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*Research Paper :*

# Ligand field parameters of some transition metal ion complexes of 1-(4-aminobenzoyl)-2-[1-(5-chloro-2-hydroxyphenyl) ethylidene] hydrazine and their anti bacterial activity

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## ABSTRACT

Potentiometric studies have been carried out on transition metal complexes of $Mn^{+2}$, $Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Zn^{+2}$ with hydrazones synthesized from 4-amino benzoic- acid hydrazide and 5-chloro-2-hydroxy acetophenone. The dissociation constants of ligand and formation constants of its metal complexes have been determined by Calvin-Bjerrum pH titration technique, as adopted by Irving and Rossotti at 27±0.1ºC and at an ionic strength of 0.1M in 60:40 (v/v) dioxane water medium. The order of the stability of complexes is $Cu^{+2} > Ni^{+2} > Co^{+2} > Mn^{+2} > Zn^{+2}$ for the ligand ACEH. All the metal complexes screened for their antibacterial activity. The result indicates that the growth of the tested organism was inhibited by most of the compounds.

**KEY WORDS :** Transition metal ion complexes, Potentiometric study

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Hydrazones are used as intermediates in synthesis [1], as functional groups in metal carbonyls [2], in organic compounds [3, 4] and in particular in hydrazone Schiff base ligands [5–8], which are among others employed in dinuclear catalysts [9]. Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelate complexes with transition metals which catalyze physiological processes [10–12]. They also act as herbicides, insecticides, nematocides, rodenticides, plant growth regulators, sterilants for houseflies, among other applications [10-13]. In analytical chemistry hydrazones find applications as multidentate ligands for transition metals in colorimetric or fluorimetric determinations [14, 15]. In continuation of our research work[16-17] on the transition metal complexes of hydrazones, we report here the results of pH metric study of the formation of metal complexes of above ligand.

## EXPERIMENTAL METHODOLOGY

4-amino benzoic acid hydrazide and 5-chloro-2-hydroxy acetophenone were synthesized by reported method [18-19]. The hydroxy hydrazones were synthesized by the equimolar mixture of ethanolic solution of hydrazide and substituted hydroxy ketone were refluxed for three hours. The mixture was poured in cold water and then filtered. The solid product thus obtained was crystallized in ethanol.

We report here the formation constant of transition metal complexes of 1-(4-aminobenzoyl)-2-[1-(5-chloro-2-hydroxyphenyl) ethylidene] [ACEH].

The pH metric titrations were carried out against 0.1M KOH solution with a Systronic digital pH meter with glass calomel electrodes to determine the pH. The meter has an accuracy of ±0.01 pH and reproducibility of ±0.02 pH in standard scale operation. The instrument was standardized against 0.05M potassium hydrogen phthalate solution (pH=4) in the beginning of each titration. The metal ion solutions were prepared from the corresponding acetate (BDH, AR) and were standardized by conventional methods [20]. Solutions of ligands were prepared in pure[ 21] dioxane. Standard carbonate free KOH (E. Merck) solution was prepared by the method of Allen and Low [22] Potassium nitrate and nitric acid were used to maintain constant ionic strength. The buffer solution was kept in a Pyrex flask and a few drops of toluene were added as a preservative. The total volume 50ml and ($\mu$ = 0.1M $KNO_3$) of each system were kept constant in the beginning of each titration. All other

chemicals used were also AR grade.

The proton ligand stability constants of Schiff bases and formation constants of their metal complexes were determined using Calvin-Bjerrum technique as modified by Irving and Rossotti [23].

The values of $\bar{n}H$ ñ and pL were calculated from the plots of pH vs volume of alkali added. Proton ligand formation curves were obtained by plotting pH vs $\bar{n}H$. Proton ligand formation constants were obtained by Bjerrum half integral values (at $\bar{n}H=0.5$) from the formation curves and were also calculated by Pointwise method. The values determined by two methods are in good agreement with each other. The metal-ligand formation curves were obtained by plotting ñ vs pL. From these curves the metal ligand formation constants ($\log K_1$ and $\log k_2$) were determined by Half Integral, Midpoint slope, Pointwise, Least square, Linear plot and Correction term methods. The values obtained by various methods are in good agreement with each other. The accuracy of the stability constant values is in the order of ±0.02.

## EXPERIMENTAL FINDINGS AND ANALYSIS

The acid-dissociation constant of the ligand was calculated from the potentiometric titration curve of nitric acid in the presence and in the absence of the ligand. The formation curve for the proton ligand system extended from 0 and 1 in the $\bar{n}H$ scale, suggest that the ligand has one dissociable proton. It is observed from the titration curve that the ligand curve start deviating from free acid curve at about pH=8.3 and the deviation increased continuously up to pH=10.4. It also indicated that hydroxyl

**Table 1 : Ligand: ACEH**

| Metal ion | Computational method | Formation constants | | | $\text{Log}(K_1/K_2)$ | $\text{Log } K_1/\text{log } K_2$ |
|---|---|---|---|---|---|---|
| | | $\text{Log } k_1$ | $\text{Log } k_2$ | Log B | - | - |
| $H^+$ | Point-wise | 8.280 | - | 8.280 | - | - |
| $Mn^{+2}$ | Half Integral | 09.98 | 08.25 | 18.23 | 1.73 | 1.209 |
| | Midpoint slope | 10.25 | 08.23 | 19.48 | 1.02 | 1.110 |
| | Pointwise | 09.68 | 08.21 | 17.89 | 1.47 | 1.179 |
| | Least square | 09.41 | 08.25 | 17.66 | 1.16 | 1.140 |
| | Linear plot | 10.73 | 09.21 | 19.94 | 1.52 | 1.165 |
| | Correction term | 08.93 | 07.25 | 16.18 | 1.68 | 1.231 |
| $Co^{+2}$ | Half Integral | 11.33 | 10.07 | 21.40 | 1.26 | 1.125 |
| | Midpoint slope | 09.73 | 08.38 | 18.11 | 1.35 | 1.161 |
| | Pointwise | 09.79 | 09.14 | 18.93 | 0.65 | 1.071 |
| | Least square | 11.30 | 10.25 | 21.55 | 1.05 | 1.102 |
| | Linear plot | 11.27 | 10.24 | 21.51 | 1.03 | 1.100 |
| | Correction term | 09.10 | 08.76 | 17.86 | 0.34 | 1.038 |
| $Ni^{+2}$ | Half Integral | 11.61 | 11.29 | 22.90 | 0.32 | 1.028 |
| | Midpoint slope | 09.01 | 08.69 | 17.70 | 0.32 | 1.036 |
| | Pointwise | 10.07 | 09.63 | 19.70 | 0.44 | 1.045 |
| | Least square | 11.58 | 10.35 | 21.93 | 1.23 | 1.118 |
| | Linear plot | 10.55 | 10.19 | 20.74 | 0.36 | 1.035 |
| | Correction term | 09.04 | 08.12 | 17.16 | 0.92 | 1.113 |
| $Cu^{+2}$ | Half Integral | 10.74 | 10.15 | 20.89 | 0.59 | 1.058 |
| | Midpoint slope | 09.92 | 08.85 | 18.77 | 1.07 | 1.120 |
| | Pointwise | 10.72 | 09.95 | 20.67 | 0.77 | 1.077 |
| | Least square | 10.89 | 09.88 | 20.77 | 1.01 | 1.102 |
| | Linear plot | 11.92 | 11.02 | 22.94 | 0.9 | 1.081 |
| | Correction term | 11.29 | 09.59 | 20.88 | 1.70 | 1.177 |
| $Zn^{+2}$ | Half Integral | 09.10 | 07.59 | 16.69 | 1.51 | 1.198 |
| | Midpoint slope | 09.80 | 08.20 | 18.00 | 1.6 | 1.195 |
| | Pointwise | 10.36 | 08.70 | 19.06 | 1.66 | 1.190 |
| | Least square | 09.96 | 08.53 | 18.49 | 1.43 | 1.167 |
| | Linear plot | 09.60 | 08.32 | 17.92 | 1.28 | 1.153 |
| | Correction term | 09.45 | 08.34 | 17.79 | 1.11 | 1.133 |

(–OH) group starts to dissociate at about pH= 10.4 to 11.9.

Irving and Rossotti expression is used to calculate proton ligand formation numbers $\bar{n}H$. The $P^K$ values were estimated from the formation curve ($\bar{n}H$ vs pH) by noting the pH at which $\bar{n}A$ =0.5. The accurate values of $P^K$=8.280 was determined by pointwise calculations. Making the use of Bjerrum-pH titration techniques as adopted by Irving and Rossotti, the stability constant of the metal complexes were determined by Half Integral, Midpoint slope, Pointwise, Least square, Linear plot and Correction term methods. The formation of metal complexes between $Mn^{+2}$, $Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Zn^{+2}$ and ligand was indicated by

– The significant departure starting from pH 3.25 to 3.39 of metal titration curves from the ligand curve and

– The change in colour from light yellow to dark yellow as pH was raised from 3.39 to 9.28.

The log K values were directly read from the formation curves ($\bar{n}H$ vs pH) using half integral method. The most accurate log K values were calculated by pointwise calculation (Table 1 and 2). The log $K_1$ and log$K_2$ values follow the order as $Cu^{+2} > Ni^{+2} > Co^{+2} > Mn^{+2} > Zn^{+2}$ for ligand ACEH. It can be seen that with the ligand studied, order of logK1 confirm the well established Irving-Williams order [24]. The values of Δlog K (log $K_1$-log$K_2$) and log $K_1$/log$K_2$ are given in Table 1. The results show that the ratio of log $K_1$/log$K_2$ is positive in all cases.

**Antibacterial activity:**

The antibacterial activity of all the synthesized compounds was tested against Escherichia coli, Bacillus subtilis and Staphylococcus aureus using nutrient agar medium (Hi-Media Laboratories, India) by the method of Tandon *et al*.(2005). The sterilized (autoclaved at 120 °C for 30 min) medium (40~50°C) was inoculated (1 ml/100 ml of medium) with the suspension (105 CFU/ml) of the microorganism (matched to McFarland barium sulphate standard) and poured into a petridish to a depth of 3~4 mm. The paper impregnated with the test compounds (50 ìg/ml in dimethyl formamide) was placed on the solidified medium. The plates were preincubated for 1 h at room temperature and incubated at 37°C for 24 h. Neomycin was used as standard for antibacterial activity. The observed zone of inhibition is presented in Table 2. Minimum inhibitory concentration (MIC) of the test compounds was determined by agar streak dilution method. A stock solution of the synthesized compound (50 ìg/ml) in dimethyl formamide was prepared and graded

**Table 2 : Antibacterial activity of the synthesized compounds**

| Compounds | Zone of inhibition in mm( MIC in µg/ml) | | |
|---|---|---|---|
| | *E. coli* | *B. subtilis* | *S. aureus* |
| ACEH | 11(34) | 11(34) | 13(30) |
| $[Mn(ACEH)_2]$ | 12(39) | 13(37) | 14(38) |
| $[Co(ACEH)_2]$ | 12(40) | 14(34) | 10(40) |
| $[Ni(ACEH)_2]$ | 12(33) | 11(37) | 12(34) |
| $[Cu(ACEH)_2]$ | 11(36) | 11(41) | 11(38) |
| $[Zn(ACEH)_2]$ | 11(32) | 11(31) | 11(30) |
| Neomycin (30 µg/disk) | 22(0.6) | 23(0.7) | 22(0.6) |

quantities of the test compounds were incorporated in specified quantity of molten sterile nutrient agar. A specified quantity of the medium (40~50°C) containing the compound was poured into a petridish to a depth of 3~4 mm and allowed to solidify. Suspension of the microorganism was prepared to contain approximately 105 CFU/ml and applied to plates with serially diluted compounds in dimethyl formamide to be tested and incubated at 37°C for 24 h. The MIC was considered to be the lowest concentration of the test substance exhibiting no visible growth of bacteria on the plate. The observed inhibition of growth in mm and MIC in ìg/ml are presented in Table 2.

**Conclusion:**

The dissociation constants of ligand and formation constants of its metal complexes have been determined by Calvin-Bjerrum pH titration technique. All the compounds moderately inhibited the growth of Gram positive and Gram negative bacteria. The antibacterial activity was evaluated by measuring the zone of inhibition in mm. In the present study, ligand was showed moderate effective against the bacteria when metal complexes Mn(II), Co(II) and Ni(II) were found to be most potent.

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