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A Contribution to the Dissociation and Association of Salicylic Acid

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The dissociation and the possible association of salicylic acid was investigated by spectrophotometric measurements and potentiometric titrations of the $2.26 \times 10^{-4}\,M$ and $4 \times 10^{-3}\,M$ acid. A discrepancy between the experimental colorimetric titration curve and the calculated one between *p*H 3 and *p*H 4 was stated. This phenomenon is explained by the assumption that some association reactions might occur. The calculation of the association constants was attempted by means of the least squares method using the titration data obtained.

The dependence of the absorption spectrum of salicylic acid on the hydrogen ion concentration was investigated by H. Schuhler[1]. The concentration of the acid was 4×10^{-4} to 10^{-5} g./l. Schuhler confirmed that between *p*H 1 and 6 salicylic acid behaves like a dibasic acid with dissociation constants $pk = 2$ *and* $pk = 3.7$. The dependence of $E\,(\lambda_1) : E\,(\lambda_2)$ on *p*H was not represented by an S-shaped curve with an inflection point at $pH = 2.9$ which, determined by classical methods, would point to the dissociation of the carboxyl group, but by a curve with a minimum at $pH = 3.5$ and a »plateau« between *p*H 4.6 and 10. Schuhler attempted to explain her results by the assumption that the dissociation of the carboxyl group is followed by a semiquinone-like transformation. One constitution would correspond to the constant at *p*H 3.7 and the other to that at *p*H 10.5.

The potentiometric titration of salicylic acid resulted, however, only one dissociation constant $pk = 3.01$ and therefore the dependence of the dissociation of salicylic acid on *p*H was reinvestigated between 224 and 340 mμ.

EXPERIMENTAL

The spectrophotometric measurements were performed with a Hilger Uvispek type spectrophotometer between 220 mμ and 340 mμ using quartz cells of 10 mm. length. The concentration of salicylic acid was $2.26 \times 10^{-4}\,M$. The constant ionic strength of 0.1 was obtained by addition of a neutral solution of $NaClO_4$. The concentration of H^+ ions was varied by addition of $0.1\,M$ $HClO_4$ or $0.1\,M$ NaOH respectively. The measurements were carried out at room temperature between *p*H 1 and 6 with a precision of 2%.

The potentiometric titrations were carried out with a Philips GM 4491 type *p*H-meter, using a glass electrode at 25° C, while purified nitrogen gas was passed through the solution. Vigorous stirring of the solution was effected from outside, using a magnetic stirrer. The temperature was kept constant within ± 0.05° C by means of a Hoeppler thermostat. The dissociation constants of the 2.26×10^{-4} and $4 \times 10^{-3}\,M$ acid at various ionic strengths were determined with *p*H values in the vicinity of the half-neutralization point. Solutions of 0.03 and 0.01 ionic strength were carefully half-neutralized and the pH measured. The accuracy of the pk determination was ± 0.01 pk for the 4×10^{-3} M solution and ± 0.02 pk for the more diluted one.

Reagents. — Salicylic acid »Merck« was recrystallized from water and dried at 50° C to constant weight. All the solutions were prepared from a 10^{-2} M stock solution. The purity of the acid was checked by titration with 0.1 N NaOH using phenolphthalein as indicator and by potentiometric titration. By the first assay the purity obtained was 99,78% and by the second one 99,5%.

Sodium perchlorate was prepared from stoichiometric quantities of $NaHCO_3$ + + $HClO_4$, CO_2 being removed by boiling and evaporation to dryness. The obtained $NaClO_4$ was recrystallized from water, dissolved in bidistilled water and diluted to a 1 M solution.

The standard 0.1 and 0.01 N carbonate free NaOH solutions, the 0.1 N perchloric acid and the synthethized $NaClO_4$ were all prepared from analytical grade reagents.

RESULTS AND DISCUSSION

The molecular extinction coeficients of salicylic acid and salicylate ion are given in the Tables I and II.

TABLE I

Molecular extinction coefficient of salicylic acid

λ	ε_{HA}	λ	ε_{HA}	Conditions of the extinction determination	Data obtained by
301	3750	238	6140	in 0.1 N $HClO_4$	the author
301	3700	238	8300	in 0.1 N HCl	H. Dannenberg[2]
307	3716	236	7245		C. M. Moser[3]
302	3620	236	8350		L. J. Edwards[4]

TABLE II

Molecular extinction coefficient of salicylate ion

λ	ε_{A^-}	λ	ε_{A^-}	Conditions of the extinction determination	Data obtained by
295	3647	231-4	4637	at $pH = 6$	the author
296	3750	230	7300	in $N/20$ NaOH	H. Dannenberg[2]
296.5	3520	228.5	6920		L. J. Edwards[3]

The values obtained concerning the absorption band at 301 mμ ond 295 mμ agreed with those in the literature but some discrepancies were found for those at 238 mμ and 230 mμ[2,3,4].This was probably due to the influence of $NaClO_4$ and $HClO_4$ which were added for the maintenance of constant ionic strength as well as for the variation of pH. (For the measurements cited in the literature the values of the ionic strength were not mentioned and we might therefore suppose that they were not kept constant by addition of neutral salts). The extinction of salicylic acid solution with and without addition of

NaClO$_4$ did not change at 301 mμ while at 238 mμ it increased on the average by 8$^0/_0$ when the concentration of NaC10$_4$ varied between 0.1 and 1 *N*.

The shift of the spectrum of salicylic acid to shorter wave lengths with increasing *p*H is represented by Fig. 1 and 1a. Up to *p*H 2 the acid is not dissociated. Consequently the bands of salicylic acid appear between 236—238 mμ and 300 and 302 mμ. At *p*H 2,9 the band at 300 mμ shifts towards shorter wave lengths. The shift of the 236 mμ band was not yet measurable because it was probably smaller than 1 mμ. Only its intensity decreased. The dissociation which begins at this moment affects more the absorption band at 300 mμ than this one at 236 mμ where the total shift is smaller too. At *p*H 3,5 the salicylate ion band appears and reaches its maximal value at *p*H 3.7. With a further increase of *p*H to *p*H 6 the position of the salicylate ion band does not change while its intensity decreases by 3$^0/_0$ for the band at 300 mμ and by 5$^0/_0$ for that at 238 mμ.

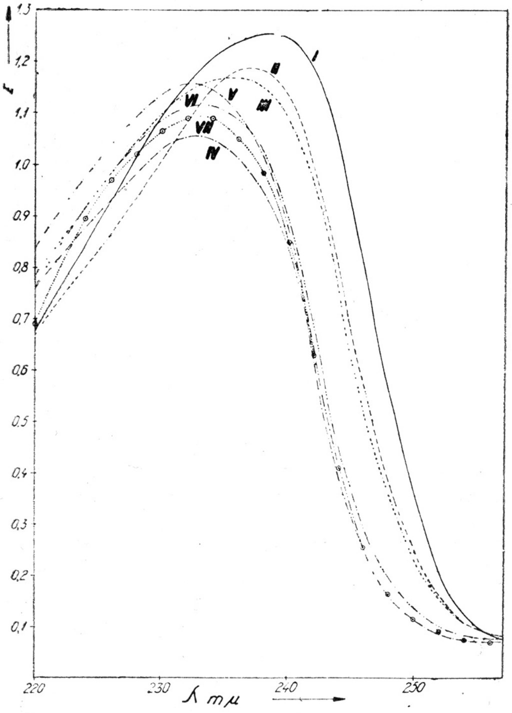


Fig. 1. Absorption spectrum of salicylic acid at different *p*H:

curve I *p*H = 1.0
curve II *p*H = 2.8
curve III *p*H = 3.0
curve IV *p*H = 3.5
curve V *p*H = 3.7
curve VI *p*H = 4.1
curve VII *p*H = 6.0

The total extinction at different H$^+$ ion concentrations for a definite wave length is equal to the sum of the extinctions of salicylic acid and its ions present:

$$E = \varepsilon_{HA}\,[HA] + \varepsilon_{A^-}\,[A^-] \qquad (1)$$

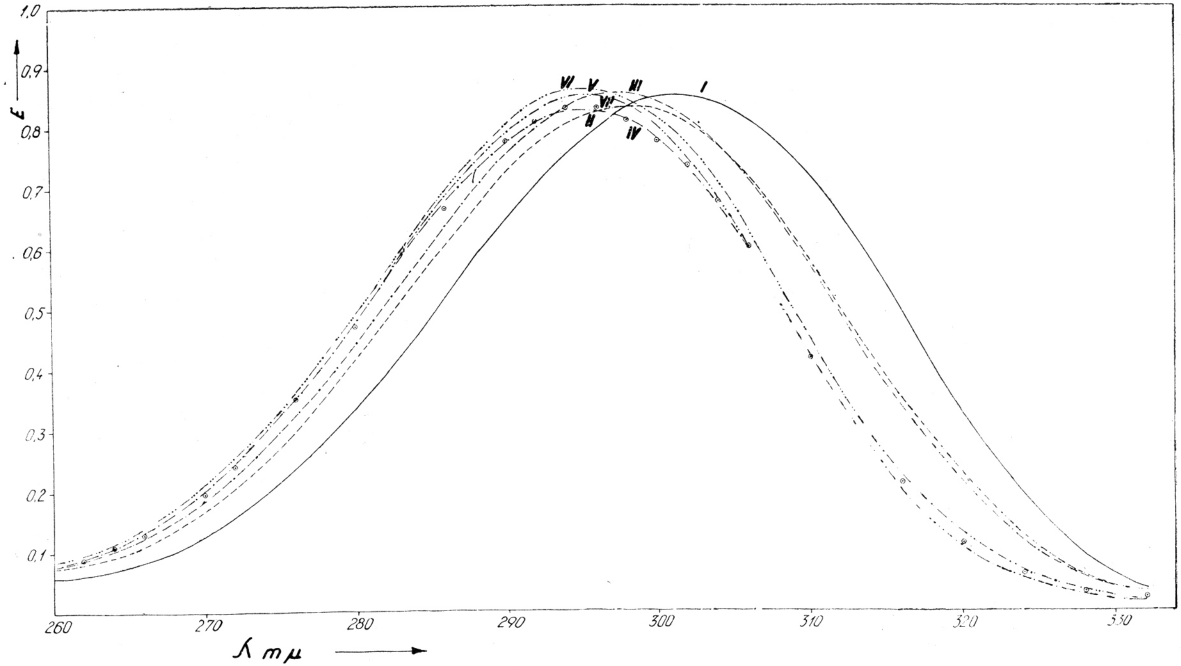


Fig. 1a. Absorption spectrum of salicylic acid at different *pH* (see Fig. 1).

If the total concentration of the acid is represented by

$$c_k = [HA] + [A^-] \tag{2}$$

and the dissociation constant by

$$k_h = \frac{[H] \cdot [A^-]}{[HA]} \tag{3}$$

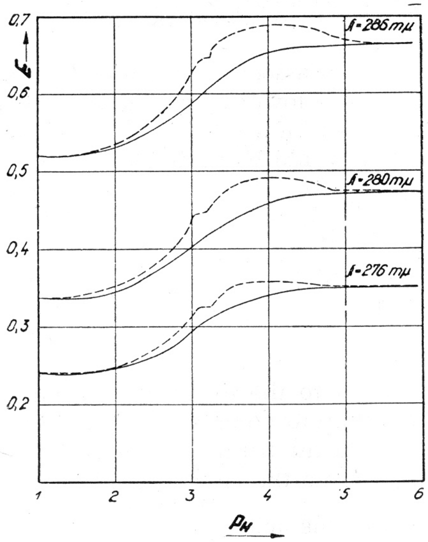
then from the equation (2) and (3) we can deduce that

$$[A^-] = \frac{k_h \cdot c_k}{[H^+] + k_h} \quad (4) \qquad [HA] = c_k \left(1 - \frac{k_h}{[H^+] + k_h}\right) \quad (5)$$

Replacing these values in the equation (1) the total extinction becomes equal to

$$E = \varepsilon_{HA} c_k \left(1 - \frac{k_h}{k_h + [H^+]}\right) + \varepsilon_{A^-} c_k \frac{k_h}{k_h + [H^+]} \tag{6}$$

If the concentration of the H^+ions, the dissociation constants k_h and the molecular extinction coefficients of salicylic acid and salicylate ions at a definite wave length are known, then the dependence of the extinction of salicylic acid on the H^+ion concentration can be calculated. Having obtained by potentiometric titrations only one constant of dissociation between pH 1 and 7 the curve calculated by equation (6) had the shape of a monobasic acid neutralization curve.



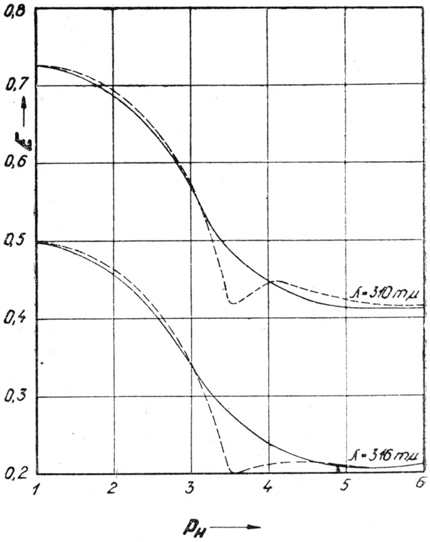


Fig. 2. Dependence of the extinction of salicylate ion on pH; ------- experimental data ———— calculated data

Fig. 3. Dependence of the extinction of salicylic acid on pH; ------- experimental data ———— calculated data

If the calculated curve is compared with this one obtained by experiments for the wave lengths, where either the dependence of the extinction of salicylic acid on *p*H (Fig. 3 and 4) ($\lambda = 310$ and 316 mμ regarding the band at 301 mμ and $\lambda = 248$ and 252 mμ for that at 238 mμ) or that of salicylate ion on *p*H (Fig. 2) ($\lambda = 276, 280$ 286 mμ concerning the band at 301 mμ) can be followed, then a discrepancy of the experimental curve between *p*H 3 and 4 could be stated. Salicylic acid behaves like a dibasic acid.

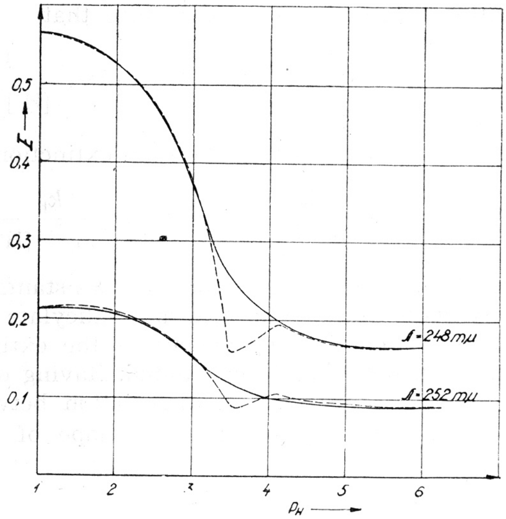


Fig. 4. Dependence of the extinction of salicylic acid on pH;
------- experimental data ———— calculated data

It is well known that carboxylic acids tend to associate in aqueous solutions and that the addition of salts may produce a lowering of the dielectric constant of the solvent and thus enhance the process of association. In aqueous solutions of salicylic acid the following reactions would be probable:

$$3\,HA \rightleftarrows 2H^+ + HAA^- + A^- \qquad (1)$$

$$3\,HA \rightleftarrows H^+ + 2A^- + HAH^+ \qquad (2)$$

$$3\,HA \rightleftarrows H^+ + A^- + HAHA \qquad (3)$$

$$3\,HA \rightleftarrows 3H^+ + A^- + AA^- \qquad (4)$$

$$3\,HA \rightleftarrows 3H^+ + 3A^- \qquad (5)$$

A change of the H^+ion concentration with regard to the dissociation occured at reactions (1), (2) and (3), and an attempt was therefore made to calculate the association constants of these reactions by means of the titration data available. For every reaction mentioned above we could define the equations of the

a) total concentration of the acid
b) electroneutrality
c) dissociation constant k_h, and
d) association constant k_a

Solving these equations we obtained two sets of equations with 2 unknowns:

$$1)\quad 3\,HA \rightleftarrows 2\,H^+ + A^- + HAA^-$$

a) $c_k = [HA] + [A^-] + 2[HAA^-]$ b) $[A^-] = [H^+] + ac_k - [HAA^-]$

c) $k_h = \dfrac{[H^+]\,[A^-]}{[HA]}$ d) $k_a = \dfrac{[A^-]\,[HA]}{[HAA^-]}$

the solving of these gives that

$$k_a([H^+]^3 + ac_k\,[H^+]^2) - k_a k_h c_k [H^+] - k_a k_h^2([H^+] + ac_k - c_k) -$$
$$- k_h(c_k - 2[H^+] - 2ac_k)^2 \cdot [H^+] = 0$$
$$Ak_a - Bk_a k_h - Ck_a k_h^2 - Dk_h = 0 \text{ respectively}$$

$$2)\quad 3\,HA \rightleftarrows H^+ + 2A^- + HAH^+$$

a) $c_k = [HA] + [A^-] + [HAH^+]$ b) $[A^-] = [HAH^+] + ac_k + [H^+]$

c) $k_h = \dfrac{[H^+]\,[A^-]}{[HA]}$ d) $k_a = \dfrac{[H^+]\,[HA]}{[HAH^+]}$

The solving of these resulted in

$$k_a k_h\,(c_k - [H^+] - ac_k) - k_a\,([H^+]\,ac_k - [H^+]^2) - [H^+]^2\,(c_k + [H^+] + ac_k) = 0$$
$$Ak_a k_h - Bk_a - C = 0 \text{ respectively.}$$

$$3)\quad 3\,HA \rightleftarrows H^+ + A^- + HAHA$$

a) $c_k = [HA^-] + [A^-] + 2[HAHA]$ b) $[A^-] = [H^+] + ac_k$

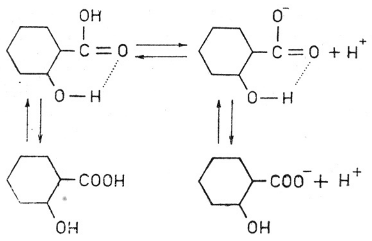
c) $k_h = \dfrac{[H^+]\,[A^-]}{[HA]}$ d) $k_a = \dfrac{[HA]\,[HA]}{[HAHA]}$

The solving of these resulted in

$$k_a k_h^2\,(c_k - [H^+] - ac_k) - k_a([H^+]^2 + [H^+]\,ac_k) - 2([H^+]^2 + [H^+]\,ac_k)^2 = 0$$
$$Ak_a k_h^2 - Bk_a - 2C = 0 \text{ respectively.}$$

If the titration data from the vicinity of the half-neutralization point were substituted in the equations obtained above (for the 4×10^{-3} and $2.26 \times 10^{-4}\,M$ acid of different ionic strengths) the resulting systems were ill conditioned. When solved by the least squares method the values of the asociation constants were determined with an error greater than 100% if the error in the experimental data was 0.1%.

It was supposed that for salicylic acid in aqueous solution the following equilibria were valid:



The H^+ atom which would, by the assumption of H. Schuhler, take part in a semiquinone-like reaction is bound in the molecule of the acid itself. Hence it is more probable that the discrepancy between the experimentaly obtained colorimetric titration curve and the calculated one is due to some of the association reactions mentioned above.

CONCLUSION

Missing some appropriate method for the determination of the association of the $2.26 \times 10^{-4}\,M$ aqueous solution of salicylic acid, the discrepancies in spectrophotometric measurements mentioned above could be explained only by the assumption that different association reactions took place. An increase of the concentration of salicylate ion between *p*H 3,5 — 4 would then be a consequence of the dissociation of the associated molecules.

GLOSSARY OF SYMBOLS

The following symbols were used in this text:

HA, A^-	for undissociated salicylic acid and salicylate ion
HAH, HAA^-, HAH	for the associated molecules
c_k	for the total concentration of salicylic acid in mol per liter
a	degree of neutralization (mols of NaOH added per mol of salicylic acid)
k_h	thermodynamic dissociation constant
k_a	association constant
ε_{HA}	molecular extinction coefficient of salicylic acid
ε_{A^-}	molecular extinction coefficient of salicylate ion
λ	wave length
E	extinction $= \log I_0/I = \varepsilon b c_k$
b	length of the light path

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IZVOD

Prilog poznavanju disocijacije i asocijacije salicilne kiseline

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Ispitivana je disocijacija i mogućnost asocijacije salicilne kiseline spektrofotometrijskim mjerenjima i potenciometrijskim titracijama kiseline koncentracije $2{,}26 \times 10^{-4}$ i $4 \times 10^{-3}\,M$. Konstatirano je odstupanje kolorimetrijske krivulje titracije dobivene računom od eksperimentalne između *p*H 3 i *p*H 4. Tu pojavu razjašnjuje pretpostavka, da se događaju različne reakcije asocijacije. Pokušalo se, da se metodom najmanjih kvadrata, s pomoću titracionih podataka, odrede konstante ravnoteže za pojedine reakcije asocijacije.

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