurements are made at 515 to 500 mμ, salicylic 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 12 p. p. m.; iron(II) does not interfere, even at a concentration of 100 p. p. m.

Salicylic acid has been known as a reagent[1] for determining iron(III), since it gives characteristic colors with iron(III). The initial investigation of the nature of the complex formation between iron(III) and salicylic acid was undertaken by Babko,[2,3] who demonstrated the formation of more than one complex in an aqueous solution. Afterward, Ågren[4] determined the equilibrium constants for the complex-forming reaction.

The present authors were interested in the color variations, from violet through red to yellow with a rise on the pH values, which had been noted in earlier analytical studies.[5,6] For the present paper, therefore, the color-forming reaction between iron(III) and salicylic acid was studied spectrophotometrically, and, further, an attempt was made to test the applicability of salicylic acid as a reagent for the spectrophotometric determination of iron(III) in the presence of iron(II).

Experimental

Reagents.—The iron(III), iron(II) and buffer solutions were prepared in manners described previously.[7] A solution of salicylic acid was prepared by dissolving a commercial product, $C_6H_4(OH)(COOH)$, in ethanol.

Apparatus.—The two spectrophotometers and the pH meter used in the present work were the same as those described previously.[7]

Procedure.—The volume of the iron(III) solution was calculated and the pH was adjusted to the required value by adding a buffer solution. After the calculated volume of the salicylic acid solution had been added, the whole was diluted to the proper volume and allowed to stand for two hours. The absorbancy was observed in a part of the resulting solution, and/or, if necessary, the absorption curve over the range from 400 to 600 mμ was recorded, while the pH was measured for the other part. Preliminary experiments showed that the solutions reached an equilibrium within two hours and showed no measurable variation thereafter for periods of less than twenty-four hours.

Results and Discussion

The Effects of pH on the Absorption Curve.—Figure 1 shows the absorption curves for the mixture of iron(III) and salicylic acid at different pH values. The absorption maxima are found at 530 mμ, independently of the pH values when those values are between 0.7 to 2.5, while they shift to a shorter wavelength when the pH rises above 3. The isosbestic point occurs at 550 mμ at pH values between 3 and 6. This behavior suggests that only one complex is formed in a strongly acid solution between pH 0.7 and 2.5, but that the formation of more than one complex may be involved in a weakly acid solution between pH 3 and 6.

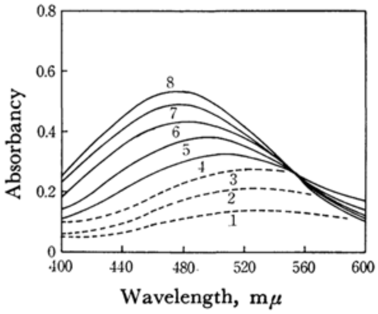

Fig. 1. Absorption curves. Solutions were 1.83×10^{-4} M in iron(III) and 7.3×10^{-3} M (for dotted line) or 1.45×10^{-2} M (for full line) in salicylic acid.
Curve 1, at pH 0.74; 2, at pH 1.71; 3, at pH 2.45; 4, at pH 3.20; 5, at pH 3.63; 6, at pH 4.04; 7, at pH 4.60; 8, at pH 5.30

The Effects of the Molar Ratio of Salicylic Acid to Iron(III).—The relations between the absorbancy and the molar ratio of salicylic acid

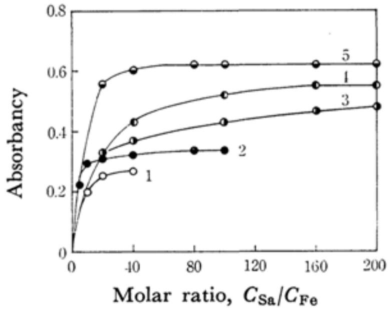

Fig. 2. Relations between absorbancy and C_{Sa}/C_{Fe}. Solutions were 1.83×10^{-4} M in iron(III) and 0.05 M in total monochloroacetate (curves 1 and 2) or 0.05 M in total acetate (curves 3, 4 and 5).
Curve, 1, at pH 2.04 for 530 mμ; 2, at pH 2.81 for 515 mμ; 3, at pH 3.51 for 490 mμ; 4, at pH 4.58 for 480 mμ; 5, at pH 5.96 for 475 mμ

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[1] F. J. Welcher, "Organic Analytical Reagents Vol. II," D. van Nostrand Co., New York (1947), p. 118.

[2] A. K. Babko, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 745 (1945); *Chem. Abstr.*, **40**, 7041 (1946).

[3] A. K. Babko, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 758 (1945); *Chem. Abstr.*, **40**, 7042 (1946).

[4] A. Ågren, *Acta Chem. Scand.*, **8**, 1059 (1954); *Chem. Abstr.*, **49**, 2929 (1955).

[5] J. P. Mehlig, *Ind. Eng. Chem. Anal. Ed.*, **10**, 136 (1938).

[6] R. O. Scott, *Aualyst*, **66**, 142 (1941).

[7] K. Ogawa and N. Tobe, This Bulletin, **39**, 223 (1966).

to iron(III) in their mixture were obtained at different pH values. The results are shown in Fig. 2. There is neither a sharp break nor a leveling-off to a constant absorbancy at any pH value for ratios up to as high as ten moles of salicylic acid to one mole of iron(III); this shows that the colored complexes are appreciably dissociated and that, hence, a large excess of salicylic acid over iron(III) is required to bring the reaction to completion.

The Composition of the Complex.—The compositions of the complexes were determined by applying the continuous variation method.[8] Figure 3 shows the results obtained at different pH values by plotting Y, the difference between the observed absorbancy and that which would be obtained if no reaction had taken place, against the ratio of the total concentration of salicylic acid, C_{Sa}, to the sum of the total concentration of iron(III) and that of salicylic acid, $C_{\mathrm{Fe}}+C_{\mathrm{Sa}}$. The maximum value of Y in curve 1 occurs at a ratio of 0.5, indicating that salicylic acid combines with iron(III) in a molar ratio of 1 to 1. In each of the curves from 2 to 5 the maximum of Y is found in the neighborhood of a ratio of 0.7, while in curve 6 it is found at a ratio of about 0.75. This indicates that complex species in which salicylic acid combines with iron(III) in molar ratios of two to one and/or three to one are formed in addition to the 1 to 1 complex, and that the molar ratio of salicylic acid to iron(III) in the complex increases with the rising pH values. This behavior is interpreted as taking place because iron(III) competes with hydrogen ions in taking away salicylate anions.

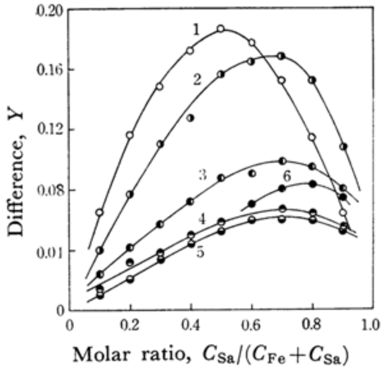

Fig. 3. Relations between Y and $C_{\mathrm{Sa}}/(C_{\mathrm{Fe}}+C_{\mathrm{Sa}})$ in the application of continuous variation method. Solutions were 4.57×10^{-4} M (curves 1 to 5) or 9.13×10^{-1} M (curves 6) in $C_{\mathrm{Fe}}+C_{\mathrm{Sa}}$ and 0.05 M in total monochloroacetate (curve 1) or 0.05 M in total acetate (curves 2 to 6).
Curve 1, at pH 2.70 for 520 mμ; 2, at pH 3.33 for 505 mμ; 3, at pH 3.80 for 500 mμ; 4, at pH 4.02 for 485 mμ; 5, at pH 4.80 for 480 mμ; 6, at pH 5.94 for 475 mμ

The Stability Constant of the Complex.—The method described by McConell and Davidson[9] was used for determining the stability constants of the complexes. Since there are three complex species in the acid solution, the reaction for the complex formation may be written in general in terms of the following successive steps:

$$\mathrm{Fe^{3+}+Sa^{2-}\rightleftarrows Fe(Sa)^{+}} \qquad (1)$$

$$\mathrm{Fe(Sa)^{+}+Sa^{2-}\rightleftarrows Fe(Sa)_2^{-}} \qquad (2)$$

$$\mathrm{Fe(Sa)_2^{-}+Sa^{2-}\rightleftarrows Fe(Sa)_3^{3-}} \qquad (3)$$

where $\mathrm{Sa^{2-}}$ denotes the salicylate anion, $\mathrm{C_6H_4(O^-)(COO^-)}$. The corresponding equilibrium constants are, then;

$$K_1=\frac{[\mathrm{Fe(Sa)^{+}}]}{[\mathrm{Fe^{3+}}][\mathrm{Sa^{2-}}]} \qquad (4)$$

$$K_2=\frac{[\mathrm{Fe(Sa)_2^{-}}]}{[\mathrm{Fe(Sa)^{+}}][\mathrm{Sa^{2-}}]} \qquad (5)$$

$$K_3=\frac{[\mathrm{Fe(Sa)_3^{3-}}]}{[\mathrm{Fe(Sa)_2^{-}}][\mathrm{Sa^{2-}}]} \qquad (6)$$

When salicylic acid is present in a large excess over iron(III), the concentration of the salicylic acid combining with iron(III) is negligible compared with its total concentration. Therefore, Eqs. 4, 5, and 6 are converted into the following:

$$K_1=\frac{[\mathrm{Fe(Sa)^{+}}]\Phi}{\{C_{\mathrm{Fe}}-([\mathrm{Fe(Sa)^{+}}]+[\mathrm{Fe(Sa)_2^{-}}]+[\mathrm{Fe(Sa)_3^{3-}}])\}C_{\mathrm{Sa}}} \qquad (7)$$

$$K_2=\frac{[\mathrm{Fe(Sa)_2^{-}}]\Phi}{[\mathrm{Fe(Sa)^{+}}]C_{\mathrm{Sa}}} \qquad (8)$$

$$K_3=\frac{[\mathrm{Fe(Sa)_3^{3-}}]\Phi}{[\mathrm{Fe(Sa)_2^{-}}]C_{\mathrm{Sa}}} \qquad (9)$$

where C_{Fe} and C_{Sa} represent the total concentrations of iron(III) and of salicylic acid respectively, and

$$\Phi=1+\frac{[\mathrm{H^+}]}{k_2}+\frac{[\mathrm{H^+}]^2}{k_1k_2} \qquad (10)$$

where k_1 and k_2 are the first and the second acid dissociation constants of salicylic acid. The absorptions of both iron(III) and salicylic acid in the solution are so weak that they are negligible compared with the absorption of the complexes over the range from 450 to 600 mμ. Therefore, the observed absorbancy, As, may be expressed as:

$$A_{\mathrm{S}}=\varepsilon_1[\mathrm{Fe(Sa)^{+}}]+\varepsilon_2[\mathrm{Fe(Sa)_2^{-}}] +\varepsilon_3[\mathrm{Fe(Sa)_3^{3-}}] \qquad (11)$$

where ε_1, ε_2, and ε_3 represent the molar absorbancy

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

[9] H. McConell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3164 (1950).

indexes of $Fe(Sa)^+$, $Fe(Sa)_2^-$, and $Fe(Sa)_3^{3-}$ respectively.

From Eqs. 7, 8, 9, and 11 the following equation is derived:

$$\frac{C_{Fe}}{As}=\frac{1}{\varepsilon_3}+\frac{F_3}{\varepsilon_3\beta_3} \tag{12}$$

where:

$$F_3=\frac{\Phi^3}{C_{Sa}{}^3}\left\{1+\frac{K_1}{\Phi}C_{Sa}+\frac{\beta_2}{\Phi^2}C_{Sa}{}^2 -\frac{C_{Fe}C_{Sa}\left(\varepsilon_1\frac{K_1}{\Phi}+\varepsilon_2\frac{\beta_3 C_{Sa}}{\Phi^2}\right)}{As}\right\} \tag{13}$$

and where β is the overall stability constant of the complex, which is expressed in general as $\beta_n=\Pi K_n$. In Eqs. 12 and 13, C_{Fe} and C_{Sa} have known values; As is an observed quantity, and ε_1, ε_2, K_1 and β_2 can be obtained from subsequent equations. If a suitable condition is chosen, the plotting of C_{Fe}/As against F_3 gives a straight line, the slope of which is $1/\varepsilon_3\beta_3$. The molar absorbancy index, ε_3, can be estimated from the intercept at $F_3=0$, which is obtained by extrapolation. In all subsequent equations, as in this, C_{Fe}/As is plotted against F terms, and the desired constants are obtained from the slopes and the intercepts of the straight lines.

If a condition is now selected where the reaction for the complex formation is represented as the two successive steps of reactions 1 and 2, $[Fe(Sa)_3{}^{3-}]$ becomes zero, and, from Eqs. 7, 8 and 11, it follows that:

$$\frac{C_{Fe}}{As}=\frac{1}{\varepsilon_2}+\frac{F_2}{\varepsilon_2\beta_2} \tag{14}$$

where:

$$F_2=\frac{\Phi^2}{C_{Sa}{}^2}\left\{1+\frac{K_1}{\Phi}C_{Sa}-\frac{\varepsilon_1 K_1 C_{Fe}C_{Sa}}{As\Phi}\right\} \tag{15}$$

Equations 14 and 15 permit the determination of both ε_2 and β_2, which are necessary for Eq. 13.

If a condition can be found where only a 1 to 1 complex is formed, both $[Fe(Sa)_2{}^-]$ and $[Fe(Sa)_3{}^{3-}]$ become zero, and, from Eqs. 7 and 11, there comes the following equation:

$$\frac{C_{Fe}}{As}=\frac{1}{\varepsilon_1}+\frac{F_1}{\varepsilon_1 K_1} \tag{16}$$

where $F_1=\Phi/C_{Sa}$, which permits the determination of both ε_1 and K_1, necessary for Eq. 14.

First, in order to determine the K_1 value, plots of Eq. 16 were applied to the data at pH 2.04 and 2.81; the results are shown in Fig. 4. Next, plots of Eq. 14 were applied to the data at pH 3.51 in order to determine β_2; the results are given in Fig. 5. Finally, β_3 was determined from the results of the application of Eq. 12 to the data at pH 5.96, as is shown in Fig. 6.

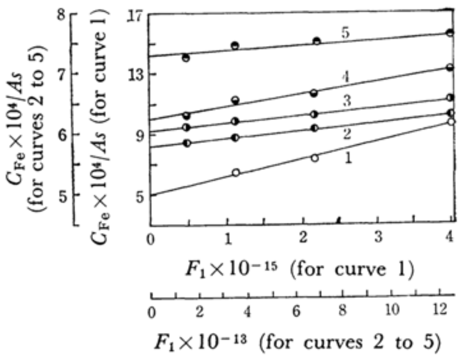

Fig. 4. Plots of C_{Fe}/As vs. F_1, keeping C_{Fe} at 1.83×10^{-4} M and varying C_{Sa} from 2.0×10^{-3} to 1.45×10^{-2} M in 0.05 M of total monochloroacetate.

Curve 1, at pH 2.04 for 530 mμ; 2, at pH 2.81 for 530 mμ; 3, at pH 2.81 for 550 mμ; 4, at pH 2.81 for 480 mμ; 5, at pH 2.81 for 460 mμ.

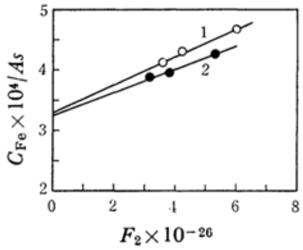

Fig. 5. Plots of C_{Fe}/As vs. F_2 at pH 3.51, keeping C_{Fe} at 1.83×10^{-4} M and varying C_{Sa} from 7.3×10^{-3} to 3.62×10^{-2} M in 0.05 M of total acetate.

Curve 1, for 460 mμ; 2, for 480 mμ.

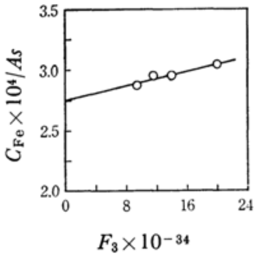

Fig. 6. Plots of C_{Fe}/As vs. F_3 at pH 5.96 for 480 mμ, keeping C_{Fe} at 1.83×10^{-4} M and varying C_{Sa} from 3.6×10^{-3} to 2.90×10^{-2} M in 0.05 M of total acetate.

In Table I are tabulated the results of the calculation of the desired constants from Figs. 4, 5 and 6. The values of the first and the second acid dissociation constants of salicylic acid used in these calculations were those described in the literature.¹⁰⁾ The logarithmic values of the stability constants calculated above are given in Table II, where they are also compared with those determined by

TABLE I. CALCULATION OF STABILITY CONSTANTS

Calculation of K_1 from Fig. 4

pH	Φ $\times 10^{-12}$	Wavelength mμ	Intercept $\times 10^4$	Slope $\times 10^{19}$	ε_1 $\times 10^{-3}$	K_1 $\times 10^{-15}$
2.04	8.07	530	5.00	1.14	2.00	4.39
2.81	0.249	460	7.30	2.58	1.37	2.83
2.81	0.249	480	6.25	6.33	1.60	0.99
2.81	0.249	530	5.80	3.95	1.72	1.47
2.81	0.249	550	6.05	3.95	1.65	1.53
					Mean	2.24

Calculation of β_2 from Fig. 5

pH	Φ $\times 10^{-10}$	Wavelength mμ	Intercept $\times 10^4$	Slope $\times 10^{31}$	ε_2 $\times 10^{-3}$	β_2 $\times 10^{-27}$
3.51	1.32	460	3.30	2.30	3.03	1.43
3.51	1.32	480	3.25	1.90	3.07	1.71
					Mean	1.57

Calculation of β_3 from Fig. 6

pH	Φ $\times 10^{-7}$	Wavelength mμ	Intercept $\times 10^4$	Slope $\times 10^{40}$	ε_3 $\times 10^{-3}$	β_3 $\times 10^{-36}$
5.96	1.47	480	2.75	1.48	3.64	1.86

TABLE II. LOGARITHMIC VALUES OF OVERALL STABILITY CONSTANTS

Method*	Medium	Temp., °C	log K_1	log β_2	log β_3	Reference
sp.	0.05 M monochloroacetate or acetate	20—25	15.35	27.20	36.27	Present
pol.	3 M $NaClO_4$	25	15.82	27.49	35.31	Ågren[4,10]

* The two abbreviations, "sp." and "pol." mean "spectrophotometric" and "polarographic" respectively.

Ågren.[4,10] The present values of log K_1 and log β_2 agree reasonable well those obtained by Ågren, while there are considerable discrepancies between them in the two values of log β_3. These discrepancies may be due to the difference in ionic strength and temperature, and also to some unknown factor such as the influence of buffer components in the equilibria.

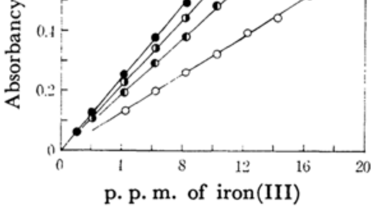

Fig. 7. Calibration curves. Solutions were 0.036 M in salicylic acid and 0.5 M in total monochloroacetate (curve 1) or 0.5 M in total acetate (curves 2 to 4).
Curve 1, at pH 2.80 for 515 mμ; 2, at pH 3.50 for 490 mμ; 3, at pH 4.50 for 480 mμ; 4, at pH 6.00 for 475 mμ

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. 7. A linear or nearly linear relation is found between the absorbancy and the concentration of iron(III) at each pH value.

The Effects of Iron(II).—As is shown in Table III, the determination of iron(III) at pH 2.80

TABLE III. SPECTROPHOTOMETRIC DETERMINATIONS OF IRON(III) BY SALICYLIC ACID IN THE PRESENCE OF IRON(II)*

pH	Fe(II) present p. p. m.	Absorbancy	Fr(III) found p. p. m.	Error %
2.80	10.2	0.262(515 mμ)	8.30	+ 2
	51.0	0.264(515 mμ)	8.30	+ 2
	102	0.267(515 mμ)	8.35	+ 2
3.50	10.2	0.372(490 mμ)	8.05	− 1
	51.0	0.389(490 mμ)	8.40	+ 3
	102	0.402(490 mμ)	8.55	+ 5
4.50	10.2	0.535(480 mμ)	9.80	+20
	51.0	0.659(480 mμ)	122	+50
	102	0.799(480 mμ)	150	+84

* The amount of iron(III) taken in each case was 8.16 p. p. m. Solutions were 0.036 M in salicylic acid and 0.5 M in total monochloroacetate or total acetate.

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[10] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants, Part I: Organic Ligands," The Chemical Society, London (1956), p. 53.

and 3.70 has a positive error of a few percentage points because of the presence of iron(II). At pH 4.50, the sensitivity is greater, but even small quantities of iron(II) produce a large positive error.

Summary

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

$$\frac{[Fe(Sa)^+]}{[Fe^{3+}][Sa^{2-}]}=2.24\times10^{15}$$

$$\frac{[Fe(Sa)_2^-]}{[Fe^{3+}][Sa^{2-}]^2}=1.57\times10^{27}$$

$$\frac{[Fe(Sa)_3^{3-}]}{[Fe^{3+}][Sa^{2-}]^3}=1.86\times10^{36}$$

Also, it has been ascertained that salicylic 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 2 to 3.

The authors wish to express their deep gratitude to Professor Sôichirô Musha of the University of Osaka Prefecture for his interest, as well as to Assistant Professor Makoto Munemori for his helpful discussions. Thanks are due also to Dr. Takeshi Nakatogawa and Dr. Natsuki Kawashima of the Hitachi Research Laboratory, Hitachi, Ltd., for their guidance and encouragement throughout this work.