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*NOTE*

# Formation Constants of 3-Hydroxynaphthalene-2-Carboxylic Acid Chelates

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3-Hydroxynaphthalene-2-carboxylic acid forms 1 : 1 complex with V(V) and Mn(II). Proton-ligand formation constants and metal-ligand formation constants were determined using Irving-Rossotti pH-titration techniques.

3-Hydroxynaphthalene-2-carboxylic acid is an efficient complexing agent. Studies on the interaction of transition metal ions[1-5] and some lanthanide ions[6] with 3-hydroxynaphthalene-2-carboxylic acid have been carried out applying various physico-chemical methods. The present note deals with the potentiometric study of complexes of V(V) and Mn(II) with 3-hydroxynaphthalene-2-carboxylic acid at 30 ± 0.1°C in dioxane-water medium (50% v/v) and at ionic strength of 0.1 M $NaClO_4$ using Calvin-Bjerrum[7,8] pH titration technique as modified by Irving-Rossotti method[9].

All the chemicals used were of AR quality and their solutions were prepared in doubly distilled $CO_2$-free water. Stock solutions of metal ions were prepared from ammonium metavanadate and manganous sulphate monohydrate and were standardised using standard procedures[10]. The solution of 3-hydroxynaphthalene-2-carboxylic acid was prepared in dioxane. A digital pH/mv meter (DPH 14, accuracy ± 0.1 pH) with glass and calomel electrode assembly was employed for pH measurements. The meter was calibrated using standard buffer of pH 4.

From the titration curves, the average number of protons associated with the reagent $\bar{n}A$, average number of ligands associated with the metal $\bar{n}$, and free ligand exponent pL were calculated by employing the relationships derived by Irving and Rossotti[9]. From $\bar{n}A$-pH relationship log $K_2^H$ was evaluated at $\bar{n}A = 1.5$ (Bjerrum half-integral method). In the case of 3-hydroxynaphthalene-2-carboxylic acid, since there are few values of $\bar{n}A$ below one, the value of log $K_1^H$ has been obtained by using the following relationship:

$$\log K_1^H K_2^H = 2pH \text{ (at } \bar{n}A = 1).$$

Pointwise calculation method and graphical method were also adopted to calculate the protonation constants of ligand.

The formation curves for the complex systems were constructed by plotting

$\bar{n}$-pL relationship. These plots indicate that the value of $\bar{n}$ is one for V(V) and Mn(II). Study of the interaction of Mn(II) with various nitrosalicylic acids reveals the formation of 1 : 1 complexes in solution[11]. The present study also reveals the formation of 1 : 1 complex of Mn(II) in solution. Bjerrum half-integral method[8] graphical method and point-wise calculation method were used to calculate log $K_1$. The values so obtained are in good agreement with each other. The average log $K_1$ values are presented in Table-1. From the values in Table-1 it is inferred that the stability of Mn(II) complex is greater than that of V(V) complex. The probable structures of 1 : 1 complexes of Mn(II) and V(V) are

$$[Mn(—OOCC_{10}H_8O—)(H_2O)_4]$$

$$[VO(OH)(—OOCC_{10}H_8O—)(H_2O)_2]$$

TABLE-1
VALUES OF THE PROTONATION CONSTANTS OF THE LIGAND AND PRACTICAL STABILITY CONSTANTS OF COMPLEXES

| Method | H | | V(V) | Mn(II) |
|---|---|---|---|---|
| | log $K_1$ | log $K_2$ | log K | log K |
| Bjerrum's half integral method | 10.90 | 3.71 | 6.05 | 6.85 |
| Point-wise calculation | 11.24 | 3.71 | 6.29 | 6.90 |
| Graphical method | 11.46 | 3.70 | 6.37 | 6.82 |
| Average values | 11.20 | 3.71 | 6.24 | 6.86 |

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