

The Complex Formation between Iron(III) Ion and Some Phenols. II. Salicylic Acid and *p*-Amino Salicylic Acid *

ALLAN ÅGREN

Department of Chemistry, Royal Pharmaceutical Institute, Stockholm, Sweden

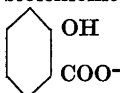
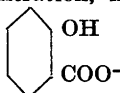
In a previous work ¹ this author has studied the complex formation between iron(III) ion and sulfosalicylic acid. The complex formation between iron(III) ion and salicylic acid and *p*-aminosalicylic acid has now been investigated.

Symbols used in the text (mC denotes millimoles/liter).

h = hydrogen ion concentration, mC.

$[]$ = concentration of substance indicated, mC.

$[]_t$ = stoichiometrical concentration, mC.

RH =  or NH₂ 

$b = \frac{[Fe^{+3}]_t - [Fe^{+3}]}{[Fe^{+3}]}$

ϵ = extinction, cm⁻¹ mC⁻¹

E = extinction, cm⁻¹.

K_a = dissociation constant of acid.

κ = complexity constant.

$\kappa' = \frac{\kappa_{11}}{h} + \frac{\kappa_{12}}{h^2} + \frac{\kappa_{22} [Fe^{+3}]}{h^2}$

κ_{nm} = complexity constants of the hydroxyl complexes $Fe_n(OH)_m$.

The signs for the electrical charges are omitted when there is no risk of confusion.

SALICYLIC ACID

Salicylic acid, like sulfosalicylic acid, forms complexes built up from one atom of iron(III) and one, two or three molecules of salicylic acid. This complex formation has been used in quantitative photometric determinations of iron ^{2,3} and salicylic acid and some derivatives of this acid ⁴.

The complexes have been studied by, among others, Babko ⁵ and Bertin-Batsch ⁶. The former, by a photometric method, has determined the dissociation constants of the three complexes. The latter has, also photometrically, determined the first dissociation constant.

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Table 1. Survey of previous investigations.

Author	FeR			FeR ₂			FeR ₃			Method	Temp.	Ionic strength
	κ_1	ϵ_1	λ	κ_2	ϵ_2	λ	κ_3	ϵ_3	λ			
Babko *	900	—	—	9.3	—	—	$1.7 \cdot 10^{-6}$	—	—	photom.	—	—
Bertin-Batsch *	1 000	1 630	—	—	—	—	—	—	—	photom.	15°	$3.6 \cdot 10^{-3}$
This work	500	1 350	530	18	3 600	480	$8 \cdot 10^{-4}$	4 300	430	photom.	25°	3.0
"	470	—	—	15	—	—	$1.5 \cdot 10^{-4}$	—	—	potentiom.	25°	3.0

* κ_n is calculated using the dissociation constant of salicylic acid $\frac{[R] \cdot h}{[RH]} = 3.6 \cdot 10^{-14}$

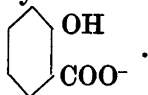
The determinations in this work are made potentiometrically and photometrically. In spite of the determinations having been made under other conditions the results agree rather well with the results of Babko and Bertin-Batsch (Table 1). The complexity constants are defined by the following equations:

$$\kappa_n = \frac{h^n [FeR_n]}{[RH]^n [Fe]} \quad (n = 1, 2 \text{ and } 3) \quad (1)$$

In a previous work¹ the following equation was shown to be valid:

$$\frac{(b - \kappa') h}{[RH]} = \kappa_1 + \kappa_2 \frac{[RH]}{h} + \kappa_3 \left(\frac{[RH]}{h} \right)^2 \quad (2)$$

By this equation the complexity constants could be calculated. The same equation is valid here if RH is



b was calculated from the redox potential of the solution. At small values of $[RH]/h$ the last term could be omitted and a straight line was obtained from which κ_1 and κ_2 were calculated. At high values of $[RH]/h$, κ_3 could then be calculated.

In the photometric determinations the following equations, derived earlier, were used:

$$\frac{c}{E} = \frac{1}{\epsilon_1} + \left[\sqrt{\frac{h(h + K_a)}{E K_a}} \right] \sqrt{\frac{1}{\epsilon_1 \kappa_1}} \quad (3)$$

This equation is valid if Fe and FeR are the only forms of iron(III) present in measurable amounts. $c = [Fe]_t = [R]_t$.

$$\frac{c}{E} = \frac{1}{\epsilon_n} + \left[\frac{h}{[RH]} \cdot \frac{E - c \epsilon_{n-1}}{E} \right] \frac{\kappa_{n-1}}{\epsilon_n \kappa_n} \quad (4)$$

This equation was used when FeR and FeR₂, or FeR₂ and FeR₃ are the only forms of iron(III) present in measurable amounts. $c = [Fe]_t$.

Experimental

Apparatus. The apparatus was the same as that in the previous work ¹.

Chemicals. Iron(II) and iron(III) perchlorate were prepared in the same manner as described before ¹. From sodium salicylate (A.R.) a solution was prepared, the concentration of which was determined bromometrically as described in the Danish Pharmacopeia (1948). To all solutions NaClO₄ (A.R.) was added to make the concentration of ClO₄⁻ 3 000 mC. Under these conditions it is assumed that the activity factors are constant and hence the concentrations may be used instead of activities in the equilibria.

Determination of the dissociation constant of salicylic acid. In acidic solutions only the carboxylic group is dissociated. The phenolic group is dissociated in alkaline solutions only. The dissociation constant of the carboxylic group was determined by titrating a 20 mC solution of sodium salicylate with perchloric acid. The hydrogen ion concentration was determined with a glass electrode. The mean value of the dissociation constant was

$$K_a = \frac{h [RH]}{[RH_2]} = 0.718 \pm 0.005 \text{ mC} = 10^{-3.86} \pm 0.01 \text{ C.}$$

Potentiometric determination of the complexity constants. The experiments were made in the following manner. A solution with known concentration of iron(III) and iron(II) and perchloric acid was titrated with a sodium salicylate solution of known concentration. At the same time an iron solution was added from another burette, whereby the total concentrations of iron(III) and iron(II) were kept constant.

Table 2. Salicylic acid. Potentiometric determination of κ_1 and κ_2 . Compare Table 3, No. 1.

[R] _t	[H] _t	h	b	$\frac{[RH]}{h}$	$\frac{(b-\kappa') h}{[RH]}$
2.186	0.647	1.177	137.03	0.332	410
3.060	0.402	0.7072	565.96	1.312	431
3.825	0.187	0.4737	1 436.3	3.219	446
4.500	-0.002	0.3537	2 773.6	5.900	470
5.100	-0.171	0.2856	4 655	9.054	514
5.637	-0.321	0.2473	6 951	12.137	573
6.120	-0.457	0.2108	10 060	16.295	617
6.557	-0.579	0.1943	13 160	19.310	682
6.955	-0.691	0.1735	17 620	23.666	745

Table 3. Salicylic acid. Survey of potentiometric determinations.

No.	Symbol	Concentrations		κ_1	κ_2	κ_3
		Fe (III)	Fe (II)			
1	○	1.273	0.433	400	14	—
2	□	1.280	1.023	510	17	—
3	△	1.173	1.502	450	20	—
4	▽	1.201	0.312	300	18	—
5	×	1.192	3.004	470	23	—
6	●	1.136	0.295	600	10	1.7 · 10 ⁻⁴
7	+	1.192	3.004	490	11	—
8	⋈	1.173	1.502	460	13	—
9	●	1.136	0.295	550	11	1.2 · 10 ⁻⁴
10	■	0.265	1.430	—	11	1.4 · 10 ⁻⁴
11	▲	0.256	0.604	500	12	1.8 · 10 ⁻⁴

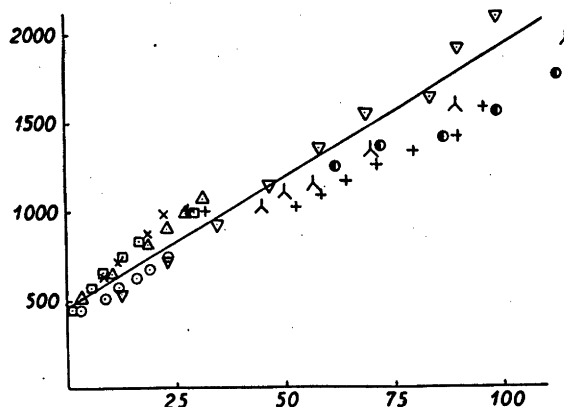


Fig. 1. Salicylic acid. Survey of potentiometric determinations of κ_1 and κ_2 . Compare Table 3. $\frac{(b-\kappa')h}{[RH]}$ vs. $\frac{[RH]}{h}$

As an example the results of one titration are given in detail in Table 2. From these values the complexity constants were calculated: $\kappa_1 = 400$, $\kappa_2 = 14$. Several such titrations were made, and the results are collected in Table 3 and Fig. 1. Some of the titrations were made at very low hydrogen ion concentrations. In these solutions the complex FeR_3 was formed. The results of these experiments are found in Fig. 2.

Photometric experiments. The values of the complexity constants, found potentiometrically, were verified by photometric determinations. These experiments also give the extinction values.

Using the values of κ_n found potentiometrically, conditions were chosen so that one or two complexes but not more were formed in appreciable amounts in the same solution.

The results of the photometric determinations are shown in Tables 4–6 and Figs. 3–5. Fig. 6 shows how iron(III) is distributed over the complexes when $[RH]/h$ is varied.

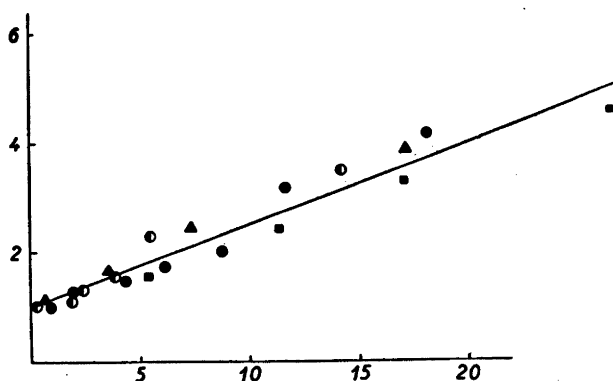


Fig. 2. Salicylic acid. Survey of potentiometric determinations of κ_2 and κ_3 . Compare Table 3. $\left(\frac{(b-\kappa')h}{[RH]} - \kappa_1\right)\frac{h}{[RH]}$ vs. $\frac{[RH]}{h}$

Table 4. Salicylic acid. Photometric determination of κ_1 . $[Fe]_t = [R]_t = 1.514 \text{ mC}$. In the left hand section are given the extinction values at 530 m μ . In the right hand section are given the extinction at different wave lengths when $h = 31.55 \text{ mC}$.

h	E	λ	E
11.29	1.339	400	0.154
16.36	1.066	425	0.191
21.42	0.848	450	0.307
26.49	0.697	475	0.426
31.55	0.565	500	0.514
36.62	0.492	530	0.565
41.68	0.413	550	0.556
46.75	0.315	575	0.505
		600	0.439

Table 5. Salicylic acid. Photometric determination of κ_2 . $[Fe]_t = 0.3805 \text{ mC}$; $[R]_t = 10.10 \text{ mC}$.

h	Extinction at wave length								
	400	425	450	460	470	480	490	500	525
1.248	0.373	0.805	1.105	1.195	1.225	1.248	1.232	1.185	1.000
1.270	0.400	0.826	1.136	1.203	1.250	1.270	1.250	1.208	1.028
1.284	0.428	0.850	1.196	1.225	1.270	1.284	1.263	1.220	1.020
1.300	0.435	0.875	1.166	1.235	1.282	1.300	1.278	1.224	1.015

Table 6. Salicylic acid. Photometric determination of κ_3 . $[Fe]_t = 0.2154 \text{ mC}$; $[R]_t = 10.10 \text{ mC}$.

h	Extinction at wave length								
	400	430	450	475	500	525	550	575	600
5.951	0.500	0.715	0.775	0.730	0.609	0.468	0.320	0.195	0.108
4.121	0.535	0.755	0.780	0.715	0.580	0.440	0.295	0.175	0.100
3.229	0.585	0.775	0.720	0.701	0.575	0.420	0.275	0.163	0.095
2.228	0.605	0.800	0.805	0.712	0.550	0.400	0.265	0.156	0.090
1.425	0.655	0.840	0.835	0.725	0.550	0.395	0.255	0.155	0.090
1.104	0.660	0.845	0.835	0.685	0.500	0.345	0.210	0.120	0.068
0.835	0.700	0.880	0.840	0.690	0.500	0.325	0.205	0.115	0.070

p-AMINOSALICYLIC ACID (PAS)

The colour reaction between iron(III) and PAS has been used in a photometric determination of Fe by Rosdahl¹¹. Like salicylic acid, PAS forms coloured complexes with iron(III) and the colour shifts as the pH is changed. In rather strong acidic solutions the colour is violet and when the hydrogen ion concentration is decreased the colour shifts through red to yellow. The violet complex is built up from one atom Fe and one molecule of PAS, which may be shown by a method introduced by Job⁷ (Fig. 7).

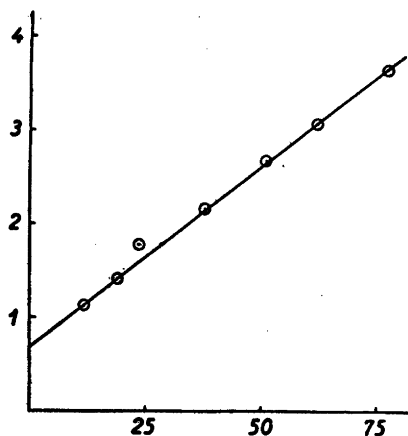


Fig. 3. Salicylic acid. Photometric determination of κ_1 .

$$\frac{c}{E} \text{ vs. } \sqrt{\frac{h(h+K_a)}{E \cdot K_a}}; c = [Fe]_t = [R]_t = 1.514 \text{ mC. } \lambda = 530 \text{ m}\mu.$$

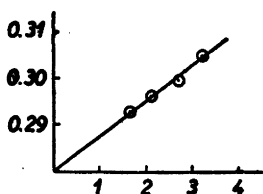


Fig. 4. Salicylic acid. Photometric determination of κ_2 .

$$\frac{c}{E} \text{ vs. } \frac{h}{[RH]} \cdot \frac{E - c \cdot \epsilon_1}{E}; c = [Fe]_t = 0.3805 \text{ mC. } [R]_t = 10.10 \text{ mC. } \lambda = 480 \text{ m}\mu.$$

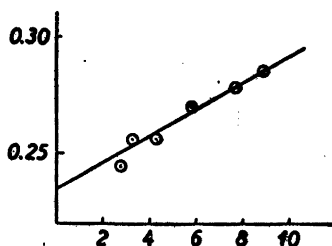


Fig. 5. Salicylic acid. Photometric determination of κ_3 .

$$\frac{c}{E} \text{ vs. } \frac{h}{[RH]} \cdot \frac{E - c \cdot \epsilon_2}{E}; c = [Fe]_t = 0.2154 \text{ mC. } [R]_t = 10.10 \text{ mC. } \lambda = 430 \text{ m}\mu.$$

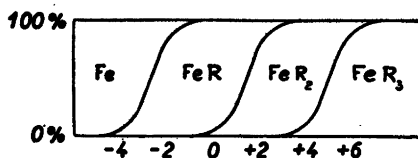
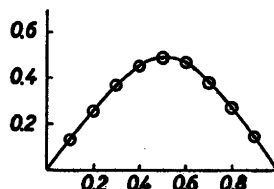


Fig. 6. Salicylic acid. Distribution of Fe(III) in per cent over Fe^{+3} , FeR^+ , FeR_2^- and FeR_3^{3-} as a function of $\log \frac{[RH]}{h}$.

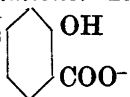
Fig. 7. PAS. Determination of composition of the violet complex.

$$E \text{ vs. } \frac{[Fe]_t}{[Fe]_t + [R]_t} ; [Fe]_t + [R]_t = 0.75 \\ mC. \quad h = 5.0 \text{ mC.}$$



When the hydrogen ion concentration is decreased, complexes built up from two and three molecules of PAS per atom Fe are formed. In order to determine the complexity constants, defined by equation (1) the same method was used as in the investigation of sulfosalicylic acid¹ and salicylic acid.

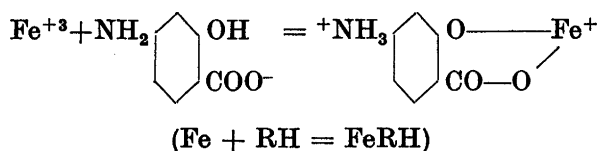
Theoretical

Potentiometric determinations. It is easy to see that equation (2) should also be valid if RH is NH_2 . When $[RH]/h$ is rather small, the last

term in this equation may be omitted. Thus a straight line should be obtained if $\frac{(b-\kappa')h}{[RH]}$ is plotted against $[RH]/h$.

During this investigation, however, it was observed that when $[RH]/h$ was very low or h rather great, the line was bent upwards (cf. Fig. 8). This was not observed with the phenols hitherto investigated. This phenomenon may be explained in the following manner.

PAS has an amino group with weakly basic properties. In acid solutions one hydrogen ion can be added, and thus there is a possibility that another complex is formed:



the equilibrium constant being

$$\kappa_{10} = \frac{[FeRH]}{[RH][Fe]} \quad (5)$$

In analogy to the complex $FeRH$ one would expect the complexes FeR_2H , FeR_3H and so on, but complexes with more than one R per Fe atom are formed only in very weakly acidic solutions and no such complexes have been found in fact.

A similar phenomenon was observed by Schwarzenbach and Willi⁸ with pyrocatechol-3,5-disulfonic acid, which forms complexes of the type FeBz and FeHBz ($\text{Bz} = \text{C}_6\text{H}_2(\text{O}^-)_2(\text{SO}_3^-)_2$). Schwarzenbach and Willi believe that the hydrogen atom is bound to the sulfonic group but not to the phenolic groups.

It is easy to show, that here equation (2) has to be changed to

$$\frac{(b-\kappa')h}{[\text{RH}]} = \kappa_{10}h + \kappa_1 + \kappa_2 \frac{[\text{RH}]}{h} + \kappa_3 \left(\frac{[\text{RH}]}{h} \right)^2 \quad (6)$$

At low h values this equation, like equation (2), gives a straight line, from which κ_1 and κ_2 may be calculated. But if the hydrogen ion concentration is appreciably increased the first term of the right member increases, which results in a bending upwards of the curve. If $[\text{RH}]/h$ is small and h increases the last two terms of equation (6) may be omitted:

$$\frac{(b-\kappa')h}{[\text{RH}]} = \kappa_{10}h + \kappa_1 \quad (7)$$

A straight line should be obtained if the left member is plotted against h . The slope of this line is κ_{10} and the intercept gives κ_1 .

When $[\text{RH}]/h$ is appreciably increased the complex FeR_3 is formed. However, the complexity constant κ_3 could not be determined potentiometrically because PAS is sparingly soluble. Thus $[\text{RH}]$ may not be increased too much, and h may not be decreased too much because the hydrolysis of Fe(III) and Fe(II) will then be too great.

Photometric determinations. The hydrogen ion concentration was kept within a range where only one or two complexes but not more were formed in appreciable amounts. This could be calculated from Fig. 9, which shows the distribution of iron between the complex forms at different h values. These curves are calculated from κ_n measured potentiometrically. The total concentration of PAS is 10 mC and the concentration of iron so low that only a very small portion of PAS is bound to the iron.

The equations used before, (3) and (4), in the photometric determinations could not be used here due to the formation of the complex FeRH . Instead the following equations are valid.

$$[\text{Fe}]_t = [\text{Fe}] + [\text{FeRH}] \quad (8)$$

$$E = \varepsilon_{10} [\text{FeRH}] \quad (9)$$

(Only Fe and FeRH are present in appreciable amounts, and only the latter has a measurable extinction at the concentration and wave length used).

If these equations are combined with equation (5) the following equation is formed:

$$\frac{[\text{Fe}]_t}{E} = \frac{1}{\varepsilon_{10}} + \frac{1}{[\text{RH}]} \frac{1}{\varepsilon_{10} \kappa_{10}} \quad (10)$$

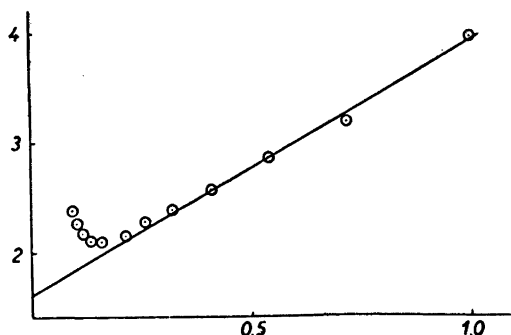


Fig. 8. PAS. Potentiometric determination of κ_1 and κ_2 . Expt. No. 3 of Table 7.

$$\frac{(b-x')h}{[RH]} 10^{-3} \text{ vs. } \frac{[RH]}{h}$$

If $[\text{Fe}]_t/E$ is plotted as a function of $1/[\text{RH}]$ a straight line should be formed, the intercept of which is $1/\varepsilon_{10}$. From the slope of the line κ_{10} could be calculated.

When FeRH and FeR are formed, the following equations are valid:

$$E = \varepsilon_{10} [\text{FeRH}] + \varepsilon_1 [\text{FeR}] \quad (11)$$

$$[\text{Fe}]_t = [\text{FeRH}] + [\text{FeR}] \quad (12)$$

(No forms of iron other than FeRH and FeR are supposed to be present). From these equations and equations (1) and (5), the following expression may be derived:

$$\frac{[\text{Fe}]_t}{E} = \frac{1}{\varepsilon_1} + \left[h \cdot \frac{E - \varepsilon_{10} [\text{Fe}]_t}{E} \right] \frac{\kappa_{10}}{\varepsilon_1 \kappa_1} \quad (13)$$

If $[\text{Fe}]_t/E$ is plotted against the expression in the square brackets a straight line should be obtained. From the slope and intercept, ε_1 and κ_1 may be calculated.

From Fig. 6 it is seen that under the conditions used there, κ_{10} may be determined within a range of $\log h$ from $+3$ to $+2$, where Fe^{+3} and FeRH but no other forms of iron are present in measurable amounts. In the range from $+1$ to 0 the expression κ_{10}/κ_1 may be determined. The expression κ_1/κ_2 cannot be determined, however, in this manner since the complexes FeR and FeR_2 cannot be formed without an appreciable amount of FeRH being present.

At h values which are so low ($\log h = -3$ to -6) that the yellow complex FeR_3 is formed, κ_3 can also be estimated. From equation (4) where $n = 3$, ε_3 and κ_3 may be determined if ε_2 and κ_2 are known. However, κ_2 could not be determined photometrically in the usual manner as shown above. Instead the following method was used.

$[\text{Fe}]_t/E$ plotted against the expression in the square brackets of equation (4) should give a straight line. This is only true if the right value of ε_2 is used.

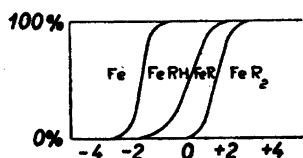


Fig. 9. PAS. Distribution of Fe(III) in per cent over Fe^{+3} , FeRH^{+2} , FeR^{+} and FeR_2^{-} as a function of $-\log h$. $[\text{R}]_t = 10 \text{ mC}$.

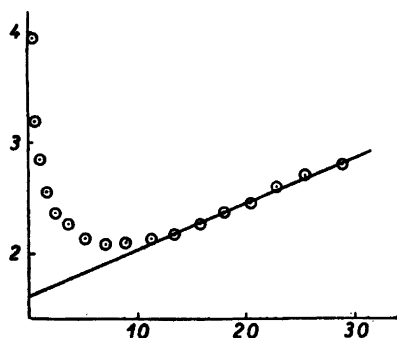


Fig. 10. PAS. Potentiometric determination of κ_{10} and κ_1 . $\frac{(b-\kappa') h}{[\text{RH}]} 10^{-3}$ vs. h .

If a wrong value is used the curve will bend in one direction or another. When several values were tried only a certain value gave a straight line but small variations in ϵ_2 gave strong deviations from the straight line. In order to calculate κ_3 the value of κ_2 found potentiometrically was used.

Experimental

Chemicals. In addition to the chemicals used before, solutions of PAS were used. These were prepared immediately before each experiment from pure PAS, which was dissolved in an excess of NaOH 100 mC. Then a calculated amount of HClO_4 100 mC was added.

Table 7. PAS. Survey of potentiometric experiments.

No.	Symbol	Concentrations		κ_{10}	κ_1	κ_2
		Fe (III)	Fe (II)			
1		0.651	0.591	1 700	1 500	—
2		0.660	0.573	1 700	—	—
3		1.663	0.595	(2 300)	1 600	43
4	○	0.558	0.507	—	1 400	24
5	□	0.651	0.591	—	1 600	21
6	△	0.660	0.573	—	2 500	32
7	×	0.669	0.573	—	2 500	38
8	+	0.669	0.573	—	2 000	43
9	Λ	1.500	0.591	—	1 400	35
10	◇	1.663	0.573	—	1 600	43
11	●	2.981	0.551	—	1 600	66

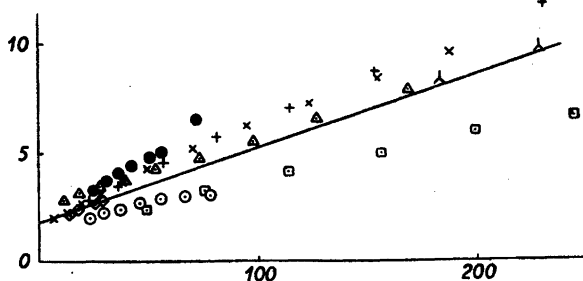


Fig. 11. PAS. Survey of potentiometric determinations of κ_1 and κ_2 . Compare Table 7.
 $\frac{(b-x')h}{[RH]}$ vs. $\frac{[RH]}{h}$.

To the solutions of PAS, as to all other solutions, NaClO_4 was added up to a concentration of 3 000 mC ClO_4^- .

Acidic solutions of PAS are not quite stable^{9,10} but at the hydrogen ion concentrations and the temperature used in this investigation the decomposition, as was experimentally proved, is insignificant.

Determination of dissociation constants. In acidic or neutral solutions the following constants are of interest:

$$K_{a1} = \frac{[RH]h}{[RH_1]} \qquad K_{a2} = \frac{[RH_2]h}{[RH_2]}$$

Table 8. PAS. Photometric determination of κ_{10} .

h	Extinction at wave length								
	400	425	450	475	500	525	550	575	600
102.7	0.174	0.265	0.417	0.532	0.589	0.575	0.500	0.400	0.296
110.6	0.155	0.240	0.380	0.499	0.541	0.522	0.462	0.358	0.260
118.7	0.141	0.230	0.350	0.459	0.493	0.490	0.424	0.328	0.238
126.8	0.132	0.212	0.324	0.422	0.462	0.460	0.390	0.301	0.218
134.9	0.123	0.199	0.301	0.392	0.437	0.420	0.360	0.279	0.201
143.1	0.105	0.180	0.276	0.358	0.396	0.382	0.332	0.254	0.185

Table 9. PAS. Photometric determination of κ_1 .

h	Extinction at wave length								
	400	425	450	475	500	525	550	575	600
0.4199	0.277	0.405	0.500	0.516	0.479	0.390	0.285	0.186	0.120
1.004	0.208	0.310	0.417	0.450	0.427	0.360	0.277	0.190	0.127
1.564	0.151	0.250	0.345	0.400	0.398	0.350	0.279	0.200	0.136
2.595	0.130	0.220	0.313	0.370	0.378	0.348	0.280	0.212	0.148
3.556	0.114	0.200	0.291	0.333	0.360	0.333	0.288	0.217	0.151
4.838	0.100	0.170	0.269	0.330	0.355	0.336	0.287	0.213	0.152
6.277	0.096	0.164	0.262	0.327	0.351	0.330	0.280	0.211	0.150

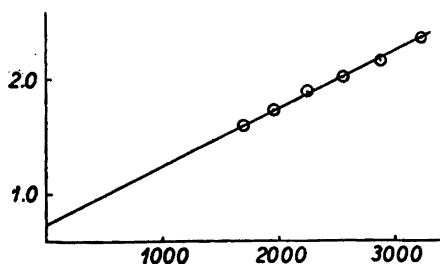


Fig. 12. PAS. Photometric determination of κ_{10} . $\frac{[Fe]_t}{E}$ vs. $\frac{1}{[RH]}$; $[Fe]_t = 0.9318$ mC, $[R]_t = 9.774$ mC. $\lambda = 500$ m μ .

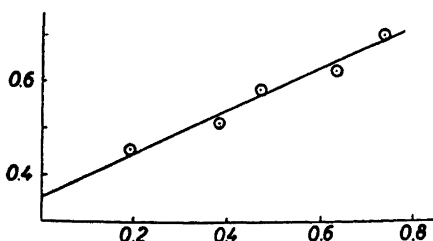


Fig. 13. PAS. Photometric determination of κ_1 . $\frac{c}{E}$ vs. $h \cdot \frac{E - c \cdot \epsilon_{10}}{E}$; $c = [Fe]_t = 0.2330$ mC. $[R]_t = 9.776$ mC. $\lambda = 475$ m μ .

They were determined by titrating a 25 mC solution of PAS-Na with $HClO_4$ 100 mC. From the titration curve obtained the constants could be calculated. Mean values are

$$K_{a1} = 8.3 \pm 0.1 \text{ mC} = 10^{-2.08 \pm 0.01} \text{ C}$$

$$K_{a2} = 0.0826 \pm 0.0005 \text{ mC} = 10^{-4.08 \pm 0.01} \text{ C}.$$

Potentiometric determinations of complexity constants. The experiments were made in complete analogy to those described under "salicylic acid". Fig. 8 shows how the formation of the complex $FeRH$ influences the results. Here $\frac{b \cdot h}{[RH]}$ is plotted as a function of $[RH]/h$. Disregarding the upwards bending of the left part of the curve one may calculate $\kappa_1 = 1\ 600$ and $\kappa_2 = 43$.

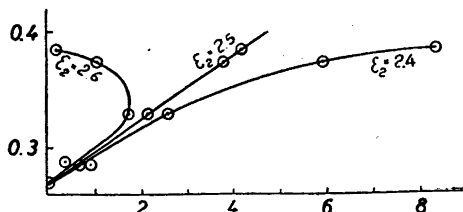
If $\frac{b \cdot h}{[RH]}$ is plotted against h instead, the curve in Fig. 10 is obtained. At high h values the complexes $FeRH$ and FeR dominate. When h is small (< 0.2 mC) FeR_2 is being formed in an appreciable amount, which results in the bending upwards of the left part of this curve. Here the following values are calculated: $\kappa_1 = 1\ 600$ and $\kappa_{10} = 2\ 300$.

Several such experiments are collected in Table 7. Nos. 1 and 2 are made in strongly acidic solutions ($h \sim 50$ mC). Fig. 11 shows those experiments from which κ_1 and κ_2 are calculated.

Table 10. PAS. Photometric determination of κ_3 .

h	Extinction at wave length						
	400	425	450	475	500	525	550
$1.412 \cdot 10^{-6}$	0.860	0.920	0.807	0.587	0.350	0.166	0.050
$2.646 \cdot 10^{-5}$	0.815	0.879	0.820	0.657	0.469	0.294	0.169
$1.202 \cdot 10^{-4}$	0.708	0.802	0.794	0.704	0.559	0.420	0.278
$5.488 \cdot 10^{-4}$	0.625	0.730	0.779	0.748	0.654	0.518	0.380
$1.035 \cdot 10^{-3}$	0.607	0.714	0.772	0.760	0.676	0.544	0.400

Fig. 14. PAS. Photometric determination of κ_3 . $\frac{c}{E}$ vs. $\frac{h}{[RH]} \cdot \frac{E - c \cdot \epsilon_2}{E} 10^6$; $c = [Fe]_t = 0.2330$ mC. $[R]_t = 9.758$ mC. $\lambda = 400$ m μ .



Photometric experiments. The results of the photometric experiments, from which κ_{10} and κ_1 are determined are shown in Tables 8 and 9. From these values the curves shown in Figs. 12 and 13 are constructed.

In order to estimate κ_3 a series of experiments was done, the results of which are shown in Table 10. Fig. 14 gives the results at 400 m μ . Three curves are drawn, which result if ϵ_2 is given the values 2.4, 2.5 and 2.6. Only the value 2.5 gives a straight line, and thus this value was taken as the right one. From this straight line ϵ_2 and κ_3 were calculated. The value of $\kappa_3 = 34$, which was determined potentiometrically, has been used in this calculation. In the same manner a straight line was constructed from the values at 425 m μ .

In the least acidic solution it is seen, that FeR_3 is almost the only complex present. Thus the extinction curve of this solution could be used to determine the extinction maximum.

Table 11 shows the collected results from the potentiometric and photometric determinations.

Table 11. PAS. Survey of the potentiometric and photometric determinations.

Complex	Potentiometric.	Photometric.		
	κ	κ	ϵ	λ_{\max}
FeRH	$1\,700 \pm 200$	$1\,500 \pm 200$	1.33	510
FeR	$1\,800 \pm 500$	$1\,200 \pm 200$	2.8	460
FeR ₂	34 ± 10	—	3.4	470
FeR ₃	—	$3.4 \cdot 10^{-4}$ $\pm 1 \cdot 10^{-4}$	4.0	425

SUMMARY

The complex formation between iron(III)ion and salicylic acid or *p*-aminosalicylic acid (PAS) has been investigated at $25.0^\circ \pm 0.1^\circ$ C in solutions with a concentration of ClO_4^- of 3 000 mC. Using potentiometric and photometric methods the complexity constants and the molar extinctions have been determined.

Salicylic acid forms the complexes FeR , FeR_2 and FeR_3 : Table 1.

PAS forms the complexes $FeRH$, FeR , FeR_2 and FeR_3 : Table 11.

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