The Complex Formation between Iron (III) Ion
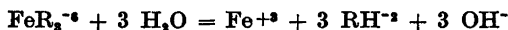
and Sulfosalicylic Acid

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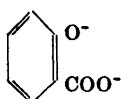
Phenols are characterized by, amongst other reactions, the colour which is formed with a solution of iron (III) chloride. The coloured substance formed is a complex built up by iron (III) ion and one or more phenol molecules.

Sulfosalicylic acid and iron (III) give a violet colour in a rather strongly acidic solution. When the pH is increased the colour shifts over orange to yellow.

Previous work. Wesp and Brode [1] made a review, the composition and colour of the complexes formed from 44 phenols and iron (III). Schwarzenbach and coworkers have written several papers concerning the stability of such complexes, most of them being cited in [2]. Foley and Anderson [3] investigated the system iron (III) + sulfosalicylic acid spectrophotometrically. They concluded that the colour change might depend upon a dissociation of the complex. In several buffer systems, having pH values up to 7.75, they found that the complex was built up from 1 molecule sulfosalicylic acid and 1 atom of iron (III). The apparent equilibrium constant $K = \dfrac{[Fe] \cdot [R]}{[FeR]}$ was found to be $1.3 \cdot 10^{-5}$ at pH 2.38 and $2.2 \cdot 10^{-5}$ at pH 5.3. [R] is here the total content of sulfosalicylic acid "without correction for ionization".

Banks and Patterson [4] in a polarographic investigation of the same complexes showed that the yellow colour obtained in neutral or alkaline solution is due to a complex built up from 1 atom iron and 3 molecules of sulfosalicylic acid. They estimated the equilibrium constant for the reaction
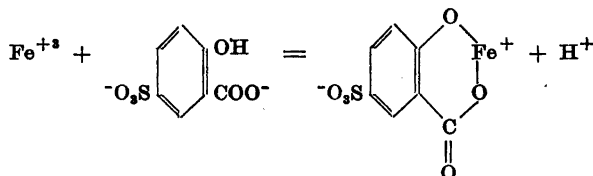
$$FeR_3^{-6} + 3 \ H_2O = Fe^{+3} + 3 \ RH^{-2} + 3 \ OH^-$$

to be $10^{-43} \ C^3$ (C = moles/litre). R is [a structure] . The ionic strength was 1 C and the temperature 25° C.

Kennard and Johnson [5] used the complex formation between iron (III) and sulfosalicylic acid in a photometric determination of iron. They showed that the three complexes have extinction maxima at 500, 460 and 420 mμ resp. and that the complexes are stable around pH 1.5, 5.0 and 8.2 resp.

THEORY

Sulfosalicylic acid is a tribasic acid. In water the sulfonic group is complete-ly ionized. Thus the ions RH_2^- and RH^{-2} are present but hardly any ions, R^{-3}, since phenols are very weak acids. When 1 molecule R is bound to Fe (III), a chelate compound is formed:

$$Fe^{+3} + \text{[structure: benzene ring with } {}^-O_3S, OH, COO^-] = \text{[structure: chelate ring with } {}^-O_3S, O, Fe^+, C=O] + H^+$$
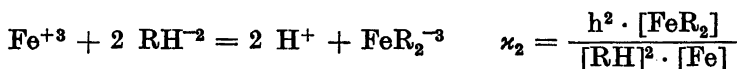
This compound is a sulfonic acid which is assumed to be completely ionized.
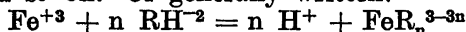
There is a possibility that the complex $FeRH^+$ is formed. The experimental results may however be explained without including this possibility in the theory.

The higher complexes are formed in an analogous manner.

This investigation was made to estimate the numerical values of the complexity constants, defined as follows:

$$Fe^{+3} + RH^{-2} = H^+ + FeR \qquad \varkappa_1 = \frac{h \cdot [FeR]}{[RH] \cdot [Fe]}$$

$$Fe^{+3} + 2\ RH^{-2} = 2\ H^+ + FeR_2^{-3} \qquad \varkappa_2 = \frac{h^2 \cdot [FeR_2]}{[RH]^2 \cdot [Fe]}$$

and so on. Or generally written:

$$Fe^{+3} + n\ RH^{-2} = n\ H^+ + FeR_n^{3-3n}$$

$$\varkappa_n = \frac{h^n \cdot [FeR_n]}{[RH]^n \cdot [Fe]} \qquad (1)$$

where h is the hydrogen ion concentration (in mC = millimoles/litre) and [ ] the concentration of the substance indicated. The signs for the electrical charges are omitted.

To estimate these complexity constants, h and [Fe] can be measured poten-tiometrically. [FeR_n] can be determined photometrically. Both these methods have been used here. The measurements were made at 25.0° C and, to all solutions, $NaClO_4$ was added up to a total concentration of 3 000 mC ClO_4^-. This ion strength was chosen because Hedström's [6] investigations on the hydrolysis of iron (III) and iron (II) are made at this ionic strength and thus his results could be used.

As shown by Sutton [7], ClO_4^- has a weak complex forming tendency but this tendency does not influence the results when the concentration of this ion is great and constant. It is assumed that the activity factors are constant and hence the concentrations may be used instead of activities in the equi-libria.

Potentiometric determinations

The concentration of free iron (III) ion was measured in the presence of a constant amount of iron (II) with a platinum electrode. The hydrogen ion concentration was measured with a glass electrode. As a reference electrode, a silver-silver chloride electrode in 100 mC NaCl and 3 000 mC NaClO$_4$ was used. Thus the electromotive force (emf) of the following cells were measured:

+ Glass electrode | H$^+$ | Reference electrode —
+ Pt | Fe^{+3}, Fe^{+2} | Reference electrode —
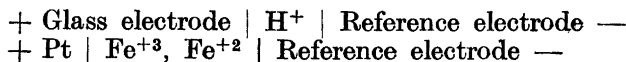
The emf of the first cell is given by the equation

$$E_{Gl} = E_{0,Gl} + 59.16 \log h + E_j$$

where $E_{0,Gl}$ is a constant (in mV) and E_j the liquid junction potential. The glass electrode used changed its potential in the theoretically expected manner, as shown by a separate titration. E_j is approximately $= -0.018$ h under conditions used in this investigation, as shown by Biedermann and Sillén [8].

The emf of the second cell is given by the equation

$$E_{Pt} = E_{0,Pt} + 59.16 \log \frac{[Fe^{+3}]}{[Fe^{+2}]} + E_j$$

where $E_{0,Pt}$ is a constant. This equation can be transformed

$$E = E_{Pt} - E_j = E_{0,Pt} + 59.16 \log \frac{[Fe]_t}{[Fe^{+2}]} - 59.16 \log (b + 1)$$

where $b = \dfrac{[Fe]_t - [Fe^{+3}]}{[Fe^{+3}]}$ and $[Fe]_t$ is the total concentration of iron (III).

If the total concentration of iron (III) and of iron (II) are each constant during an experiment, this equation can be written

$$E = E_0 - 59.16 \log (b + 1)$$

where $E_0 = E_{0,Pt} + 59.16 \log \dfrac{[Fe]_t}{[Fe^{+2}]}$

In order to calculate the complexity constants the following equation was used:

$$[Fe]_t = [Fe] + [FeOH] + [Fe(OH)_2] + 2[Fe_2(OH)_2] + [FeR] + [FeR_2] + \\ + [FeR_3] \qquad (2)$$

The hydroxyl complexes were found by Hedström [6] and the equilibrium constants are defined by

$$\varkappa_{nm} = \frac{h^n \cdot [Fe_n(OH)_m]}{[Fe]^n}$$

By combining equations (1) and (2):

$$[Fe]_t = [Fe] + \frac{\varkappa_{11}[Fe]}{h} + \frac{\varkappa_{12}[Fe]}{h^2} + 2\frac{\varkappa_{22}[Fe]^2}{h^2} + \varkappa_1 \frac{[RH]}{h} + \\ + \varkappa_2 \frac{[RH]^2}{h^2} + \varkappa_3 \frac{[RH]^3}{h^3}$$

or by transforming

$$\frac{[Fe]_t - [Fe]}{[Fe]} = b = \varkappa' + \varkappa_1 \frac{[RH]}{h} + \varkappa_2 \frac{[RH]^2}{h^2} + \varkappa_3 \frac{[RH]^3}{h^3} \qquad (3)$$

where the small correction term $\varkappa'$ is defined by

$$\varkappa' = \frac{\varkappa_{11}}{h} + \frac{\varkappa_{12}}{h^2} + 2 \frac{\varkappa_{22}[Fe]}{h^2}$$

The numerical values of the equilibrium constants of the hydroxyl complexes are, according to Hedström, $\varkappa_{11} = 0.90$, $\varkappa_{12} = 0.49$ and $\varkappa_{22} = 1.22$.

If the last term of equation (3) is assumed to be very small compared with the other terms, the following equation is obtained:

$$(b - \varkappa') \frac{h}{[RH]} = \varkappa_1 + \varkappa_2 \cdot \frac{[RH]}{h} \qquad (4)$$

The value of the left member can be calculated from experimental data. If this member is plotted against the function $[RH]/h$ a straight line should be obtained, the intercept being $\varkappa_1$ and the slope $\varkappa_2$.

In order to calculate $[RH]$ the dissociation constant of sulfosalicylic acid must be known:

$$K_a = \frac{[RH] \cdot h}{[RH_2]} \qquad (5)$$

Further, the following equations are valid:

$$[R]_t = [RH] + [RH_2] + [FeR] + 2 [FeR_2] + 3 [FeR_3] \qquad (6)$$

$$h = [H]_t - [OH]_t + [FeR] + 2 [FeR_2] + 3 [FeR_3] - [RH_2] + [FeOH] + \\ + 2 [Fe(OH)_2] + 2 [Fe_2(OH)_2] \qquad (7)$$

where $[R]_t$ is the stoichiometrical concentration of sulfosalicylic acid and $[H]_t$ and $[OH]_t$ are the stoichiometrical concentrations of hydrogen ion and hydroxyl ion resp.

From equations (6) and (7) the following equation is obtained:

$$[R]_t - h = [RH] + 2 [RH_2] - [H]_t + [OH]_t - [FeOH] - 2 [Fe(OH)_2] - \\ - 2 [Fe_2(OH)_2] \qquad (8)$$

or

$$[RH] \cdot \left(1 + \frac{2h}{K_a}\right) = [R]_t + [H]_t - [OH]_t - h + [FeOH] + 2 [Fe(OH)_2] + \\ + 2 [Fe_2(OH)_2]$$

From this equation $[RH]$ may be calculated.

When the values of $\varkappa_1$ and $\varkappa_2$ had been estimated as mentioned above, the value of $\dfrac{[RH]}{h}$ was increased, usually by decreasing h. At sufficiently low h values the complex FeR_3 was formed. Now $\varkappa_3$ could be estimated from equation (3), which could be transformed:

$$\left[(b - \varkappa') \frac{h}{[RH]} - \varkappa_1\right] \frac{h}{[RH]} = \varkappa_2 + \varkappa_3 \cdot \frac{[RH]}{h} \qquad (9)$$
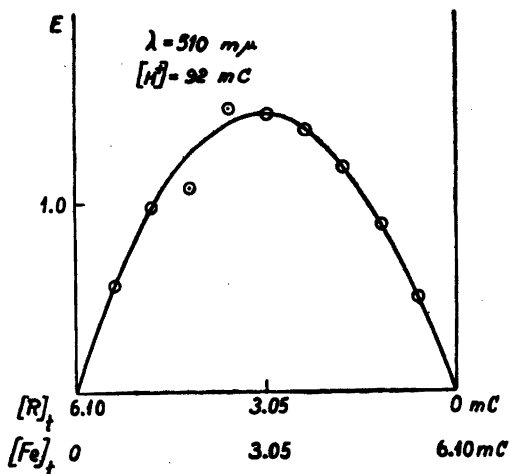
Fig. 1. Extinction (E) of various mixtures of Fe (III) and sulfosalicylic acid.

Here too a straight line should be formed when the left member is plotted against $\dfrac{[RH]}{h}$. The intercept will give the value of $\varkappa_2$ and the slope $\varkappa_3$.

Complexes with more than three R per iron atom have not been found in this investigation. This is in agreement with the supposition that chelate compounds are formed. As Fe(III) has the coordination number six, only three molecules R can be bound to one atom of Fe.

Photometric determinations

The values of the complexity constants which have been estimated poten-tiometrically have also been verified photometrically.

According to Job [9] the composition of a complex may be determined by the method of continuous variations. Using the same method the complexity constants may also be calculated. — In acid solution (pH about 2) sulfosalicylic acid and Fe (III) form a violet solution with extinction maximum at 510 mμ. By Job's method it was shown that this complex is built up from 1 molecule of R and 1 atom of Fe (Fig. 1). The measurements have not been used to calculate the complexity constant.

The same method could not be used to determine the composition of the orange and the yellow complexes formed at higher pH values. This is because the different complexity constants are so close to each other. Even if most of the iron (III) is in one complex form, a certain amount will be in another form (Fig. 2). The different complexes also have their extinction maxima so near each other (Fig. 3) that the extinction at one wave length will result from at least two different complexes. Another reason why Job's method could not be used is that, when the concentration of R is low, Fe (III) will be hydrolyzed or even precipitated.
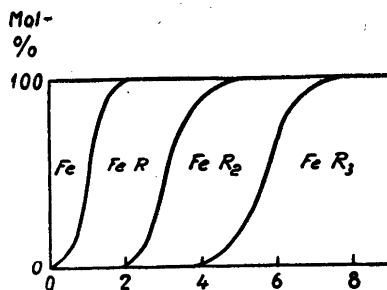
Fig. 2. *Distribution of* Fe (III) *(in percent) over* Fe^{+3}, FeR, FeR_2^{-3} *and* FeR_3^{-6}, *as a function of log* h *(h in mC).*

Another photometric method has been used instead to estimate the complexity constants. The principle is the same as that used by Heller and Schwarzenbach [10] but is modified here so that it may be also used when two complexes absorb light at the same wave length.

If only *one* complex is formed the following equations are valid:

$$\varkappa_n = \frac{h^n \cdot [FeR_n]}{[RH]^n \cdot [Fe]} \tag{1}$$

$$[Fe]_t = [Fe] + [FeR_n] = c_1 \tag{10}$$

(No appreciable amounts of hydroxyl complexes are formed)

$$[R]_t = [RH] + [RH_2] + n[FeR_n] = c_2 \tag{11}$$

$$E = \varepsilon_n \cdot [FeR_n] \tag{12}$$

$$\frac{[RH] \cdot h}{[RH_2]} = K_a \tag{5}$$

where E = the extinction of the solution in a 1 cm cell ε_n = the molar extinction.
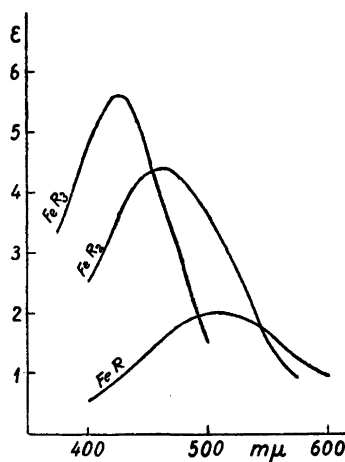

Fig. 3. *Extinction curves of the three complexes* FeR, FeR_2^{-3} *and* FeR_3^{-6}.

By substitution in (1) the following equation is obtained:

$$\varkappa_n = \frac{h^n \cdot \dfrac{E}{\varepsilon_n}}{\left(c_2 - n\, \dfrac{E}{\varepsilon_n}\right)^n \left(\dfrac{K_a}{h + K_a}\right)^n \left(c_1 - \dfrac{E}{\varepsilon_n}\right)} \tag{13}$$

Two cases may be distinguished:

1. If $c_2 \gg c_1$ the term $n\, \dfrac{E}{\varepsilon_n}$ in the denominator can be neglected and one obtains:

$$\frac{c_1}{E} = \frac{1}{\varepsilon_n} + \left[\frac{h^n}{c_2^n \left(\dfrac{K_a}{h + K_a}\right)^n}\right] \cdot \frac{1}{\varkappa_n \varepsilon_n} \tag{14}$$

If c_1/E is plotted against the expression in the square brackets a straight line is obtained. The intercept equals $\dfrac{1}{\varepsilon_n}$ and the slope is $\dfrac{1}{\varepsilon_n \varkappa_n}$.

2. If $\dfrac{1}{n}\, c_2 = c_1 = c$ equation (13) gives:

$$\frac{c}{E} = \frac{1}{\varepsilon_n} + \left(\frac{1}{\varepsilon_n \varkappa_n}\right)^{\frac{1}{n+1}} \cdot \left[\left(\frac{h}{nE\, \dfrac{K_a}{h + K_a}}\right)^{\frac{n}{1+n}}\right] \tag{15}$$

A straight line is obtained if $\dfrac{c}{E}$ is plotted against the function in the square brackets. The intercept is $\dfrac{1}{\varepsilon_n}$ and the slope $\left(\dfrac{1}{\varepsilon_n \varkappa_n}\right)^{\frac{1}{1+n}}$.

On the other side, if the iron forms *two* different complexes which both contribute to the extinction at one wave length, and no other forms of iron are present, the following equations are obtained:

$$\frac{\varkappa_n}{\varkappa_{n-1}} = \frac{h \cdot [FeR_n]}{[RH] \cdot [FeR_{n-1}]} \tag{16}$$

$$E = \varepsilon_n \cdot [FeR_n] + \varepsilon_{n-1} \cdot [FeR_{n-1}] \tag{17}$$

$$[Fe]_t = [FeR_n] + [FeR_{n-1}] = c \tag{18}$$

These equations may be combined to give

$$\frac{c}{E} = \frac{1}{\varepsilon_n} + \frac{\varkappa_{n-1}}{\varepsilon_n \varkappa_n} \cdot \left[\frac{h}{[RH]} \cdot \frac{E - c\, \varepsilon_{n-1}}{E}\right] \tag{19}$$

where $\dfrac{c}{E}$ is a linear function of the expression in the square brackets. When $n = 1$ this equation will be identical with (14) and (15) if $\varepsilon_{n-1} = \varepsilon_0 = 0$.

By chosing suitable pH ranges from Fig. 2 it is thus possible to estimate the complexity constants $\varkappa_1$, $\varkappa_2$ and $\varkappa_3$ photometrically.

EXPERIMENTAL

Apparatus. The measurements were made with an apparatus essentially the same as that described by Forsling, Hietanen and Sillén [11]. Nitrogen was passed through the reaction mixture, the gas being first freed from oxygen using a Meyer-Ronge [12] oven and then from carbon dioxide using soda-lime. In order to avoid evaporation the gas was bubbled through a 3 000 mC solution of $NaClO_4$.

The potential of the glass electrode was measured with a valve potentiometer (type Radiometer PHM 3). The redox potential was measured with a potentiometer having a sensitivity of 0.01 mV.

The photometric measurements were made with a Beckman spectrophotometer model B.

Chemicals. A solution of iron (II) perchlorate was made by Lindstrand's [13] method from perchloric acid (A.R.) and iron (II) sulfide (A.R.) Iron (III) perchlorate was made by adding perchloric acid and hydrogen peroxide. The concentrations of the solutions were determined cerimetrically, if necessary after passage through a cadmium reductor. The concentration of ClO_4^- was determined using an ion exchange technique. The hydrogen ion concentration was determined by difference, $([H^+] = [ClO_4^-] - 3 [Fe^{+3}] - 2 [Fe^{+2}])$.

Sodium perchlorate was made from perchloric acid (A.R.) and sodium carbonate (A.R.) added in deficit. After removing the carbonic acid using nitrogen gas, the solution was carefully neutralized with NaOH (A.R.). The concentration was determined using an ion exchange technique.

Sulfosalicylic acid was neutralized with one equivalent of sodium carbonate (A.R.) in hot solution. On cooling, the monosodium salt of sulfosalicylic acid crystallized and the salt was washed with a little water, alcohol and ether. After redissolving in water, sodium carbonate (A.R.) was added and the concentration was determined using an ion exchange technique.

Determination of the dissociation constant of sulfosalicylic acid. Before the complexity constants could be calculated, the dissociation constant, K_a, of the acid had to be determined. To a known amount of the di-sodium salt of the acid, an excess of perchloric acid was added and the solution titrated with NaOH using a quinhydrone electrode. From nine points of the titration curve, K_a was calculated. The mean value of these calculations was taken as K_a (Table 1).

Table 1. Determination of the dissociation constant, K_a, of sulfosalicylic acid.

$[R]_t$	$[H]_t$	h	K_a
19.00	14.90	3.355	2.17
18.57	12.25	2.410	2.14
18.36	10.97	2.039	2.15
18.16	9.72	1.685	2.12
17.97	8.49	1.365	2.07
17.77	7.29	1.141	2.15
17.40	4.97	0.694	2.13
17.04	2.75	0.344	2.09
16.87	1.67	0.206	2.17
			M = 2.13 ± 0.06 mC

Potentiometric experiments

The measurements were made in the following manner. A solution of Fe (II) and Fe (III) perchlorate which was acidified with a suitable amount of $HClO_4$, was "titrated" with a solution of the disodium salt of sulfosalicylic acid. At the same time an iron solution was added, so that the total concentrations of Fe (II) and Fe (III) were kept constant during the experiment. After each addition the emf was determined and it was usually found that equilibrium was attained after 15 minutes.

Table 2. Potentiometric determination of the complexity constants $\varkappa_1$ and $\varkappa_2$.

$[R]_t$	E	E_{Gl}	b	h	$\dfrac{[RH]}{h}$	$(b - \varkappa')\dfrac{h}{[RH]}$
1	2	3	4	5	6	7
*	442.3					
2.900	302.7	− 73.9	227.93	1.523	0.4429	512
5.510	258.2	− 81.6	1 292.9	1.128	1.996	647
7.871	233.4	− 87.4	3 396.0	0.900	4.351	781
10.018	215.0	− 91.0	6 951.2	0.783	6.991	994
11.978	200.2	− 94.3	12 367	0.688	10.193	1 213
13.775	187.2	− 97.7	20 512	0.603	14.21	1 443
15.428	177.1	− 99.5	30 391	0.562	17.61	1 726
16.954	168.0	−101.8	43 018	0.514	21.91	1 963
18.367	160.4	−104.2	58 215	0.468	26.94	2 161
19.679	153.3	−106.1	76 744	0.435	31.84	2 410

* Too many figures are given in the tables in order not to introduce an appreciable error in the calculations.

The results of one experiment of this kind are given in some detail in Table 2. The results of the same experiment can be found in Table 3 (No. 5). In the first column of Table 2 the total concentration of sulfosalicylic acid is given. Column 2 shows the redox emf in mV. The first value (E_0) is the emf of the same solution with no sulfosalicylic acid added but to which a sufficient amount of perchloric acid was added in order to depress the hydrolysis of iron ($[H^+] = 67.5$ mC). The diffusion potential is eliminated. Column 3 gives the potential of the glass electrode. The other columns need no explanation.

Several other experiments were done in the same manner, but the conditions were varied in one respect or another. All of these experiments are collected in Table 3 and Fig. 4. In experiments 3—6 in this table the concentration of iron (III) was almost unaltered, but the concentration of iron (II) was varied from 1,5 to 14,3 mC. In spite of this variation the values of $\varkappa_1$ and $\varkappa_2$ show no trend, which shows that iron (II) does not form detectable amounts of a complex with sulfosalicylic acid under these conditions.

Table 3. Survey of experiments for the calculation of $\varkappa_1$ and $\varkappa_2$ potentiometrically.

No.	Symbol	Concentrations			$\varkappa_1$	$\varkappa_2$
		Fe (II)	Fe (III)	H+		
1	+	0.7	3.35	0.4	420	62
2	人	0.7	7.53	0.3	490	65
3	×	1.5	1.65	0.3	450	55
4	⊡	3.1	1.84	0.2	550	43
5	⊙	6.5	1.75	0.3	550	63
6	⬛	14.3	1.85	0.2	410	54
7	◐	0.7	0.67	22	507	—
					M = 482 ± 70	56 ± 9
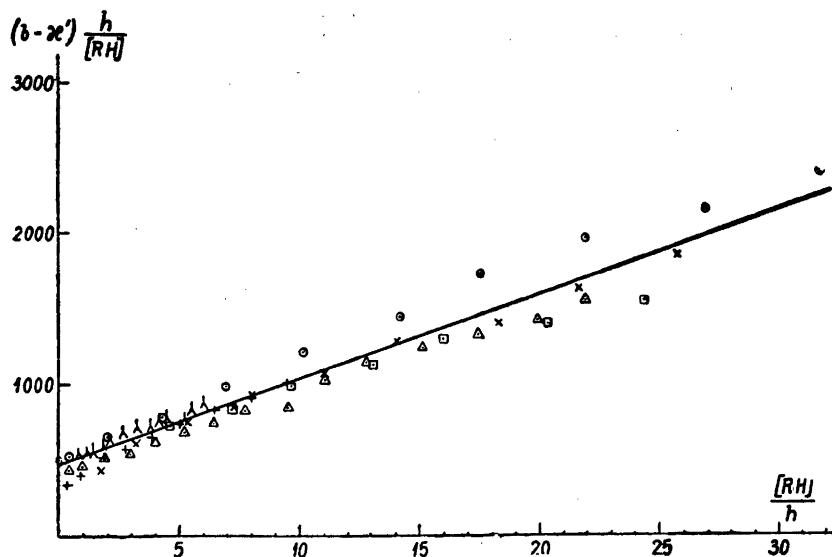
Fig. 4. Potentiometric determination of $\varkappa_1$ and $\varkappa_2$. Various total concentrations of Fe (III) and Fe (II). Compare Table 3.

In the experiments in Table 3 the concentration of iron (III) varied from 0.67 to 7.5 mC. No trend in the variation of $\varkappa$ can be seen and thus there seem to be no multinuclear complexes.

As may also be seen in Table 3 a variation in hydrogen ion concentration did not result in a variation in $\varkappa$. From this fact, it may be concluded that no appreciable amount of the complex FeRH is formed.

In the experiments performed to estimate the value of $\varkappa_3$ a technique, which differed in some respects from the preceding one, was used. Now a certain amount of sulfosalicylic acid was added to the iron solution in the beginning of the experiment. Then the hydrogen ion concentration was

Table 4. Potentiometric determination of the complexity constants $\varkappa_2$ and $\varkappa_3$.

$[R]_t$	$[OH]_t$	E	E_{Gl}	b	h	$\dfrac{[RH]}{h}$	$(A-\varkappa_1)\dfrac{h}{[RH]}$
1	2	3	4	5	6	7	8
		532.3					
48.62	1.792	98.0	-151.5	$2.193 \cdot 10^7$	0.0743	588.2	62.6
46.78	2.671	67.0	-169.1	$7.330 \cdot 10^7$	0.0374	1 138.2	56.2
45.08	3.487	20.0	-190.0	$4.566 \cdot 10^8$	0.0166	2 466	74.9
43.50	4.245	-55.0	-220.0	$8.459 \cdot 10^9$	0.00516	7 570	147.5
42.75	4.605	-116.0	-243.0	$9.087 \cdot 10^{10}$	0.00211	18 040	279.2

$$A = (b-\varkappa')\frac{h}{[RH]}$$
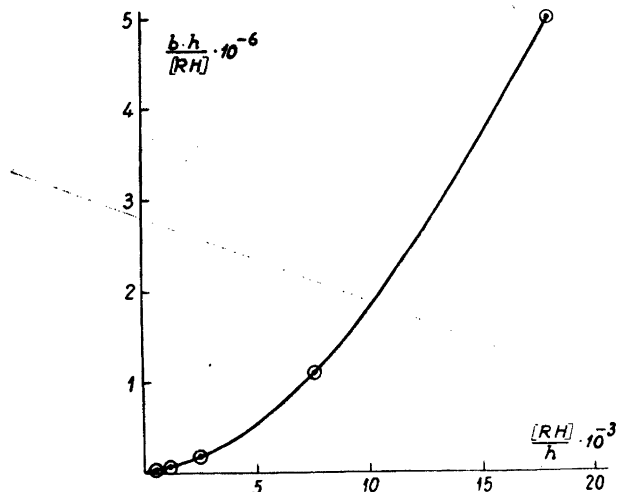
Fig. 5. Potentiometric determination of $\varkappa_2$ and $\varkappa_3$.

changed by adding NaOH. At the same time an iron solution was added so that the total concentrations of iron (II) and iron (III) were unchanged during the experiment. Such a titration is shown in Table 4. Column 1 shows the total concentration of sulfosalicylic acid which decreases a little during the titration due to the dilution of the solution. Column 2 shows the stoichiometrically calculated concentration of hydroxyl ion if no hydrolysis or complex formation occurred. Column 8 gives the left member of equation (9). Fig. 5 shows the same experiment graphically, the expression $\dfrac{b \cdot h}{[RH]}$ being the dependent variable. Here the curve is bent upwards, which shows that the complex FeR_3 is being formed. If the expression $\left(\dfrac{b \cdot h}{[RH]} - \varkappa_1 \right) \dfrac{h}{[RH]}$ is the dependent variable the curve is a straight line, from which $\varkappa_2$ and $\varkappa_3$ may be calculated.

The results of several such experiments are collected in Table 5.

Table 5. Survey of experiments for the calculation of $\varkappa_2$ and $\varkappa_3$ potentiometrically. Total concentration of Fe (III) = 1.575, of Fe (II) = 0.158 mC.

$\varkappa_2$	$\varkappa_3$
48	—
42	0.013
52	—
46	0.005
50	0.014
M = 48 ± 6	0.011 ± 0.06

Table 6. Photometric determination of $\varkappa_1$. $[R]_t = 9.92$ mC, $[Fe]_t = 0.3024$ mC.

$[H]_t$	h	$[RH]$	E	$\dfrac{[Fe]_t}{E}$	$\dfrac{h}{[RH]}$
41.4	32.0	0.622	0.530	0.571	51.4
62.0	52.4	0.388	0.490	0.617	135.1
82.7	73.0	0.276	0.399	0.758	264
103.1	92.3	0.236	0.328	0.922	391
123.7	113.9	0.183	0.267	1.133	622

Photometric experiments

Using the value of $\varkappa_n$ calculated above, Fig. 2 was constructed. This figure shows in which form iron (III) is present at different "pH" values (strictly speaking, log h values). The curves are drawn on the assumption that the total concentration of sulfosalicylic acid is 10 mC and that the concentration of iron is so low that only an insignificant amount of sulfosalicylic acid is used for complex formation. From this figure the suitable "pH" values may be chosen in the photometrical determinations of the complexity constants.

In the estimation of the value of $\varkappa_1$ the "pH" range chosen was 0.94—1.50. From Fig. 2 it may be seen that in this range there is hardly any FeR_2 formed. To a certain solution of iron (III) and sulfosalicylic acid there were added varying amounts of perchloric acid. Then 3 000 mC $NaClO_4$ was added up to a certain volume. The hydrogen ion concentration and the extinction at 510 mμ were then determined. The results are shown in Table 6 and Fig. 6 curve 1. From this curve the following values are calculated: $\varepsilon_1 = 2.0$; $\varkappa_1 = 480$.

The experiment which was carried out in order to estimate the value of $\varkappa_2$ was made in the same way as the preceding one. The amounts of perchloric acid were chosen so that the "pH" values varied between the limits, 3.54 and 3.88. In this range, as may be seen in Fig. 2, only the complexes FeR and FeR_2 are present in measurable amounts. The extinctions were measured at 460 mμ. The results are shown in Table 7 and Fig. 6 curve 2, from which the values $\varepsilon_2 = 4.4$ and $\varkappa_2 = 52$ may be calculated.
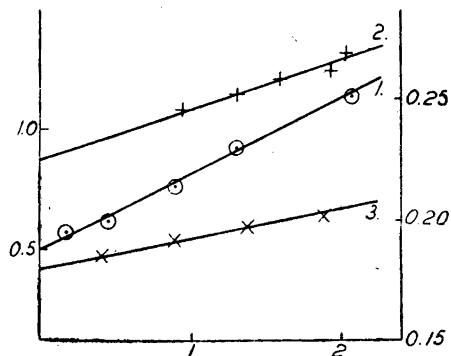

Fig. 6. Photometric determination of $\varkappa_n$.

$$\dfrac{[Fe]_t}{E} \ vs. \ \dfrac{h}{[RH]} \cdot \dfrac{E - [Fe]_t \cdot \varepsilon_{n-1}}{E} \cdot a.$$

Curve 1: $n = 1$; $a = 3 \cdot 10^2$; scale to the left
Curve 2: $n = 2$; $a = 10^{-2}$; scale to the right
Curve 3: $n = 3$; $a = 10^{-5}$; scale to the right.

Table 7. Photometric determination of $x_2 \cdot [R]_t = 9.92$ mC $[Fe]_t = 0.3024$ mC.

$[H]_t$	h	[RH]	E	$\dfrac{[Fe]_t}{E}$	$\dfrac{h}{[RH]} \cdot \dfrac{E-[Fe]_t \cdot \varepsilon_1}{E}$
0.234	0.133	8.91	1.228	0.2462	0.00941
0.487	0.183	8.72	1.205	0.2510	0.01308
0.741	0.223	8.63	1.173	0.2578	0.01584
0.994	0.270	8.49	1.152	0.2625	0.01927
1.247	0.291	8.54	1.125	0.2688	0.02032

In the photometric determination of x_3, the "pH" range, 6.18—6.94, was chosen. Here most of the iron is transformed to FeR_3. No measurable amount of FeR is present. The experiment was made in an analogous manner to the foregoing ones. But, instead of adding perchloric acid, varying amounts of NaOH were added to the iron sulfosalicylic acid solution. The extinctions were measured at 425 mμ. The results are collected in Table 8 and Fig. 6 curve 3. From this curve the values $\varepsilon_3 = 5.6$ and $x_3 = 0.008$ may be calculated.

The values which were found photometrically agree fairly well with those found by potentiometrical measurements.

Table 8. Photometric determination of $x_3 \cdot [R]_t = 9.92$ mC $[Fe]_t = 0.151$ mC.

$[OH]_t$	h	[RH]	E	$\dfrac{[Fe]_t}{E}$	$\dfrac{h}{[RH]} \cdot \dfrac{E-[Fe]_t \cdot \varepsilon_2}{E}$
0.464	$6.56 \cdot 10^{-4}$	9.455	0.746	0.2027	$1.879 \cdot 10^{-5}$
0.489	$4.43 \cdot 10^{-4}$	9.431	0.768	0.1969	$1.370 \cdot 10^{-5}$
0.515	$2.68 \cdot 10^{-4}$	9.405	0.790	0.1914	$0.887 \cdot 10^{-5}$
0.541	$1.14 \cdot 10^{-4}$	9.379	0.820	0.1844	$0.409 \cdot 10^{-5}$

Figure 7 shows how the complex composition of an iron solution varies with the expression $\dfrac{[RH]}{h}$. This figure is more generally valid than Fig. 2, which only shows the conditions at a certain total concentration of sulfosalicylic acid.
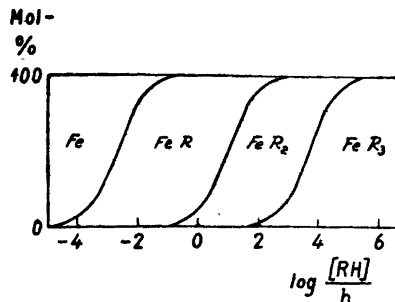

Fig. 7. Distribution of Fe (III) (in percent) over Fe^{+3}, FeR, FeR_2^{-3} and FeR_3^{-6}, as a function of $\log \dfrac{[RH]}{h}$.

SUMMARY.

The complex formation between iron (III) and sulfosalicylic acid has been investigated. At 25.0° C and in a 3 000 mC solution of ClO_4^- the following constants have been determined:

1. The dissociation constant of sulfosalicylic acid (RH_3; cf. p. 266)

$$K_a = \frac{[H^+] \cdot [RH^{-2}]}{[RH_2^-]} = 2.13 \pm 0.06 \text{ mC} = 10^{-2.67 \pm 0.01} \text{ C.}$$

2. The equilibrium constants of the following reactions (both potentiometrically and photometrically):

Reaction	Equilibrium constants	
	potentiometric.	photometric.
$Fe^{+3} + RH^{-2} = H^+ + FeR$	$480 \quad \pm 70$	$480 \quad \pm 80$
$Fe^{+3} + 2\ RH^{-2} = 2\ H^+ + FeR_2^{-3}$	$50 \quad \pm 15$	$52 \quad \pm 10$
$Fe^{+3} + 3\ RH^{-2} = 3\ H^+ + FeR_3^{-6}$	0.011 ± 0.006	0.008 ± 0.002

3. The molar extinctions and the wave length of maxim. absorption:

Complex	Molar extinction $cm^{-1} \cdot mole^{-1} \cdot l$	Wave length $\lambda_{max}.$
FeR	$2 \cdot 10^3$	$510 \text{ m}\mu$
FeR_2^{-3}	$4.4 \cdot 10^3$	$460 \text{ m}\mu$
FeR_3^{-6}	$5.6 \cdot 10^3$	$425 \text{ m}\mu$

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