The Co-ordinate Compounds of Iron with Some Hydroxycarboxylic Acids

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Sulphosalicylic acid has widely been used for the colorimetric determination of ferric iron in solutions, but of the details of physicochemical properties of the complex formed by co-ordination of hydroxycarboxylic acid of this sort we have only rudimentary information at present. The present work was carried out with the purpose of clarifying some properties of co-ordinate compounds of tri-valent iron with sulphosalicylic acid and related substances, dealing in particular with the determination of the number of ligands chelating with iron and the equilibrium constants between them. The compounds studied were salicylic, sulphosalicylic and 2-hydroxy-3-naphthoic acids, which all, with their hydroxyl group situated in the ortho position to the carboxyl group, form stable complexes with iron.

Methods

The concentration of the complexes formed in solutions was determined spectrophotometrically, using an Adam Hilger monochrometer for visible region combined with the photo-multiplier-tube 931-A. The thickness of the cell compartments used was 1 cm. The mixture of ethanol and water (1:1 in volume) was generally used as the solvent, the purpose of which was to prevent the precipitation of the complexes formed. The standard solution of iron was prepared by dissolving pure iron wire into dil. hydrochloric acid by heating. The ferrous ion in the solution was oxidized by $KClO_3$.

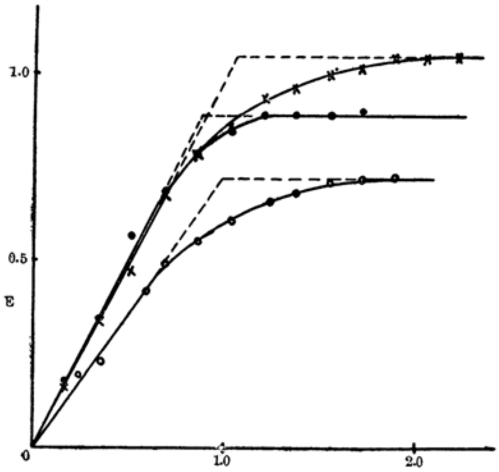
The reaction between acids and iron was observed by the following procedure. 5 cc. of the alcoholic solution of hydroxycarboxylic acid was added to 5 cc. of ferric iron aq. solution. After a while, the absorbance, $E=\log_{10}I_0/I$ (I_0, incident light; I, transmitted light) of the solution was observed at the wave-length of the absorption maximum of the complex formed. As the equal amounts of solutions were mixed together, the solution at the beginning of reaction contained half the concentrations of each component in the original solution, which were denoted by C_f (concentration of iron in g. atoms/l.) and C_h (concentration of hydroxycarboxylic acids in mol./l.), respectively.

Results

(1) Determination of the Number of Chelating Ligands.—By a preliminary experiment it was confirmed that the positions of absorption maxima shown by the complexes of sulphosalicylic acid, salicylic acid and 2-hydroxy-3-naphthoic acid were 5100 Å., 5300 Å. and 5900 Å., respectively, in 50% ethanol aq. solution. For sulphosalicylic acid, the absorption maximum was measured in water, which was found to be 4900 Å. The absorbance E of the reaction mixtures was measured using monochromatic light corresponding to the absorption maximum of each complex.

Using a definite concentration of iron solution

($C_f=0.91\times10^{-3}$) the change of E in function of C_h was followed. The experimental curves shown in Fig. 1 indicate that at lower concentrations of C_h, E is proportional to C_h, but with the increase of C_h, E increases more slowly and finally reaches a constant value. It was confirmed that the maximum value of E did not increase any more, even when solid hydroxycarboxylic acid was added to the mixture.

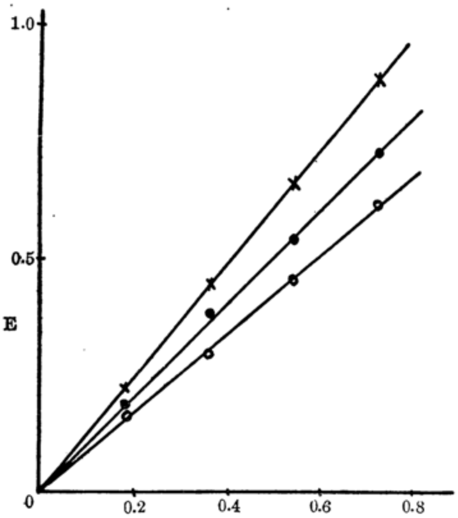


C_h in 10^{-3} mol./l. unit.
● Sulphosalicylic acid
× 2-Hydroxy-3-naphthoic acid
○ Salicylic acid

Fig. 1.

It is obvious that, in the region of linear proportionality, almost all of the hydroxycarboxylic acid added had co-ordinated with iron, while after reaching a constant value of E, almost all of the iron ion was bound. Hence, the value of C_h at the crossing point of the two dotted extrapolated lines shown in Fig. 1 must indicate the upper-most quantity of hydroxycarboxylic acid which can chelate with all iron ions present. These values of C_h were found to be 0.98 for salicylic acid, 0.90 for sulphosalicylic acid and 1.05 for 2-hydroxy-3-naphthoic acid, which all coincide with the value of C_f within the experimental error. A similar experiment was carried out with sulphosalicylic acid, using pure water as solvent. Also in this case, the molecular ratio of chelating agent to iron was found to be one to one.

In Fig. 2 are shown the results of experiments in which the change of E in function of C_f at a definite value of C_h (4.0×10^{-3}) was determined. The distinct linear ascent of the curves shows that under the conditions studied all iron ions have been bound by hydroxycarboxylic acids. The values of tangents of these lines also indicate that the combinations occur at the ratio of one to one.



C_f in 10^{-3} g.-atoms/l. unit.
● Sulphosalicyilc acid
× 2-Hydroxy-3-naphthoic acid
○ Salicylic acid

Fig. 2.

(2) The equilibrium constant between iron and hydroxycarboxylic acids.—In so far as Beer's law holds, the concentration of a complex in solution must be proportional to the absorbance E of the solution; namely,

$$E=A[\mathrm{HFe}] \tag{1}$$

where (HFe) stands for the concentration of chelated compounds and A for the proportionality constant. The value of A may be estimated either from the value of C_f and the maximum value of E in the experiment shown in Fig. 1, or from the tangent of straight lines in Fig. 2. The values of A thus obtained were 850 for salicylic acid, 1020 for sulphosalicylic acid and 1230 for 2-hydroxy-3-naphthoic acid.

Since the number of ligands chelating with one iron ion was found to be one, the equilibrium between the reaction components may be represented by

$$\mathrm{H}+\mathrm{Fe}\rightleftarrows\mathrm{HFe}$$

$$K=\frac{[\mathrm{HFe}]}{[\mathrm{H}][\mathrm{Fe}]} \tag{2}$$

where H represents the molecule of hydroxycarboxylic acid and K the equilibrium constant. Since C_f and C_h are the concentrations at the beginning of reaction, they are

$$C_f=[\mathrm{Fe}]+[\mathrm{HFe}] \tag{3}$$

$$C_h=[\mathrm{H}]+[\mathrm{HFe}] \tag{4}$$

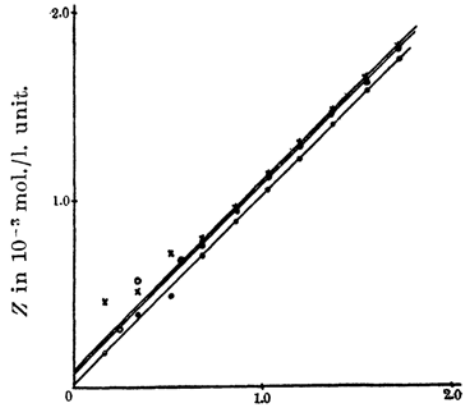
Substituting equations (3) and (4) in equation (2), we get

$$[\mathrm{HFe}]^2-(C_f+C_h+1/K)[\mathrm{HFe}]+C_fC_h=0$$

Dividing this equation by [HFe], we obtain

$$Z \equiv [\mathrm{HFe}] + C_f\left(\frac{C_h}{[\mathrm{HFe}]} - 1\right) = C_h + \frac{1}{K} \qquad (5)$$

By applying the data shown in Fig. 1 to this equation, the value of K can be calculated; namely, if we plot the values of Z of the left-hand side of equation (5) against the values of C_h, the points must be on a straight line having a slope of unity and the intersection across the ordinate should be $1/K$. As will be seen from Fig. 3, the linear relationship holds satisfactorily except for the cases of very low concentrations. From the reciprocals of the intersections determined by the method of least square, the values of K of salicylic acid and 2-hydroxy-3-naphthoic acid were found to be 13,900 and 10,900, respectively.



C_h in 10^{-3} mol./l. unit.

● Sulphosalicylic acid

× 2-Hydroxy-3-naphthoic acid

○ Salicylic acid

Fig. 3.

As for the value for sulphosalicylic acid, the intersection was so close to the origin of co-ordinates that the value of K could not be estimated accurately by the above method. Therefore, a resort was had to the following procedure to determine the value in this case. If the mixture contains two kinds of hydroxy-carboxylic acids, H_1 and H_2, the equilibrium to be established between them and the iron ion will be;

$$H_1 + Fe \rightleftarrows H_1Fe$$
$$H_2 + Fe \rightleftarrows H_2Fe$$

Therefore,

$$\frac{K_1}{K_2} = \frac{[H_1Fe](C_2 - [H_2Fe])}{[H_2Fe](C_1 - [H_1Fe])} \equiv K' \qquad (6)$$

where

$$C_1 = [H_1Fe] + [H_1]$$
$$C_2 = [H_2Fe] + [H_2]$$

and K' stands for K_1/K_2.

If the concentrations of the H_1Fe and H_2Fe are estimated experimentally, K' can be calculated, and if K_2 is known K_1 may be obtained from K' and K_2.

As the hydroxycarboxylic acid (H_2) with known equilibrium constant (K_2) we used 2-hydroxy-3-naphthoic acid, which was mixed with sulphosalicylic acid (H_1) in 5 cc. of alcoholic solution and this was added to 5 cc. of iron aq. solution. The absorbances of the solution were measured at the two wave-lengths corresponding to the absorption maxima of H_1Fe and H_2Fe. The values of absorbance thus obtained, which may be denoted by E_1 and E_2, respectively, cannot be regarded as being proportional to the concentrations of the corresponding complexes formed, because the two absorption bands are appreciably broad and overlap with each other at both wavelengths. The situation is schematically illustrated in Fig. 4, where the curve I+II is the absorption curve of the solution obtained, which is thought to be the sum of the curves of I and II for H_1Fe and H_2Fe existing in the solution. The actual absorbance, which is proportional to the concentration of each complex is denoted by E_1' and E_2', respectively, in Fig. 4. Therefore, E_1 and E_2 may be reduced to E_1' and E_2' by solving the following equations;

$$E_1 = E_1' + \frac{E_1''}{E_2'} E_2'$$

$$E_2 = E_2' + \frac{E_2''}{E_1'} E_1'$$

where E_1'' and E_2'' are the absorbances of H_2Fe and H_1Fe at the wave-lengths corresponding to the absorption maxima of H_1Fe and H_2Fe, respectively. The ratios E_1''/E_2' and E_2''/E_1', which can be determined experimentally, may be regarded to be constant independent of the concentrations. From the values of E_1' and E_2' thus obtained, the concentrations of H_1Fe and H_2Fe were calculated using the constant A already determined for each complex.

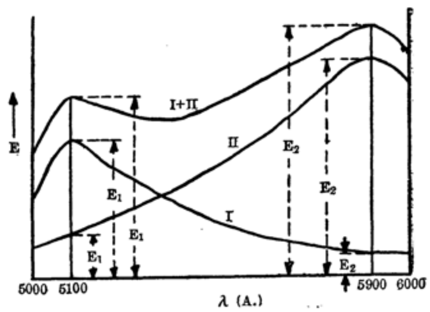


Fig. 4.

Experiments conducted with varying concentrations of H_1, H_2 and Fe, yielded the results shown in Table 1. As may be seen, the value K' calculated from different sets of experiment showed an excellent agreement, giving a mean value of $K'=2.84$. Since K_2 is 10,900, the value of K_1 (equilibrium constant of Fe-sulphosalicylic acid-complex) is 31,000.

Table 1.

C_1	C_2	C_f	K'
0.720×10^{-3}	0.720×10^{-3}	0.720×10^{-3}	2.76
0.480 〃	0.720 〃	0.480 〃	2.82
0.720 〃	0.480 〃	0.480 〃	2.87
0.688 〃	0.688 〃	0.480 〃	2.90

A similar experiment carried out using salicylic acid and 2-hydroxy-3-naphthoic acid gave the results: (K_1 for salicylic acid):(K_2 for 2-hydroxy-3-naphthoic acid)$=1.30$. This value coincides fairly well with the value 1.28 calculated from the K-values which have already been determined separately for both substances.

Discussions and Summary

Chelating action of salicylic, sulphosalicylic and 2-hydroxy-3-naphthoic acids towards iron was investigated quantitatively, and it was found that they combine with one-to-one molecular ratio with iron. In order for these substances to be used as colorimetric reagents for the determination of iron, it is desirable that the reagents as well as their complexes be well soluble in water, and that the equilibrium contants of the complexes be sufficiently large so that the proportionality between the absorbance caused by complex and the concentration of iron or chelating agent may hold in a wide range. In this respect sulphosalicylic acid may be regarded as most suitable, among the three hydroxycarboxylic acids studied, as a reagent for iron determination. In view of the fact that the introduction of sulphonyl group into salicylic acid caused the increase of K, it may be expected that a more suitable iron reagents would be obtained by further introduction of sulphonyl group in salicylic acid.

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