

3. BHATTACHARYA, P. K. & THAKER, B. I., *J. Indian chem. Soc.*, **52** (1975), 454.
4. BHATTACHARYA, P. K. & MOHANKUMAR, V. B., *Indian J. Chem.*, **13** (1975), 928.
5. BHATTACHARYA, P. K. & KOHLI, R. K., *Bull. chem. Soc. Japan.*, **49** (1976), 2872.
6. BHATTACHARYA, P. K., THAKER, B. T., MOHANKUMAR, V. B. & KOHLI, R. K., *Bull. chem. Soc. Japan* (accepted).

Studies in Tautomeric Equilibrium Schemes: 3-Amino-5-sulpho- & 5-Amino-3-sulpho- salicylic Acids

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The pK values of dissociation of the various groups in 3-amino-5-sulpho- and 5-amino-3-sulphosalicylic acids have been determined at 30° and $\mu = 0.1M$ ($NaClO_4$) in aqueous medium by Calvin-Bjerrum potentiometric titration technique. The pK_1 , pK_2 and pK_3 were ascribed to the dissociation of the $-COOH$, $-NH_3^+$ and $-OH$ groups respectively. A tautomeric equilibrium scheme is drawn for the dissociation of the various species and the equilibrium constants for these steps have been calculated with the help of the Hammett's relationship. The dissociation of the $-COOH$ group prior to the NH_3^+ is confirmed. Attempt has been made to understand the possible hydrogen bonding in the various species formed.

AMINOSULPHOSALICYLIC acids have four dissociable groups. It is very well known¹ that the $-SO_3H$ group dissociates at $pH < 1.0$. Above this pH , aminosulphosalicylic acid is, therefore, expected to exhibit a zwitterion type structure. Under these circumstances it would be interesting to examine the priority of the dissociating groups. In amino acids, the dissociation of the $-COOH$ group prior to that of NH_3^+ has been confirmed by Laidler and Bunting². We have carried out such a study to examine the equilibrium constants of various equilibria, including the tautomeric one, through which the system passes at various pH values. This study is an extension of our earlier work on the pK values of substituted salicylic acids in aqueous medium³.

The ligands 3-amino-5-sulphosalicylic acid (3-A-5-SSA) and 5-amino-3-sulphosalicylic acid (5-A-3-SSA) were of AR grade (Schuchardt Munchen).

The details regarding the instrumentation and the procedure of the Calvin-Bjerrum potentiometric titrations are given in an earlier communication⁴.

The mathematical expressions adopted to calculate pK values are given earlier⁴. The accuracy of the pK values was 0.03 to 0.05.

The pK of the $-SO_3H$ group being nearly 1.0, an increase in $[H^+]$ on the addition of the ligand to free perchloric acid ($\sim 10^{-3}M$) was expected. Actually the initial pH for the acid and acid + ligand solutions, without any addition of alkali, were iden-

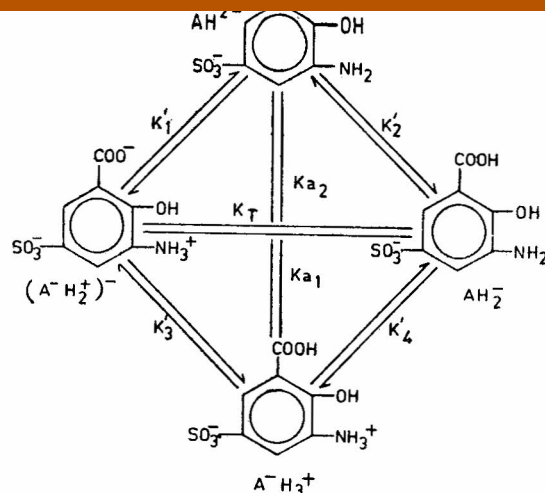


Fig. 1 — The tautomeric equilibrium scheme for 3-A-5-SSA

tical. This means that H^+ ions liberated from the $-SO_3H$ group have combined with the basic $-NH_2$ group to form a zwitterion.

The pK values 2.58, 4.38 and 15.75 of 3-A-5-SSA and 2.26, 4.23 and 16.17 of 5-A-3-SSA are due to the dissociations of the $-COOH$, $-NH_3^+$ and $-OH$ groups. The values of 15.75 and 16.17 are certainly due to $-OH$ group. The remaining two values, therefore, need to be fixed. Whether the pK_1 is due to the $-COOH$ or $-NH_3^+$ was initially decided by comparing the experimental values with the theoretically expected ones. The pK_1 expected for 3-A-5-SSA on the basis of the Hammett's relation is 2.45 (pK_{COOH} for 5-SSA is 2.49 and σ_{m-NH_2} is -0.04)⁵. The observed value 2.58 being in good agreement with the expected one, the dissociation of $-COOH$ prior to $-NH_2$ group was anticipated. This speculation was further confirmed by studying the tautomeric equilibrium of the various possible species. A total of seven equilibrium constants can be defined in this system, as shown in Fig. 1. The constants are related by the mathematical expression:

$$K_T = \frac{K'_1}{K'_2} = \frac{K'_4}{K'_3}$$

and

$$K_{a1} \times K_{a2} = K'_2 \cdot K'_4 = K'_1 \cdot K'_3$$

The values of K'_1 , K'_2 , K'_3 and K'_4 can be predicted from the knowledge of Hammett's substituent constants σ and the reaction constants ρ . Literature survey revealed that the σ values for the various substituting groups of benzoic acid are known while the reliable values of σ for aniline dissociation are not available. The constants K'_2 and K'_3 were, therefore, calculated mathematically and were further utilized to get K'_1 and K'_4 by the expressions given above.

The calculated pK'_3 is 1.8 ($\sigma_{o-HO} = 1.22$, $\sigma_{m-NH_2} = 1.13$, $\sigma_{m-SO_3} = 0.05$ and ρ for benzoic acid is 1.0)⁶. The magnitude of pK'_2 was 3.0. The values of K_T thus obtained are presented in Table 1.

TABLE 1 — pK' AND $\log K_T$ VALUES FOR AMINOSULPHONIC ACIDS

Acid	pK'_1	pK'_2	pK'_3	pK'_4	$pK_{a_1} + pK_{a_2}$	$\log K_T$
3-A-5-SSA	5.16	3.00	1.80	3.96	6.96	2.16
5-A-3-SSA	4.49	3.00	1.80	3.29	6.49	2.49

TABLE 2 — VALUE OF THE RATIO $[A^-H_2^+]/[A^-H_3^+]$ AT VARIOUS pH VALUES

pH	2.0	2.5	3.0	3.5	4.0
$\frac{[A^-H_2^+]}{[A^-H_3^+]}$	1.16	5.00	15.90	50.12	158.50

The following conclusions were drawn from the observed values:

- (i) The values of K_T are almost identical for both the acids.
- (ii) For both the acids, $pK'_3 < pK'$. The dissociation of the $-\text{COOH}$ group prior to that of $-\text{NH}_3^+$ is, therefore, confirmed.

This is in agreement with the conclusions drawn by Laidler².

- (iii) The magnitude of the ratio $\frac{[A^-H_2^+]}{[A^-H_3^+]}$ at various pH values is given in Table 2.

It can be inferred from the values that the concentration of $[A^-H_2^+]$ increases with pH . As the concentration of $[A^-H_2^+]$ increases, the concentration of the tautomer AH_2^+ will also increase. Once a sufficient active mass of $A^-H_2^+$ species is formed, the further dissociation of this species will commence. K_T being smaller than K'_1 , the possibility of $A^-H_2^+$ dissociating to give $A^-H_3^+$ would be greater than the formation of AH_2^+ by equilibrium K'_1 .

Hydrogen bonding in aminosulphonic acids: (i) 3-A-5-SSA — In the species $A^-H_3^+$, the hydrogen bonding would be between the phenolic $-\text{OH}$ and the carboxylic group. At this point the hydrogen bonding between $-\text{OH}$ and the nitrogen of the $-\text{NH}_3^+$ group is not possible as the nitrogen atom has no lone pair of electrons available. In the species $A^-H_2^+$ formed by the dissociation of $-\text{COOH}$, the hydrogen bonding would be still powerful as now it is between the $-\text{COO}^-$ and the $-\text{OH}$ groups.

For the species AH_2^+ , the hydrogen bonding would be preferably between the $-\text{OH}$ and $-\text{NH}_2$ groups and not between $-\text{COOH}$ and $-\text{OH}$. The $-\text{COOH}$ group, therefore, remains free to dissociate.

(ii) 5-A-3-SSA — For the species $A^-H_3^+$, the possibility of hydrogen bonding between $-\text{OH}$ and $-\text{SO}_3^-$ is greater than between the $-\text{COOH}$ and the $-\text{OH}$ groups. This is because sulphonyl group is negatively charged. The hydrogen bonding thus formed would be present in all other species shown in the tautomeric scheme (Fig. 1).

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References

1. PATEL, S. K., SONI, K. P. & BHAT, J. M., *Indian J. Chem.*, **10** (1972), 445.
2. LAIDLER, K. J. & BUNTING, P. S., *The chemical kinetics of enzyme action* (Clarendon Press, Oxford), 1972, 49.

3. JAHAGIRDAR, D. V. & KHANOLKAR, D. D., *Indian J. Chem.*, **13** (1975), 168.
4. JAHAGIRDAR, D. V. & KHANOLKAR, D. D., *J. inorg. nucl. Chem.*, **35** (1973), 921.
5. BERLIN, G. B. & PERRIN, D. D., *Quart. Rev.*, **75** (1966), 1.

Spectrophotometric Study of the Complexes of Fe(III) with Salicylhydroxamic Acid & Its Substituted Derivatives

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Spectrophotometric investigations on complexation reactions of Fe^{3+} with salicylhydroxamic acid (SHA) and 5-chloro, 5-bromo, 5-nitro, 5-methyl, 4-chloro, 4-bromo and 4-iodo-salicylhydroxamic acids in 50% v/v alcohol-water mixtures by Varella's method of isosbestic points and by Job's method of continuous variations as modified by Vosburgh and Gould have led to some interesting observations. Fe^{3+} with these ligands forms a 1:1 complex at $[\text{H}^+] \sim 1M$ and a 1:2 complex in the pH range 1 to 2. Above pH 2.5, instead of an expected 1:3 complex, another 1:1 complex is formed. This is explained by giving an appropriate complexation mechanism. The conditional and thermodynamic metal-ligand stability constants for the 1:1 complex formed at higher pH are given.

SALICYLHYDROXAMIC acid (SHA) and its substituted derivatives are known complexing and analytical reagents¹⁻¹³. Ghosh and Bhaduri have studied the iron(III)-SHA system, in solution, by potentiometric² as well as spectrophotometric³ methods. We have earlier undertaken systematic potentiometric and spectrophotometric investigations of metal chelates of SHA and its substituted derivatives¹⁴⁻¹⁷. During our spectrophotometric studies on colour reactions of iron(III) with substituted SHAs, we came across some interesting observations, which are recorded in this paper.

The details regarding the procedure adopted and ligands employed are given in an earlier paper¹⁶. A stock solution of ferric nitrate (BDH, AR) was prepared and standardized spectrophotometrically. Doubly distilled ethanol was used in the preparation of test solutions. The spectrophotometric measurements were taken on a Unicam SP-500 spectrophotometer. The B readings (pH -meter readings in the mixed solvent, i.e. 50% v/v ethanol-water mixture) were converted into thermodynamic values by applying the corrections given by Aditya and coworker¹⁸ and the thermodynamic values are mentioned throughout the text.

Spectrophotometric measurements — Varella's method of isosbestic points¹⁹ was used to study the mechanism of the complex formation between Fe^{3+} and various substituted SHAs. Absorption curves for solutions containing Fe^{3+} ($2.0 \times 10^{-4}M$) and the ligand ($4.0 \times 10^{-3}M$) identical in all respects except for their pH were obtained. The absorption curves (Fig. 1) can be divided into two groups, one