


STUDIES OF STABILITY CONSTANT OF N'-((5-CHLORO-3-METHYL-1-PHENYL-PYRAZOL-4-YL) METHYLENE) ISONICOTINOHYDRAZIDE WITH TRANSITION METAL IONS AT 303K.
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Article Received on 20/05/2017

Article Revised on 10/06/2017

Article Accepted on 01/07/2017

ABSTRACT

The interaction of transition metal ion with of N'-((5-chloro-3-methyl-1-phenyl-Pyrazol-4-yl) methylene) isonicotinohydrazide drug have been investigated by pH metric titration at 0.08 M ionic strength at room temperature in 30% Ethanol-Water mixture. The data obtained use to estimate the values of proton-ligand stability constant (P^k) and Metal -ligand stability constant ($\log K$). It is observed that transition metal ion form 1:1, 1:2 complexes with all the systems.

KEYWORD: *The interaction isonicotinohydrazide stability constant ($\log K$).*
INTRODUCTION

The studies of metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ion in the biological kingdom.

In the earlier papers extensive data base on metal complexes with substituted heterocyclic drugs was presented.

Narwade et.al.^[1] studies the Formation and Stability constant of thorium (IV) complex with some substituted pyrazolines. Mathieu W.A. Steenland et.al.^[2] studies stability constant of Cu(II) and Ni(II) complexes of trans-dioxopentaaza macrocycles in aqueous solution by different technique. Hong-Wen Gao et.al.^[3] has studied the stability constant of Cu (II) and Co (II) complexes with CNBAC in water sample spectrophotometrically. Tuba Sismanoglu^[4] have studied the stability constant of binary complexes of Nicotinamide with Mn (II) by pH metrically. He also determines change in free energy, change in enthalpy and change in entropy from stability constant at different temperature. Tekade et.al.^[5] have been studied complex formation of Cu (II) and Co (II) metal ion complex with substituted isoxazolines. O.Yamauchi et.al.^[6] studied stability constant of metal complexes amino acids with charged side chain by pH-metrically. Hayati Sari et.al.^[7] studied the stability constant of glyoxime derivative and their Nickel, Copper, Cobalt and Zinc complexes potentiometric and theoretically.

After review of literature survey the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the chelating properties of substituted heterocyclic drugs under suitable condition with lanthanide by pH metrically.

Experimental Details

The Schiff base ligands were synthesized according to literature process.^[10-12] The structures were confirmed by NMR, IR and purity of these compounds was verified by TLC and melting points.

The stock solution of Schiff base was prepared in 30 % Ethanol-Water mixture by dissolving the requisite quantity of the ligands in a minimum volume of solvent subsequently diluted to the final volume. The ligands were acidified with HClO_4 in a 30 % Ethanol-Water mixture and the overall ionic strength of solution was constant maintains by adding (0.1M) NaClO_4 . The solutions were titrated with standard NaOH (0.2N) solution.

The following three solutions were titrated separately against standard NaOH

1. Free HClO_4 (A).
2. Free HClO_4 + Ligand (A+L).
3. Free HClO_4 + Ligand +Metal ion (A+L+M).

The pH meter reading were taken after fixed interval until stable reading was obtained and data obtained from

each titration is plotted as pH Vs volume of NaOH added.

MATERIALS AND METHOD

pH measurement were carried out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at room temperature. Metal ions solution were prepared in triply distill water and concentration estimated by standard method.^[8] The solution of drug prepared in solvent. The pH metric reading in 30% ethanol – water mixture were converted to $[\text{H}^+]$ value by applying the correction proposed by Van Uitert Haas.

The overall ionic strength of solution was constant and calculated by the equation

$$\text{C}_i \text{Z}_i^2$$

The concentration of other ion in addition to Na^+ and ClO_4^- were also taken into consideration.

RESULT AND DISCUSSION

Substituted heterocyclic drugs may be ionized as acid having replaceable H^+ ion from -NH group. Therefore it is represented as HL i.e.

Table-1: Determination of proton- ligand stability constant (pK) at 0.08M ionic strength

| System | Constant pK | |
|----------|---------------|------------------------|
| | Half integral | Point wise calculation |
| Ligand-1 | 9.2 | 9.04. ± 0.05 |

METAL -LIGAND STABILITY CONSTANT (Log k)

Metal-ligand stability constant of transition metal ion chelate with drug were determined by employing Bjerrum calvin P^{H} metric titration method as adopted by



The titration data used to construct the curves between volume of NaOH and P^{H} . They are called acid-ligand titration curves.

It is observed from titration curves for all systems ligand start deviating from the free acid curves at $\text{P}^{\text{H}} 5.0$ and deviating continuously up to $\text{P}^{\text{H}} = 10$. The deviation shows that dissociation of proton in substituted drugs.

The average number of proton associated with the ligand (n_A) was determined from free acid and acid – ligand titration curves employing the equation of Irving and Rossotti.^[9] The P^k values were determined from formation curves (n_A v^s P^{H}) by noting the P^{H} at which $n_A = 0.5$. The accurate values of pk were calculated by point wise calculations which are presented in table -1. The pK values are found.

Irving and Rossotti. The formation of chelate between transition metal ion with drug was indicated by the significant separation starting from pH =5.0 for transition metal ion with ligand -1.

Table-2: Determination of metal –ligand stability constant (logK) of transition metal ion with drug at 0.08M ionic strength.

| stem | Logk ₁ | Logk ₂ | Logk ₂ - Logk ₁ | Logk ₂ / Logk ₁ |
|---------------|-------------------|-------------------|---------------------------------------|---------------------------------------|
| Fe(II)-Ligand | 5.5 | 8.0 | 2.5 | 1.45 |
| Co(II)-Ligand | 5.3 | 7.3 | 2 | 1.38 |
| Ni(II)-Ligand | 5.0 | 6.85 | 1.85 | 1.37 |
| Cu(II)-Ligand | 5.4 | 7.15 | 1.75 | 1.32 |
| Zn(II)-Ligand | 5.4 | 7.2 | 1.8 | 1.33 |

The result shows the ratio of Logk₂ / Logk₁ is positive in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule.

ACKNOWLEDGEMENTS

The Authors are thankful to Principal, Shri. V. S. Naik College, Raver for providing necessary facilities and for kindly cooperation.

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