

# The pH Equilibria of the 3-Bromo-5-sulfosalicylate Ion in Alkaline Solution

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The pH equilibria of the 3-bromo-5-sulfosalicylate ion,  $\text{HC}^{2-}$ , in alkaline solution have been studied at 25 °C and 3 M sodium (perchlorate) medium by means of potentiometric titrations using a glass electrode. The total concentration of  $\text{HC}^{2-}$  ranged from 5 to 100 mM. An emf correction for the glass electrode has been applied in the pH range 9–11.5. The data were evaluated with a "curve-fitting" method, and the results were refined with the generalized least squares computer program LETAGROP ETITR. The systematic errors in  $E_0$  and in the analytical concentrations were adjusted together with the formation constant  $\beta_{-11}$ . The data are best explained by



$$\log \beta_{-11} = -10.467 \pm 0.001$$

There was no evidence of the presence of dimeric complexes.

In order to investigate the complexation of the 3-bromo-5-sulfosalicylate ion,  $\text{HC}^{2-}$ , with metal ions, it is necessary to examine the equilibria between  $\text{HC}^{2-}$  and hydrogen ions in aqueous solution. In a previous investigation<sup>1</sup> the author determined the acidity constant for the carboxyl group of the acid,  $\text{H}_2\text{C}^-$ , and showed that the dimers  $\text{H}_4\text{C}_2^{2-}$  and  $\text{H}_3\text{C}_2^{3-}$  coexist with  $\text{H}_2\text{C}^-$  in acidic solution. Since the phenolic hydroxyl group is dissociated in alkaline solution only, it is also necessary to investigate the pH equilibria of the  $\text{HC}^{2-}$  ion in alkaline solution, not only in order to determine the acidity constant of the phenolic group, but also to investigate the formation of dimers.

The most common symbols are listed below for reference:

$C$	total concentration of disodium 3-bromo-5-sulfosalicylate $\text{Na}_2\text{HC}$ .
$c$	concentration of free $\text{HC}^{2-}$ .
$H$	total concentration of hydrogen ion (stoichiometric hydrogen ion concentration in excess of $\text{HC}^{2-}$ ).
$h$	concentration of free $\text{H}^+$ .
$Z$	the average number of protons released per $\text{HC}^{2-}$ .
$\beta_{-pr}$	equilibrium constant for the reaction $p\text{H}^+ + r\text{HC}^{2-} \rightleftharpoons \text{H}_{(p+r)}\text{C}_r^{(2r-p)-}$ .
$U_H$	$\sum (H_{\text{calc}} - H_{\text{tot}})^2$ .
$\sigma(\beta)$	standard deviation (in $\beta$ ).
$V_0, H_0, C_0$	volume, $H$ and $C$ in the initial solution $S_0$ .
$V_t, H_t, C_t$	volume, $H$ and $C$ in the buret solution T.
$E$	emf in mV.
$\delta H, \delta H_0$	analytical errors in $H$ and $H_0$ .
$f_c$	analytical error factor for $C$ . $f_c = C_{\text{tot}}/C$ .

## EXPERIMENTAL

**Chemicals.** Sodium perchlorate and disodium 3-bromo-5-sulfosalicylate solutions were prepared and analysed as described elsewhere.<sup>1</sup>

Perchlorate acid (Merck *p.a.*) was standardized against tris(hydroxymethyl)aminomethane GR or recrystallized borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

Sodium hydroxide was prepared from 50 % NaOH by dilution and was standardized against standard perchloric acid and against recrystallized potassium hydrogen phthalate. The results obtained from the two methods agreed to within  $\pm 0.1$  %.

Borax. A.R. was recrystallized from water under 55 °C.

Table 1. Summary of the titrations in 3 M Na(ClO<sub>4</sub>).Concentrations in mM.<sup>a</sup>

Titr. No.	H <sub>0</sub>	C <sub>0</sub>	H <sub>T</sub>	H <sub>T</sub> ' (Backtitr.)	C <sub>T</sub>	C <sub>T</sub> ' (Backtitr.)
Series I						
1a	0	12.0	-25.17		12.0	
2a+3a(Backtitr.)	0	20.0	-41.46	50.51	20.0	20.0
4a	0	30.0	-63.67		30.0	
5a	0	40.0	-82.92		40.0	
6a	0	50.0	-109.6		50.0	
Series II						
1b	0.03	5.016	-18.53		5.033	
2b+3b(Backtitr.)	0.03	10.05	-27.70	56.59	9.970	10.06
4b	0.03	19.97	-65.46		20.03	
5b	0.03	29.99	-87.46		29.99	
6b	0.03	99.93	-306.2		99.81	

<sup>a</sup> In each titration  $V_T$  ml of the buret solution T, with  $H_T$  and  $C_T$ , were added to  $V_0$  ml of an initial solution  $S_0$ , with  $H_0$  and  $C_0$ .

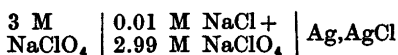
*Emf measurements and apparatus.* The experiments were carried out as two series (I and II) of potentiometric titrations at 25 °C in a nitrogen atmosphere. New stock solutions were used for each series.

In each titration, the total concentration of disodium 3-bromo-5-sulfosalicylate,  $C$ , was kept constant and the total hydrogen ion concentration,  $H$ , was varied by the addition of NaOH solution, the pH changing from 9 to 11.5. The values of  $C$  ranged from 0.005 to 0.100 M. All solutions were made 3 M in Na<sup>+</sup> by adding NaClO<sub>4</sub> to keep activity factors constant so that in the application of the law of mass action concentrations might be used instead of activities. A summary of the titrations is given in Table 1. All solutions listed in Table 1 were prepared from boiled doubly distilled water. The solutions containing NaOH were freshly prepared under N<sub>2</sub> atmosphere.

The cell used for the emf measurements can be described schematically:



The reference half cell had the composition



The titration vessel and the "Wilhelm bridge" used were kept in a paraffin oil thermostat at  $25.0 \pm 0.02$  °C. The emf of the cell in series I was measured with a Radiometer PHM 52 (accuracy  $\pm 0.1$  mV) and in series II with a digital voltmeter HP 3450A (sensitivity of 1  $\mu$ V). The emf measurements for series II were performed with the automatic titrator described by Gobom and Kovács.<sup>2</sup>

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The glass electrode was a Jena type U. Since glass electrodes do not usually respond perfectly to changes in pH in alkaline solutions containing high concentrations of Na<sup>+</sup>, a correction was necessary. The pH response of the glass electrode was standardized against a hydrogen electrode. If the glass electrode behaved as a hydrogen electrode, the difference between the emf of the hydrogen electrode and that of the glass electrode,  $\Delta E (= E_H - E_G)$ , would be constant in the relevant pH range. The method used to determine  $\Delta E$  was that described by Olin.<sup>3</sup> As is apparent from fig. 1  $\Delta E$  varied about  $\pm 0.1$  mV at pH < 9 and increased gradually for pH > 9. The correction to  $E_G$ ,  $E_{\text{corr}}$ , was then calculated as the difference in  $\Delta E$  from the value corresponding to pH = 9. A plot of the corrections,  $E_{\text{corr}}$ , (in mV to be added) as a function of  $E_G$  for the Jena type U glass electrode in alkaline solution (pH

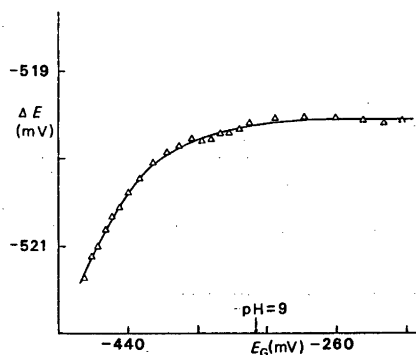


Fig. 1.  $\Delta E (= E_H - E_G)$  as a function of  $E_G$  for the Jena type U glass electrode.

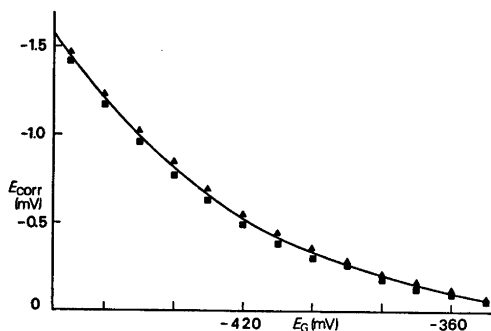


Fig. 2. The corrected emf,  $E_{\text{corr}}$ , as a function of  $E_G$  for the Jena type U glass electrode.  $\text{Na}^+ = 3 \text{ M}$ . pH from 9 to 11.5. Curves 1 (■) and 2(▲) were obtained before and after the titration series II, respectively.

9 to 11.5) containing 3 M  $\text{Na}^+$  is shown in Fig. 2. The correction curves 1 and 2 were obtained before and after titration series II, respectively. Mean values of  $E_{\text{corr}}$  from curves 1 and 2 were used to correct the measured  $E_G$  values in the titration series II (curve 3).

The voltage departures of the glass electrode in alkaline solution are time-dependent and vary with the condition of the surface of the glass electrode. However, as the pH was relatively low (under 11.5) no significant changes in  $E_{\text{corr}}$  were observed during a month.

From the corrected emf,  $h$  was calculated by means of the equation

$$E_G = E_0 + 59.156 \log h + E_j \quad (1)$$

where  $E_0$  is a constant for the electrodes used and  $E_j$  is the liquid junction potential, which can be expressed as a function of  $[\text{OH}^-]$ , i.e.  $E_j = j_{\text{alk}}[\text{OH}^-]$ . Here,  $j_{\text{alk}}$  is a constant  $\approx 8 \text{ mV/M}$  in 3 M  $\text{NaClO}_4$ ,  $[\text{OH}^-] = K_w h^{-1}$  and  $K_w = 6.03 \times 10^{-16} \text{ M}^2$ .<sup>4,5</sup>  $E_0$  was determined by measuring the emf of a buffer solution, which contained 0.01 M borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) in 3 M  $\text{NaClO}_4$  medium, after each main titration was finished. As the pH of the buffer solution was known, i.e. pH=9.00, the value of  $E_0$  could be calculated from eqn. (1).

The pH for 0.01 M  $\text{Na}_2\text{B}_4\text{O}_7$  in 3 M  $\text{NaClO}_4$  medium was calculated from the relation  $\beta = [\text{H}^+]$ , where  $\beta$  is the equilibrium constant for the reaction:  $\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{B}(\text{OH})_4^- + \text{H}^+$  i.e.

$$\beta = [\text{B}(\text{OH})_4^-] [\text{H}^+] / [\text{B}(\text{OH})_3] \quad (2)$$

According to Ingri<sup>6</sup> only the mononuclear complex  $\text{B}(\text{OH})_4^-$  is formed in 3 M  $\text{NaClO}_4$  medium at low boric acid concentrations ( $\leq 0.025 \text{ M}$ ). Thus, in the 0.01 M  $\text{Na}_2\text{B}_4\text{O}_7$

solution only the  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  species are present. From the mass and charge balances:

$$[\text{B}(\text{OH})_4^-] = 0.02 + [\text{H}^+] - [\text{OH}^-] \quad (3)$$

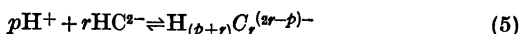
$$[\text{B}(\text{OH})_4^-] + [\text{B}(\text{OH})_3] = 0.04 \quad (4)$$

As the value of the pH in this solution is about 9, the values of  $[\text{H}^+]$  and  $[\text{OH}^-]$  in (3) are small in comparison with 0.02 and can be neglected. Hence

$$[\text{B}(\text{OH})_4^-] = [\text{B}(\text{OH})_3] = 0.02 \text{ and } \beta = [\text{H}^+]$$

As the value of  $\log \beta$  obtained by Ingri is  $\log \beta = -9.00 (\pm 0.02)$ , the pH for 0.01 M  $\text{Na}_2\text{B}_4\text{O}_7$  solution is  $9.00 \pm 0.02$ .

In the evaluation of the equilibrium constants for  $\text{Na}_2\text{HC}$  in alkaline solution,  $\text{H}^+$  and  $\text{HC}^2-$  were chosen as components. The general equilibria and formation constants are



$$\beta_{pr} = [\text{H}_{(p+r)}\text{C}_r^{(2r-p)-}] h^{-p} b^{-r} \quad (6)$$

Since  $h$ ,  $C$  and  $H$  are known, it is possible to calculate the auxiliary function,  $Z$ , which is the average number of  $\text{H}^+$  released per  $\text{HC}^{2-}$ , from the relation

$$CZ = h - H - K_w h^{-1} \quad (7)$$

## TREATMENT OF DATA AND RESULTS

The experimental data were first evaluated by the "curve-fitting" method for determining the formation constant  $\beta_{-11}$ . The results were

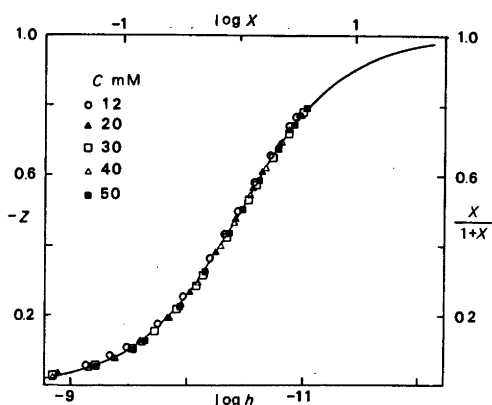


Fig. 3. Experimental data in series I plotted as  $(-Z, \log h)_c$ . The curve is a normalized curve  $(X/(1+X), \log X)$  corresponding to  $\log \beta_{-11} = -10.46$

then refined with the generalized least squares program LETAGROP ETITR.<sup>7</sup>

*Curve-fitting method.* As is shown in Fig. 3, the experimental data from series I, plotted as  $-Z=f(\log h)_C$ , fit the normalized curve  $X/(1+X)=f(\log X)$ , (where  $X=\beta_{-11}h^{-1}$ ), calculated for the single complex  $C^{3-}$  according to reaction (5) with  $p=-1$ ,  $r=1$ . This indicates that only the mononuclear complex  $C^{3-}$  is formed in alkaline solution. The equilibrium constant  $\beta_{-11}$  ( $=[C^{3-}]hc^-$ ) was then estimated as  $\log \beta_{-11}=-10.46$  from Fig. 3 according to  $\log X=\log \beta_{-11}-\log h$ .

*LETAGROP method.*  $\beta_{-pr}$  were sought as the values which gave a minimum for the error squares sum  $U=\sum(H_{\text{calc}}-H_{\text{tot}})^2$ . The program also permits adjustment of the experimental errors, such as small corrections to  $H$ ,  $C$ ,  $E_0$  etc. The data in series I and II were treated separately. Initially,  $\beta_{-11}$  was refined with no correction of the experimental quantities, the following results being obtained:

Series I.  $\log \beta_{-11}=-10.468 \pm 0.008$ ,  $\sigma(H)=0.152 \times 10^{-3}$  M,  $U_H=2.94 \times 10^{-6}$  M<sup>2</sup>

Series II.  $\log \beta_{-11}=-10.487 \pm 0.003$ ,  $\sigma(H)=0.407 \times 10^{-3}$  M,  $U_H=35.94 \times 10^{-6}$  M<sup>2</sup>

The presence of the dimeric complex  $HC_2^{5-}$  was then investigated. In this calculation both  $\beta_{-11}$  and  $\beta_{-12}$  were varied. Since a negative value was obtained for  $\beta_{-12}$ , it did not seem likely that  $HC_2^{5-}$  was present. The calculations were then performed under several conditions for the further refinement of  $\beta_{-11}$ . In each calculation, a number of systematic errors were adjusted alternately with  $\beta_{-11}$ . The resulting "best" set of values for  $U_H$ ,  $\sigma(H)$ ,  $\beta_{-11}$ ,  $E_0$ ,

$\delta H$  and  $f_C$  etc. is given in Tables 2 and 3.\*

By comparing the values of  $U_H$  and  $\sigma(H)$  obtained in different calculations (Table 2), it can be seen that the best fit (the lowest values of  $U_H$  and  $\sigma(H)$ ) is obtained in calculations 2 and 6, in which the standard deviations of  $H$ ,  $\delta H$ , are 0.0179 and 0.0449 mM, respectively. The relative errors,  $(H_{\text{calc}}-H_{\text{exp}})/H_{\text{exp}}$  or  $(Z_{\text{calc}}-Z_{\text{exp}})/Z_{\text{exp}}$ , in calculations 2 and 6 are less than 0.5% for most experimental points (about 93% of 347 points) and there are no obvious systematic errors.

The adjustment indicated in Table 3 seems to be reasonable. The value of  $f_C$  indicates that the correction to  $C$  is about 2% in series I, and 3% in series II (except for  $C=0.005$  M, where it is about 6%) and that the ratio of  $\delta H$  to  $C$  is less than 0.5% in most titrations. The corrections to  $C$  and  $H$  are feasible in view of the uncertainties in the chemical analyses.

The adjustment of  $E_0$  (below 1.2 mV for most titrations) shown in Table 3 would appear to be reasonable, considering the accuracy of the  $E_0$  determination.

The final value of  $\beta_{-11}$  is the mean value obtained from calculations 2 (or 3) and 6, i.e.  $\log \beta_{-11}=-10.467 \pm 0.001$ . This  $\beta_{-11}$  value has been used, together with the constants determined previously,<sup>1</sup>  $\log \beta_{11}=2.028$ ,  $\log \beta_{12}=2.537$  and  $\log \beta_{22}=4.739$ , to calculate the distribution of 3-bromo-5-sulfosalicylic acid present in the different species (cf. Fig. 4).

\* The output from LETAGROP calculations can be obtained on request.

Table 2. Equilibrium constant for the reaction  $HC_2^{5-} \rightleftharpoons H^+ + C^{3-}$  calculated by LETAGROP with adjustment for  $E_0$ ,  $\delta H_0$ ,  $\delta H$ , and  $f_C$ , 25°C, 3 M Na(NaClO<sub>4</sub>),  $U_H=\sum(H_{\text{calc}}-H_{\text{tot}})^2$ .

Calculation	$U \times 10^6$ (M <sup>2</sup> )	$\sigma(H) \times 10^3$ (M)	$\log \beta_{-11} \pm 3\sigma$	Systematic errors adjusted with $\beta_{-11}$
Series I (128 points)				
1	0.0765	0.0261	$-10.492 \pm 0.002$	$\delta H, f_C$
2	0.0367	0.0179	$-10.473 \pm 0.002$	$\delta H_0, f_C, E_0$
3	0.0377	0.0181	$-10.473 \pm 0.001$	$\delta H, f_C, E_0$
Series II (219 points)				
4	2.289	0.1028	$-10.505 \pm 0.004$	$\delta H, f_C$
5	1.778	0.0939	$-10.456 \pm 0.020$	$\delta H_0, f_C, E_0$
6	1.759	0.0449	$-10.464 \pm 0.001$	$\delta H, f_C, E_0$

Table 3.  $E_0$ ,  $\delta H_0$ ,  $\delta H$ , and  $f_C$  calculated by LETAGROP for the "best fit" for the calculations listed in Table 2.

Titr. No.	$E_0$ mV (from exp.)	$E_0 \pm 3\sigma$ mV	$\delta H_0 \pm 3\sigma$ mM	$\delta H \pm 3\sigma$ mM	$f_C \pm 3\sigma$
Calculation 1					
1a	198.90			$0.165 \pm 0.032$	$1.0311 \pm 0.0064$
2a	199.15			$0.137 \pm 0.025$	$1.0237 \pm 0.0031$
3a	199.15			$0.059 \pm 0.042$	$1.0331 \pm 0.0063$
4a	198.80			$0.168 \pm 0.021$	$1.0190 \pm 0.0016$
5a	199.00			$0.084 \pm 0.025$	$1.0228 \pm 0.0015$
6a	198.84			$0.011 \pm 0.042$	$1.0196 \pm 0.0020$
Calculation 2					
1a		$199.08 \pm 0.22$	$0.103 \pm 0.012$		$1.0231 \pm 0.0031$
2a		$198.73 \pm 0.07$	$0.086 \pm 0.058$		$1.0192 \pm 0.0010$
3a		$198.40 \pm 0.43$	$0.052 \pm 0.025$		$1.0272 \pm 0.0073$
4a		$197.98 \pm 0.18$	$0.131 \pm 0.025$		$1.0192 \pm 0.0024$
5a		$197.91 \pm 0.22$	$0.077 \pm 0.039$		$1.0240 \pm 0.0030$
6a		$197.47 \pm 0.26$	$0.054 \pm 0.062$		$1.0231 \pm 0.0033$
Calculation 3					
1a		$199.10 \pm 0.24$		$0.101 \pm 0.013$	$1.0182 \pm 0.0031$
2a		$198.71 \pm 0.27$		$0.083 \pm 0.025$	$1.0175 \pm 0.0037$
3a		$198.23 \pm 1.87$		$0.052 \pm 0.097$	$1.0268 \pm 0.0038$
4a		$197.91 \pm 0.21$		$0.134 \pm 0.028$	$1.0176 \pm 0.0026$
5a		$197.83 \pm 0.26$		$0.082 \pm 0.046$	$1.0238 \pm 0.0034$
6a		$197.44 \pm 0.26$		$0.053 \pm 0.062$	$1.0228 \pm 0.0031$
Calculation 4					
1b	201.56			$0.062 \pm 0.017$	$1.0617 \pm 0.0066$
2b	202.77			$0.055 \pm 0.036$	$1.0364 \pm 0.0066$
3b	202.77			$0.156 \pm 0.046$	$1.0344 \pm 0.0101$
4b	200.90			$0.159 \pm 0.083$	$1.0374 \pm 0.0076$
5b	201.13			$0.235 \pm 0.104$	$1.0252 \pm 0.0060$
6b	202.16			$0.582 \pm 0.181$	$1.0255 \pm 0.0033$
Calculation 5					
1b		$197.48 \pm 0.50$	$0.097 \pm 0.017$		$1.0772 \pm 0.0046$
2b		$201.13 \pm 0.32$	$-0.034 \pm 0.022$		$1.0358 \pm 0.0034$
3b		$201.58 \pm 0.08$	$0.082 \pm 0.005$		$1.0237 \pm 0.0010$
4b		$199.22 \pm 0.24$	$-0.014 \pm 0.036$		$1.0369 \pm 0.0023$
5b		$199.00 \pm 0.41$	$0.045 \pm 0.100$		$1.0282 \pm 0.0035$
6b		$199.00 \pm 0.37$	$-0.505 \pm 0.295$		$1.0257 \pm 0.0034$
Calculation 6					
1b		$200.82 \pm 0.78$		$-0.005 \pm 0.027$	$1.0581 \pm 0.0073$
2b		$201.54 \pm 0.36$		$-0.029 \pm 0.025$	$1.0362 \pm 0.0037$
3b		$202.05 \pm 0.21$		$0.073 \pm 0.012$	$1.0238 \pm 0.0026$
4b		$199.79 \pm 0.25$		$-0.019 \pm 0.038$	$1.0356 \pm 0.0023$
5b		$199.56 \pm 0.42$		$0.038 \pm 0.102$	$1.0265 \pm 0.0037$
6b		$199.55 \pm 0.38$		$-0.515 \pm 0.303$	$1.0270 \pm 0.0035$

## DISCUSSION

That the dimeric complex  $\text{HC}_2\text{O}_4^{2-}$  does not exist in alkaline solution is to be expected, since it is generally recognized that the inter-

molecular hydrogen bond is responsible for the association of carboxylic acids, water and phenols *etc.* In acidic solution the formation of the dimers  $\text{H}_4\text{C}_2\text{O}_4^{2-}$  and  $\text{H}_3\text{C}_2\text{O}_4^{3-}$  can be explained

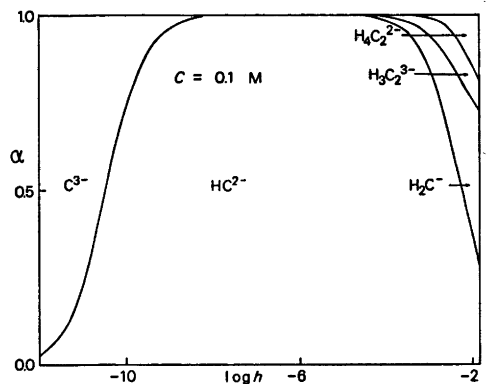


Fig. 4. The distribution of 3-bromo-5-sulfosalicylate between different species plotted versus  $\log h$ . The calculations were performed with HALTAFALL<sup>9</sup> assuming  $\log \beta_{-11} = -10.467$ ,  $\log \beta_{11} = 2.028$ ,  $\log \beta_{12} = 2.537$  and  $\log \beta_{22} = 4.739$ . At a given  $\log h$  the fraction of  $HC^{2-}$  present in each species is represented by the segment of a vertical line falling within the corresponding area.

by similar reasoning as for salicylic acid.<sup>8</sup> The dimeric hydrogen bonding between the carboxyl groups is strong enough to overcome competition from hydrogen bonding between acid and water molecules, and intramolecular hydrogen bonding between the *ortho*-hydroxyl group and the adjacent carboxyl group. The latter bond has been shown to exist in the salicylate ion.<sup>8</sup> A similar result would be expected for the 3-bromo-5-sulfosalicylate ion  $HC^{2-}$ . In alkaline solution, the carboxyl group is completely dissociated. Only the proton in the phenolic hydroxyl group would be available for hydrogen bonding. The absence of dimers in alkaline solution therefore suggests that either intramolecular hydrogen bonding or intermolecular hydrogen bonding between the phenolic hydroxyl group and water molecules is strong.

Table 4. Acidity constants.

	$\log \beta_{11}$ ( $pK_{a1}$ )	$-\log \beta_{-11}$ ( $pK_{a2}$ )	Ref.
Salicylic acid	3.173	13.12	8,10
5-Sulfosalicylic acid	2.67	11.74	11
3-Bromo-5-sulfosalicylic acid	2.028	10.467	1

No proton would then be available for dimeric hydrogen bonding.

By comparing the values of the acidity constants,  $\log \beta_{11}$  ( $pK_{a1}$ ) and  $-\log \beta_{-11}$  ( $pK_{a2}$ ), for salicylic acid, 5-sulfosalicylic acid and 3-bromo-5-sulfosalicylic acid (Table 4), it is seen that both the substituents  $-\text{Br}$  and  $-\text{SO}_3^-$  show an acid strengthening effect on both carboxyl and phenolic hydroxyl groups in the substituted acids. The effect is greater on the phenolic hydroxyl group. This strengthening effect can be explained in terms of the inductive and conjugative (or resonance) effects of the substituents, and by their influence on the intramolecular hydrogen bonding between the carboxyl and phenolic hydroxyl groups.

The  $-\text{Br}$  group has an electron withdrawing (or attracting) inductive effect (the  $-I$ -effect) and an electron releasing resonance effect, (the  $+M$ -effect). The  $-\text{SO}_3^-$  group has the  $-I$  effect and an electron withdrawing resonance effect,  $-M$ .

The acid strengthening effect of  $-\text{SO}_3^-$  on the phenolic hydroxyl group in the substituted salicylic acid can be attributed to its electron withdrawing resonance effect and a small inductive effect; the former is a result of an effective conjugation between  $-\text{SO}_3^-$ , a benzene ring and a hydroxyl group (see Fig. 5). Both the resonance and the inductive effects weaken the bonding between O and H of the hydroxyl groups, and consequently

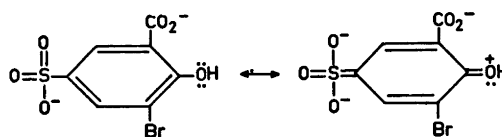


Fig. 5. The conjugation between  $-\text{SO}_3^-$ , a benzene ring and a hydroxyl group.

increase the acid strength.

The  $-Br$  group in the *ortho*-position to the hydroxyl group shows an apparent acid strengthening effect on the hydroxyl group in the substituted salicylic acid. This effect can be interpreted as due to a greater electron-withdrawing inductive effect. There is no electron-releasing resonance effect,  $+M$ , since direct conjugation is not possible.

Both  $-SO_3^-$  and  $-Br$  groups also show an acid strengthening effect on the carboxyl group, though this effect is a little weaker than that on the phenolic hydroxyl group. The protolysis of the carboxyl group in salicylic acid is dependent on intramolecular hydrogen bonding between the *ortho*-hydroxyl group and the adjacent carboxyl group, since the formation of the intramolecular hydrogen bond makes the anion more stable than the undissociated acid. In the substituted salicylic acid, the hydrogen bond is strengthened by the stabilization of the phenolic hydroxyl ion, due to the  $-M$  conjugative effect of the  $-SO_3^-$  group and the  $-I$  inductive effect of the  $-Br$  group on the phenolic hydroxyl group, thereby enhancing the acid strength of the carboxyl group in the substituted salicylic acid. In addition to this indirect acid strengthening effect, a weak electron withdrawing inductive effect of both  $-SO_3^-$  and  $-Br$  groups situated in the *meta*-position to the carboxyl group would be expected.

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