The Complex Formation between Iron(III)Ion and Some Phenols. IV. The Acidity Constant of the Phenolic Group

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By an ultra violet photometric method the dissociation constant of the phenolic group of some phenols has been determined. Among them, the following phenols have not been studied before: sulfosalicylic acid, *p*-amino salicylic acid, *p*-amino salicylamide and salicylamide.

In order to determine the dissociation constants of very weak acids, several methods have been used. King and Marion [1] used the catalytic effect of hydroxyl ion, Konopik and Eberl [2] made colorimetric determinations using colour indicators while photometric determinations in ultraviolet light (UV) have been used by others [3, 20]. Potentiometric or conductometric methods are not useful for the study of very weak acids.

This author has investigated the complex formation between iron(III)ion and the following phenols: sulfosalicylic acid [4], salicylic acid, *p*-amino salicylic acid (PAS)[5], salicylaldehyde, *o*-hydroxyacetophenone, salicylamide, methyl salicylate [6] and *p*-amino salicylamide (PAS-amide) [21]. In this investigation the dissociation constant of the phenolic group of these substances and of ordinary phenol has been determined. The values of these constants lie between the limits 10^{-9} and 10^{-14} C. Thus, the stronger ones of these acids could be studied by potentiometric measurements, but this could not easily be done with the weaker ones. Further, some of the substances concerned are sparingly soluble and this fact will make potentiometrical methods impractical. Hence all the substances were studied by photometric measurements in UV. Vandenbelt and coworkers [20] have demonstrated the agreement between photometric and potentiometric measurements where both could be used.

The results of previous work on the dissociation of the phenolic group of the substances studied here are collected in Table 1. Most of the substances have been studied in UV. Some recent works in this field are collected in Table 2. By comparing Table 1 and Table 2 it may be seen that in only two of the works cited have the measurements been used to determine the dissociation constant. This method has also been used by for example Flexser and coworkers [12], who studied some very weak acids and bases.

Table 1. *Survey of previous investigations.*

Substance	Method	Temp.	pK_a $(=3-\log K_a)$	Ref.
Salicylic acid	Colorim.	room	13.4	2
	»	19	13.64	15
	Potentiom.	30	12.38	16
o-Hydroxyacetophenone	UV photom.	25	10.17	20
Methyl salicylate	Kinetic	25	11	17
Phenol	UV photom.	room	9.89	3
	»	25	9.87	20
	Electrom.	18	9.92	13
	Potentiom.	20	9.98	14
Salicylaldehyde	»	—	9.5	18
	(50 % dioxan)			
	UV photom.	25	8.10	20

The authors cited in Table 1 have not used the same conditions as the present author used in his investigations on the complex formation with iron(III)-ion. The value given for methyl salicylate is very old and is said by the authors to be only approximate. For the substances studied previously by other authors, the results of the present author are given in Table 9, but no details on the measurements.

Studies of sulfosalicylic acid, PAS, PAS-amide and salicylamide in order to determine the dissociation constant of the phenolic group have not previously been performed. The results are given here in Table 9, with details in Tables 4—8.

THEORETICAL

When a phenol dissociates to phenolate there is usually a change in the UV absorption. Both the wave length of maximum extinction and maximum extinction itself become larger. In some cases there is a considerable change (about 20—50 mμ, cf. Fig. 4) and the dissociation is then measured at the wave length where the phenolate has its maximum extinction.

In other cases, for example salicylic acid, PAS, and PAS-amide, the wave length shift is very small (5—10 mμ, Figs. 2 and 3) but the extinction value is

Table 2. *Substances previously studied in UV.*

Substance	Ref.
Phenol	3, 20
Salicylic acid	8
Methyl salicylate	19
Salicylaldehyde	8, 19, 20
o-Hydroxyacetophenone	8, 20
Salicylamide	8
PAS	9, 10, 11

considerably changed. If the measurements are made at the wave length where the phenolate or phenol has its extinction maximum, the accuracy in the results will be rather small. Instead the measurements ought to be made at a wave length, where the extinction of phenolate is great and that of phenol is small. But as this is not the case near a maximum or minimum, large errors may be introduced if the wave length is only slightly changed during a series of measurements. If the apparatus is not changed the calculated value of the dissociation constant may be accurate, but the extinction value will be of little theoretical or practical interest.

The dissociation constant of a phenol is defined in the following equation

$$K_a = \frac{h\,[R]}{[RH]} \tag{1}$$

where h is the hydrogen ion concentration, $[RH]$ and $[R]$ are the concentration of phenol and phenolate, respectively. All concentrations are expressed in mC ($=$ millimoles/liter). All electrical charges are omitted.

The total concentration, $[R]_t$, of the phenol is

$$[R]_t = [R] + [RH] \tag{2}$$

It is assumed that no other forms are present in measurable amounts, as for example RH_2 or RH_3. This is true for all substances studied in this work at such h-values where the phenolic group is appreciably dissociated.

The extinction, E, at a definite wave length is

$$E = \varepsilon_R\,[R] + \varepsilon_{RH}\,[RH] \tag{3}$$

where ε is extinction per mC and cm.

From equations (1)—(3) the following equation is derived

$$\frac{[R]_t}{E} = \frac{1}{\varepsilon_R} + \left[h\,\frac{E - \varepsilon_{RH}\,[R]_t}{E} \right] \frac{1}{K_a\,\varepsilon_R} \tag{4}$$

If $[R]_t/E$ is plotted against the expression within the brackets a straight line should be obtained, the intercept being $1/\varepsilon_R$ and the slope $1/K_a\,\varepsilon_R$.

If ε_{RH} is also unknown, several values may be tried. Only the right value will give a straight line (compare a previous work by this author [5]).

APPARATUS AND CHEMICALS

In the photometric measurements an Uvispek photometer with 1 cm quartz cells was used. For the determination of hydrogen ion concentration, a glass electrode was used and as a reference a silver-silver chloride electrode. In solutions with large concentrations of hydroxyl ion, a hydrogen-platinum black electrode was used. The hydrogen gas was freed from oxygen using a Meyer-Ronge [22] oven. In order to avoid evaporation of the solution to be measured, the gas was bubbled first through a 3 000 mC solution of $NaClO_4$.

The measurements were made at $25.0° \pm 0.1°$ C. Further details are described in previous works [4],[5]. All experiments were made in solutions with a total concentration of 3 000 mC ClO_4^-. In this medium it is assumed that the activity factors are constant and hence that the concentrations may be used instead of activities in the equilibria.

The purity of the phenol used was controlled according to the Swedish Pharmacopeia Ed. XI. From this substance a 90 % solution was prepared and the concentration determined bromometrically according to Pharmacopeia Danica 1948. This stock solution was then diluted with water and $NaClO_4$.

Table 3. *Determination of the ionic product of water,* K_w.
Mean value $0.70 \cdot 10^{-8} \pm 0.05 \cdot 10^{-8}$ $(mC)^2 = 10^{-14.15 \pm 0.01}$ C^2.

[OH]$_t$	$h \cdot 10^{10}$	$K_w \cdot 10^{8}$
2.822	24.90	0.703
4.614	14.78	0.682
8.809	7.868	0.693
12.64	5.522	0.698
16.15	4.321	0.698
19.38	3.641	0.706
22.36	3.153	0.705
25.12	2.805	0.705
27.69	2.535	0.702
30.07	2.318	0.697
32.30	2.161	0.698
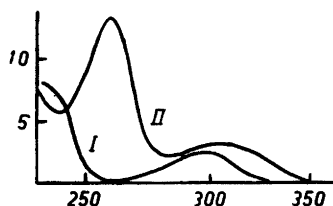
Fig. 1. *Sulfosalicylic acid.* ε vs. λ in mμ.
  Curve I: The phenol,
  $^-SO_3 \cdot C_6H_3(COO^-)OH$.
  Curve II: The phenolate,
  $^-SO_3 \cdot C_5H_3(COO^-)O^-$.
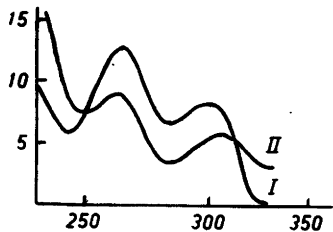
Fig. 2. *PAS.* ε vs. λ in mμ.
  Curve I: The phenol,
  $NH_2 \cdot C_6H_3(COO^-)OH$.
  Curve II: The phenolate,
  $NH_2 \cdot C_6H_3(COO^-)O^-$.
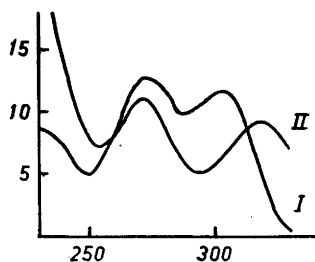
Fig. 3. *PAS-amide.* ε vs. λ in mμ.
  Curve I: The phenol,
  $NH_2 \cdot C_6H_3(CONH_2)OH$.
  Curve II: The phenolate,
  $NH_2 \cdot C_6H_3(CONH_2)O^-$.
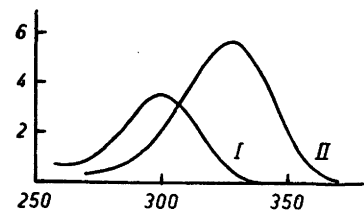
Fig. 4. *Salicylamide.* ε vs. λ in mμ.
  Curve I: The phenol,
  $C_6H_4(CONH_2)OH$.
  Curve II: The phenolate,
  $C_6H_4(CONH_2)O^-$.

Table 4. Sulfosalicylic acid. $\lambda = 260$ mμ. $[R]_t = 0.0916$ mC. In this case $\varepsilon_{RH} = 0$.
Results: $\varepsilon_R = 13.3$ mC^{-1} cm^{-1}. $K_a = 1.83 \cdot 10^{-9}$ mC.

$[OH]_t$	$h \cdot 10^9$	E	$\dfrac{[R]_t}{E}$
0.886	9.96	0.189	0.485
1.329	6.11	0.284	0.323
1.772	4.41	0.353	0.259
2.215	3.44	0.419	0.219
2.658	2.83	0.481	0.190
3.543	2.08	0.521	0.176
4.429	1.65	0.628	0.146
5.314	1.36	0.692	0.132

Table 5. PAS. $\lambda = 325$ mμ. $[R]_t = 0.2618$ mC.
Results: $\varepsilon_R = 3.1$ mC^{-1} cm^{-1}. $K_a = 1.82 \cdot 10^{-11}$ mC.

$[OH]_t$	$h \cdot 10^{11}$	E	$\dfrac{[R]_t}{E}$	$h \dfrac{E - \varepsilon_{RH}[R]_t}{E} 10^{11}$
79.0	8.86	0.191	1.37	5.84
118.5	5.91	0.243	1.08	4.33
197.5	3.54	0.320	0.818	2.82
395.2	1.77	0.440	0.595	1.51
592.8	1.18	0.525	0.499	1.03
790.4	0.886	0.561	0.467	0.783

Table 6. PAS-amide. $\lambda = 330$ mμ. $[R]_t = 0.1312$ mC. In this case $\varepsilon_{RH} = 0$.
Results: $\varepsilon_R = 6.67$ mC^{-1} cm^{-1}. $K_a = 7.7 \cdot 10^{-7}$ mC.

$h \cdot 10^7$	E	$\dfrac{[R]_t}{E}$
18.54	0.329	0.399
6.634	0.469	0.280
3.922	0.577	0.227
2.650	0.649	0.202
1.850	0.705	0.186
1.216	0.753	0.174

Table 7. Salicylamide. $\lambda = 330$ mμ. $[R]_t = 0.1488$ mC.
Results: $\varepsilon_R = 5.75$ mC^{-1} cm^{-1}. $K_a = 1.28 \cdot 10^{-6}$ mC.

$h \cdot 10^7$	E	$\dfrac{[R]_t}{E}$	$h \dfrac{E - \varepsilon_{RH}[R]_t}{E} 10^7$
14.18	0.432	0.344	12.47
10.07	0.505	0.295	9.03
6.979	0.576	0.258	6.35
5.172	0.622	0.239	4.74
4.443	0.644	0.231	4.08
3.818	0.670	0.222	3.52

Table 8. Methyl salicylate. $\lambda = 330\ m\mu$. $[R]_t = 0.2196\ mC$.
Results: $\varepsilon_R = 5.71\ mC^{-1}\ cm^{-1}$. $K_a = 6.5 \cdot 10^{-8}\ mC$.

$h \cdot 10^8$	E	$\dfrac{[R]_t}{E}$	$h\dfrac{E - \varepsilon_{RH}\,[R]_t}{E}\,10^8$
10.44	0.509	0.431	9.46
7.741	0.601	0.365	7.12
5.626	0.688	0.319	5.23
3.540	0.866	0.254	3.34
1.914	1.010	0.217	1.82
1.140	1.069	0.205	1.09
0.9065	1.090	0.201	0.87

PAS-amide was made according to Jensen and coworkers [23]. Its melting point was 160° C. The solutions were made up immediately before use.

The quality of the other chemicals used has been described earlier [4-6].

MEASUREMENTS

Some of the phenols studied are appreciably dissociated at rather small hydroxyl ion concentrations. In these cases the hydrogen ion concentration was determined directly. In other cases where large hydroxyl ion concentrations were needed a direct measurement of the hydrogen ion concentration was avoided. Here the h values were calculated from the stoichiometrical concentration of hydroxyl ion and the ionic product of water, the value of which was determined in the medium used. A solution of $NaClO_4$ was "titrated" with NaOH of known concentration and the hydrogen ion concentration determined with the hydrogen electrode. The results of such a titration are given in Table 3.

The extinction curves of sulfosalicylic acid, PAS, PAS-amide and salicyl-amide are shown in Figs. 1—4. The extinction of undissociated phenol was measured in a neutral or weakly alkaline solution. Under these conditions the carboxyl group of sulfosalicylic acid and PAS is not appreciably dissociated since the dissociation constant is 2.13 and 0.0826 mC, respectively [4, 5]. Thus, no other forms of the substances were present in measurable amounts. The extinction of the phenolate ion was calculated from the measurements in strongly alkaline solutions and equation (4).
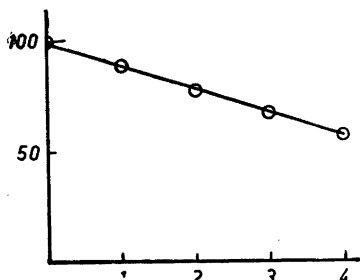
Fig. 5. Methyl salicylate. Extinction at 330 $m\mu$ (in per cent) vs. time (in hours).

Table 9. Survey of the results of this investigation.

Substance	K_a	pK_a ($= 3 - \log K_a$)
PAS	$(1.8 \pm 0.2) \cdot 10^{-11}$	13.74 ± 0.05
Salicylic acid	$(7.6 \pm 0.5) \cdot 10^{-11}$	13.12 ± 0.05
Sulfosalicylic acid	$(1.8 \pm 0.2) \cdot 10^{-9}$	11.74 ± 0.05
o-Hydroxyacetophenone	$(1.5 \pm 0.2) \cdot 10^{-8}$	10.82 ± 0.05
Methyl salicylate	$(6.5 \pm 0.8) \cdot 10^{-8}$	10.19 ± 0.07
Phenol	$(3.0 \pm 0.3) \cdot 10^{-7}$	9.52 ± 0.05
PAS-amide	$(7.7 \pm 0.8) \cdot 10^{-7}$	9.11 ± 0.05
Salicylamide	$(1.3 \pm 0.2) \cdot 10^{-6}$	8.89 ± 0.05
Salicylaldehyde	$(1.6 \pm 0.2) \cdot 10^{-6}$	8.80 ± 0.05

The results of the measurements in solutions of varying alkalinity are given in Tables 4 and 5 for sulfosalicylic acid and PAS, respectively. In these experiments the hydrogen ion concentration was calculated from the ionic product of water.

PAS-amide, salicylamide and methyl salicylate are stronger acids than the two foregoing ones. Here buffer solutions of sodium bicarbonate and sodium hydroxide were used to fix the hydrogen ion concentration. The measurements in these cases were made with the glass electrode or the hydrogen electrode. The results are given in Tables 6—8.

These three substances are not quite stable in alkaline solutions but may be hydrolyzed to the corresponding carbonic acid. If the change in extinction is due to hydrolysis the change is supposed to be slow and should not reverse when the solution is acidified again. The amides were studied in this respect but no change could be found within three hours. When acidified again the calculated extinction value was obtained.

The change in extinction may be due to a dissociation of the amide group. When benzamide was studied no change in extinction could be found even in very strongly alkaline solution. Thus this reaction is improbable.

Methyl salicylate is hydrolyzed more easily under the conditions used here. In order to estimate the speed of this reaction the extinction of one solution in 100 mC NaOH was measured during four hours. In Fig. 5, the decreasing values (in per cent) obtained are shown. For the determination of the dissociation constant more weakly alkaline solutions were used and the extinction was measured within five minutes. During this time the hydrolysis is surely not greater than 1 % and thus does not appreciably influence the results.

All the dissociation constants determined in this work are collected in Table 9.

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