# Formation Constants of Binary Complexes of Hg(II) with Substituted Salicylic Acids

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The formation constants of 1:1 and 1:2 (metal:ligand) binary complexes of mercury(II) with salicylic ($H_2SA$), 5-chlorosalicylic (5-Cl-$H_2SA$), 3,5-dibromosalicylic (3,5-diBr-$H_2SA$), 3,5-diiodosalicylic (3,5-diI-$H_2SA$), 3,5-dinitrosalicylic (3,5-diNO$_2$-$H_2SA$) and thiosalicylic (thio-$H_2SA$) acids have been determined pH-metrically in 70% (v/v) aq. ethanol using Irving-Rossotti technique. The trend in the formation constants values has been explained on the basis of basicity of the ligands.

The physicochemical properties and the antimicrobial activities of the solid ternary complexes of Hg(II) with 8-hydroxyquinoline and various salicylic acids were reported in our earlier communication[1]. In continuation of these studies we now report the formation constants of the binary complexes of Hg(II) with various salicylate ions employing Irving-Rossotti pH-titration technique[2]. Due to low solubility of these chelates in water, measurements have been carried out in 70% (v/v) aq. ethanol.

All the chemicals used were of AR grade. Mercuric nitrate, Hg(NO$_3$)$_2$ (Sarabhai Chemicals) was used as such. The ligands used were: salicylic ($H_2SA$); 5-chlorosalicylic (5-Cl-$H_2SA$); 3,5-dibromosalicylic (3,5-DiBr-$H_2SA$); 3,5-diiodosalicylic (3,5-diI-$H_2SA$); 3,5-dinitrosalicylic (3,5-diNO$_2$-$H_2SA$); and thiosalicylic (thio-$H_2SA$) acids.

Toshniwal-Moellor glass electrode (accuracy ±0.01) was used in combination with an Elico digital Mhos pH-meter model PE 133. The electrode was calibrated with buffers of pH 4.00 and 9.20 (30°C). To get correct hydrogen ion concentration in the non-aqueous medium calibration of the glass electrode was done as described by Uitert et al[3]. All the measurements were carried out under nitrogen atmosphere at 30±0.1°C and $\mu$=0.05 M (NaClO$_4$) using the experimental set-up described elsewhere[4].

The following solutions (total volume, 50 ml each) were prepared in 70% (v/v) aq. ethanol and titrated against carbonate-free NaOH (0.1580 M): (A) 0.009556 M HClO$_4$ + 0.05 M NaClO$_4$; (B) A + 0.005 M salicylic/substituted salicylic acids; (C) B

+ 0.001 M Hg(II). The significant departure of the metal complex titration curve starting from pH = 3.0 from the corresponding reagent curve, indicated complex formation.

Proton-ligand formation number $\bar{n}_A$ was determined as described elsewhere[5]. The pK values (pH in the range, 1 < $\bar{n}_A$ < 2) of salicylic acids were determined by pointwise calculation method. The average pK$_1$ values obtained (Table 1) are in agreement with the literature values. Since this method is not suitable for the determination of pK$_2$ values of salicylic acids ($\bar{n}_A$ being constant in the pH range 5-10) the pK$_2$ for salicylic acids were determined using the equation pK$_1$ + pK$_2$ = 2pH which holds good at $\bar{n}_A$ = 1.00. The same procedure was also adopted by Kabadi et al[6] to calculate pK$_2$ of salicylic acid in 75% dioxane-water medium. The pK$_2$ values thus obtained are also given in Table 1 along with the literature values.

Metal-ligand stability constants of 1:1 (log $K_{HgSA}^{Hg}$) and 1:2 (log $K_{HgSA2}^{HgSA}$) complexes were obtained from the formation curves ($\bar{n}$ versus pL) by noting the values of pL at which $\bar{n}$ = 0.5 and 1.5 respectively. The method of pointwise calculations was adopted to get the accurate values.

It can be seen from the Table 1 that the pK$_1$ and pK$_2$ values of chloro, bromo, iodo and nitro substituted salicylic acids, as expected, are lower than those of salicylic acid.

Hg(II) ion has a 5$d^{10}$-configuration and hence forms tetrahedral complexes involving 6s6p$^3$ orbitals for bonding leaving a completely non-bonding shell ($d_\gamma^4$,

Table 1—Proton-Ligand Stability Constants of Ligands and Metal-Ligand Stability Constants of 1:1 and 1:2 (Hg-Ligand) Complexes*

| Ligand | pK$_1$[†] | pK$_2$[†] | log $K_{HgSA}^{Hg}$ | log $K_{HgSA2}^{HgSA}$ |
|---|---|---|---|---|
| $H_2SA$ | 4.20 | 13.25 | 11.62 | 7.91 |
| | (3.12)[5] | (13.30)[5] | | |
| 5-Cl-$H_2SA$ | 2.70 | 12.19 | 11.52 | 6.66 |
| | (2.69)[5] | (12.22)[5] | | |
| 3,5-diBr-$H_2SA$ | 2.48 | 10.39 | 9.64 | 5.65 |
| | (2.55)[5] | (10.43)[5] | | |
| 3,5-diI-$H_2SA$ | 3.81 | 11.20 | 9.52 | 6.95 |
| | (3.80)[7] | (11.20)[7] | | |
| 3,5-diNO$_2$-$H_2SA$ | 1.56 | 7.68 | 7.24 | 4.91 |
| | (1.31)[5] | (7.00)[5] | | |
| thio-$H_2SA$ | 5.40 | 9.49 | 15.98 | 9.76 |
| | (5.44)[8] | (9.52)[9] | | |

Accuracy of the order of ±0.2 units.
†Values given in parenthesis are the literature values.

$d_\varepsilon^6$) which can cause least perturbation to preferred stereochemistry. The $Hg^{2+}$ ion, although roughly as large as $Cd^{2+}$, has considerably greater polarising power and hence can form stronger complexes, in which it functions as a class-B acceptor or soft acid.

The overall formation constants ($\log \beta = \log K_{HgSA}^{Hg}$ $+ \log K_{HgSA2}^{HgSA}$) of Hg(II) complexes, decrease in the order: thio-$H_2SA$ > $H_2SA$ > 5-Cl-$H_2SA$ > 3,5-diBr-$H_2SA$ > 3,5-diI-$H_2SA$ > 3,5-diNO$_2$-$H_2SA$.

Thus the electron withdrawing substituents in salicylic acid decrease the electron density at the site of coordination, resulting in less stable complexes with Hg(II). When $pK_1 + pK_2$ of the salicylic acids are plotted against $\log \beta$ of the complexes most of the points fall on a linear curve with unit slope, except in the case of mercury-thiosalicylato complex which has a very high $\log \beta$ value. This deviation is understandable since thiosalicylate ion with sulphur as the donor atom having vacant $d\pi$ orbital may act as a better $\pi$-acceptor than the other salicylate ions, thereby resulting in the formation of a stronger complex.

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