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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 $p$H VALUES

| $p$H | 2·0 | 2·5 | 3·0 | 3·5 | 4·0 |
|------|------|------|------|------|------|
| $\dfrac{[A^-H_2^+]}{[A^-H_3^+]}$ | 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 —COOH group prior to that of —NH$_3^+$ is, therefore, confirmed.

This is in agreement with the conclusions drawn by Laidler[2].

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

It can be inferred from the values that the concentration of $[A^-H_2^+]$ increases with $p$H. 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 $A^-H_2^+$ 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 —OH and the carboxylic group. At this point the hydrogen bonding between —OH and the nitrogen of the -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 —COOH, the hydrogen bonding would be still powerful as now it is between the —COO$^-$ and the —OH groups.

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

(ii) 5-A-3-SSA — For the species $A^-H_3^+$, the possibility of hydrogen bonding between —OH and —SO$_3^-$ is greater than between the —COOH and the —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).

Our sincere thanks are due to Dr D. D. Khanolkar for his keen interest and constant encouragement.

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## 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 Vareille'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 $[H^+] \sim 1M$ and a 1 : 2 complex in the $p$H range 1 to 2. Above $p$H 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 $p$H are given.**

SALICYLHYDROXAMIC acid (SHA) and its substituted derivatives are known complexing and analytical reagents[1-13]. Ghosh and Bhaduri have studied the iron(III)-SHA system, in solution, by potentiometric[2] as well as spectrophotometric[3] methods. We have earlier undertaken systematic potentiometric and spectrophotometric investigations of metal chelates of SHA and its substituted derivatives[14-17]. 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 paper[16]. 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 ($p$H-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 coworker[18] and the thermodynamic values are mentioned throughout the text.

*Spectrophotometric measurements* — Vareille's method of isosbestic points[19] 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 $p$H were obtained. The absorption curves (Fig. 1) can be divided into two groups, one
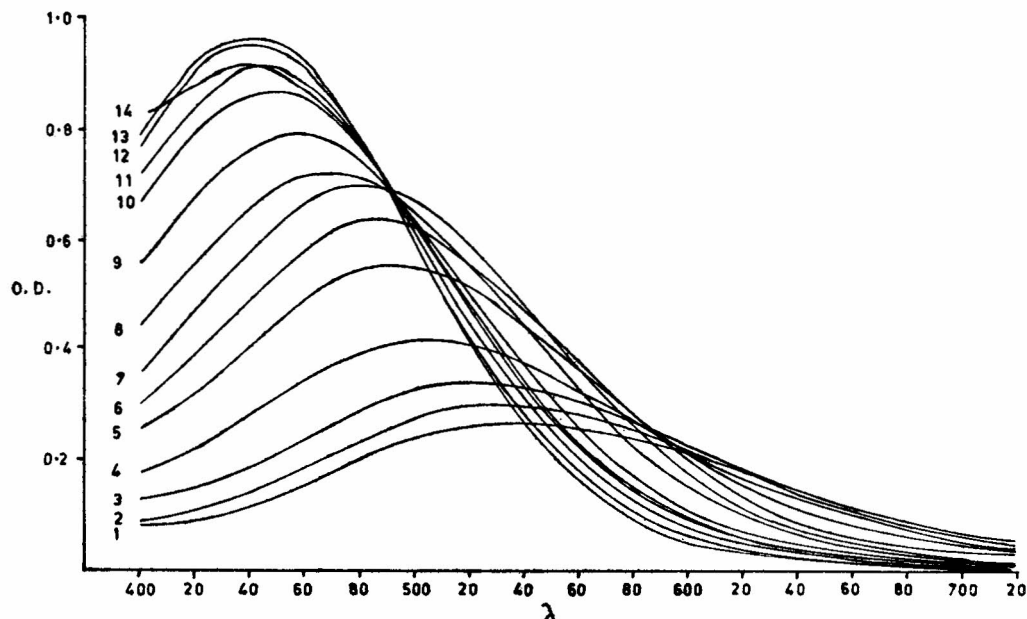
Fig. 1 — Plots of OD vs λ for $Fe^{3+}$-SHA system at various acidities and $p$H values [(1) $2M$, (2) $1M$, (3) $p$H 0·70, (4) 1·30, (5) 1·85, (6) 2·25, (7) 2·70, (8) 3·28, (9) 3·78, (10) 4·15, (11) 4·47, (12) 5·25, (13) 6·50 and (14) 7·45]

intersecting at 595 nm (isosbestic point-I) and the other intersecting at 490 nm (isosbestic point-II). This indicated the presence of three different complex species present in the $p$H range studied. A similar pattern of absorption curves as that of $Fe^{3+}$-SHA system was obtained for the metal chelates of $Fe^{3+}$ with the remaining ligands except 5-$NO_2$SHA where only one isosbestic point (at 590 nm) was obtained.

To understand the nature of complexation at various $p$H values, plots similar to those of McBryde[20] were drawn. A representative plot for $Fe^{3+}$-SHA system is given in Fig. 2. It was concluded from these plots that: (i) only 1:1 complex is formed below $p$H 1·0, (ii) in the $p$H range 1·0 to 2·5, a mixture of 1:1 and 1:2 complexes is present, and (iii) above $p$H 2·5, 1:3 complex is present. Confirmation was provided by determining the compositions of these complexes by Job's method of continuous variations as modified by Vosburgh and Gould[21]. Job's method was carried out in the concentration range $10^{-4}$ to $10^{-5}M$ for $Fe^{3+}$ chelates where the Beer's law was applicable. The compositions of the complexes were determined at a number of $p$H values ranging from 0·3 to 3·5. The values of $\bar{D}$ (where $\bar{D}$ = OD of the complex —OD of the ligand —OD of the metal ion) were plotted against % composition of the metal ion. The M:L ratio at which the maximum value of $\bar{D}$ was observed was obtained at various values of $p$H. The consolidated data for all the systems are given in Table 1.

It has been observed that for all the systems 1:1 complex is formed at $[H^+]{\sim}1M$. The formation of the 1:2 complex starts around $p$H 1·0 and continues upto $p$H 2·5. Later on instead of an expected decrease, an increase in the M:L ratio is observed. Thus at $p$H 2·5, the complex formed is 1:1 and not 1:3 as is expected from Fig. 2.
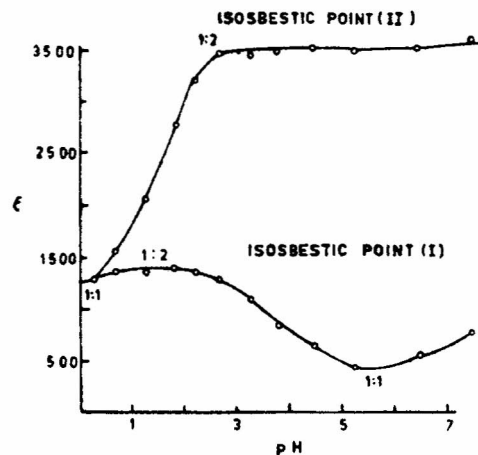


Fig. 2 — Plots of $\epsilon$ vs $p$H for $Fe^{3+}$-SHA system at the isosbestic point-I (λ = 595 nm) and isosbestic point-II (λ = 490 nm)

The formation of a 1:1 complex instead of a 1:3 complex is interesting and can be explained if the interactions between the metal ion and the ligand molecule are probed in.

*Complexation mechanism* — In highly acidic solutions $\{[H^+]{\sim}1M\}$, the molecule of SHA ($H_2L$) can take up a proton to convert the —NH to $NH_2^+$ group. The ligand species present in solution can, therefore, be designated as ($H_3L^+$). The formation of a 1:1 chelate takes place by the interaction:

$$Fe^{3+}+H_2L^+ \rightleftharpoons FeH_2L^{3+}+H^+$$
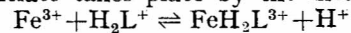
The formation of the 1:2 complex may be shown by the reaction:

$$FeH_2L^{3+}+H_3L^+ \rightleftharpoons Fe(H_2L)_2^{3+}+H^+$$
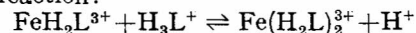
The 1:2 complex thus formed would be unstable because (i) it is formed from two positively charged species, and (ii) there is no reduction on the charge of the ferric ion even though it is complexed.

TABLE 1 — FRACTION OF METAL ION AT THE PEAK IN JOB'S CURVES FOR $Fe^{3+}$ CHELATES OF SUBSTITUTED SHAs AT VARIOUS $p$H VALUES

| System | [H+] | | $p$H | | | | |
|---|---|---|---|---|---|---|---|
| | 2$M$ | 1$M$ | 1·0 | 2·0 | 2·5 | 3·0 | 3·5 |
| $Fe^{3+}$-SHA | 0·49 | 0·50 | 0·49 | 0·37 | 0·33 | 0·38 | 0·49 |
| $Fe^{3+}$-5-CH$_3$SHA | — | 0·50 | 0·45 | 0·42 | 0·34 | 0·48 | 0·50 |
| $Fe^{3+}$-5-ClSHA | 0·50 | 0·50 | — | 0·43 | 0·46 | — | 0·50 |
| $Fe^{3+}$-5-BrSHA | 0·50 | 0·49 | — | 0·40 | 0·50 | — | 0·50 |
| $Fe^{3+}$-5-NO$_2$SHA | — | 0·50 | 0·48 | — | 0·49 | — | 0·50 |
| $Fe^{3+}$-4-ClSHA | 0·49 | 0·50 | 0·49 | 0·44 | 0·45 | 0·49 | — |
| $Fe^{3+}$-4-BrSHA | — | 0·49 | 0·49 | 0·44 | 0·45 | 0·49 | 0·50 |
| $Fe^{3+}$-4-ISHA | — | 0·48 | — | 0·42 | 0·45 | — | 0·50 |

Above $p$H 2·0, the ligand molecule is present mainly as $H_2L$ ($pK_{NH_3^+} = 1·33$)[2]. The interaction between $Fe^{3+}$ and $H_2L$ can be shown as:

$$Fe^{3+} + H_2L \rightleftharpoons FeLH^{2+} + H^+$$
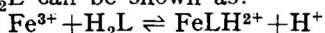
The formation of the 1:1 complex, $FeH_2L^{3+}$ in the highly acidic medium can be imagined in two ways: (i) a four-membered ring in which Fe is attached to the nitrogen of the —N.OH group and oxygen of the C=O group and (ii) a five-membered ring system in which Fe is attached to oxygen of the —N.OH group and oxygen of the C=O group. The formation of the chelate ring as envisaged in process (ii) will result in a stable complex because of its suitable ring size and covalent nature of the M—O bonds. In process (i), however, the chelation will be weak. The chelation pattern of the 1:2 complex would be similar to that of the 1:1 complex. Thus four-membered ring systems are formed on both the sides of the $Fe^{3+}$ ion. The formation of the 1:2 chelate is taking place in a small range cf $p$H, i.e. 1 to 2. The complete dissociation of the $NH_2^+$ group to form a neutral ligand would occur around $p$H 2·0. The 1:2 chelate being unstable would perhaps dissociate at $p$H 2·0 to give back free ligand molecule. Thus the formation of 1:1 chelate above $p$H 2·0 is due to the displacement of H$^+$ ions from either the phenolic —OH or the —NH group giving rise to a six-membered or a five-membered ring system respectively.

In the case of 5-NO$_2$SHA, the isosbestic point around 490 nm is not observed. The absence of this point shows the absence of 1:2 complex. This is expected because the nitro group being $\sigma$ and $\pi$ electron acceptor, would make $NH_2^+$ group significantly acidic. The isosbestic point should, therefore, be ascribed to the equilibrium between the two 1:1 complexes. This assumption was supplemented by the observations that peaks in Job's curves were obtained around 0·5 for this system (Table 1).

*Metal-ligand stability constants* — The conditional metal-ligand stability constants of the 1:1 complex formed at higher $p$H values were obtained using Job's method. The thermodynamic log $K$ values were obtained by the procedure given by McBryde[20] and are given in Table 2. The thermodynamic stability constants of the first two complex species were not determined as the $pK_{NH_3^+}$ could not be calculated with accuracy even with the potentiometric titrations.

Authors wish to express their deep sense of gratitude to Dr D. D. Khanolkar, Senior Professor

TABLE 2 — PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS

[Temp., 27°; $\mu = 0·00$; medium: 50% v/v alcohol-water]

| Ligand | $pK_1$ | $pK_2$ | $\beta_{12}$ | Log $K$ | |
|---|---|---|---|---|---|
| | | | | Conditional | Thermodynamic |
| SHA | 7·88 | 10·59 | 18·47 | 3·49 | 13·77 |
| 5-CH$_3$SHA | 7·96 | 10·61 | 18·57 | 3·93 | — |
| 5-ClSHA | 7·03 | 10·15 | 17·18 | 3·85 | — |
| 5-BrSHA | 7·18 | 10·24 | 17·14 | 3·85 | — |
| 5-NO$_2$SHA | 4·69 | 9·57 | 14·26 | 4·54 | — |
| 4-ClSHA | 7·10 | 10·33 | 17·43 | 3·87 | 13·65 |
| 4-BrSHA | 6·80 | 10·21 | 17·01 | 4·12 | 13·93 |
| 4-ISHA | 6·95 | 10·25 | 17·20 | 4·32 | 13·78 |

The $pK_1$ and $pK_2$ values were determined potentiometrically by Calvin-Bjerrum titration technique.

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