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***Research Article***

# STUDIES OF STABILITIES OF SCHIFF BASE OF (5 - HYDROXY - 3 - METHYL - 1 - (2, 4- DINITROPHENYL) – PYRAZOL – 4 - YL) (PHENYL) METHANONE AND 4-AMINO ANTIPYRINE COMPLEXES WITH METAL IONS IN MIXED SOLVENT AT 0.1 M IONIC STRENGTH AND 303 K BY PH-METRIC METHOD

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## ABSTRACT

The formation of complexes of Schiff base of (5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl)(phenyl) methanone and 4-amino antipyrine with metal ions at constant ionic strength ($\mu = 0.1M$) in 70% 1, 4 dioxane-water mixture was investigated at 303K by pH-metric titration. The values of proton-ligand stability constant (pK) and metal-ligand stability constant (logK) obtained from the data. It is observed that the metal ions form 1:1 and 1:2 complexes with Schiff base of (5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 4-amino antipyrine.

***Keywords:*** *Stability Constant, 5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl) (phenyl)-methanone, 4-amino antipyrine, Schiff Base*

## INTRODUCTION

A large number of substituted pyrazole derivatives are prepared and tested for variety of biological activities like anti HIV (Michael and Carolyn, 2000), anti-inflammatory (Bekhit *et al.,* 2000), antimicrobial (Freddy and Fernandes, 1988), fungicidal (Itaru and Kazuhiko, 2003) etc. Pyrazolyl and pyrazolyl-derived ligands can form relevant coordination compounds with different metal ions. Copper complexes have been extensively studied, especially dinuclear and polynuclear species, as mimics of the proteins hemocyanin and tyrosinase or as compounds with interesting catalytic and magnetic properties (Sharma *et al.,* 2005). In most of these complexes, copper ions are linked by N, N'-bridging pyrazolato anions, or coordinated by one nitrogen atom of the pyrazole ring. However, recently an unusual coordination mode of this type of ligand was described, where nitrogen atoms of the pyrazole rings are not bound to copper, but involved in strong intramolecular hydrogen bonds (Jadeja *et al.,* 2004). The ionic strength is one of the important characteristic of solution. It measures the concentration of ions in that solution. It affects the proton-ligand stability constant (pK) and metal-ligand stability constant (log K). 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 Schiff base of (5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 4-amino antipyrine with metal ions under suitable condition by pH metrically.

## MATERIALS AND METHODS

### *Determination of Stability Constants*

The equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) with combine glass electrode are use to measure the pH at temperature 303 K. The solution of Schiff base was prepared in 1, 4 dioxane solvent. The Solution of metal nitrate was prepared in distill water and concentration was estimated by standard method. All metal nitrates used are Pure (99.9% Pure) and obtained from Sigma Aldrich Chem. Co., U.S.A. The pH metric reading in 70% 1, 4 dioxane -water mixture were converted to [H+] value by applying the correction proposed by Van *et al.,* (1953). The overall ionic strength of solution was constant (0.1M) maintains by adding $KNO_3$. All the solutions were titrated with standard NaOH (0.2N) solution at constant ionic strength. The titration was carried out in double wall glass jacketed titration cell connect to the constant temperature circulating bath. The temperature of reaction cell is constant by circulating water from Thermostat ($0.1^0$C). The experimental procedure involved pH metric titrations of solutions of –

1. Free $HNO_3$ (A)
2. Free $HNO_3$ + Ligand (A+L)
3. Free $HNO_3$ + Ligand +Metal ion (A+L+M)

Data obtained from each titration is plotted as pH Vs volume of NaOH added and corresponding volume at successive pH for each set is determined and calculated.

## RESULTS AND DISCUSSION

Schiff base of (5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 4-amino antipyrine may be ionized as acid having replaceable H+ ion from -OH group. Therefore it is represented as HL i.e.

$$HL \longrightarrow H^+ + L^-$$

The titration data used to Plot the graph between volume of NaOH and pH. 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 pH = 2.5 and deviating continuously up to pH = 11. The deviation shows that dissociation of proton in Schiff base. 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 (1953).

The pK values were determined from formation curves (n**A** V/s pH) by noting the pH at which n**A** = 0.5. The accurate values of pK were calculated by point wise calculations which are presented in Table 1.

**Table 1: Determination of proton-ligand stability constant (pK) of Schiff base at 0.1 M ionic strength**

| System | Constant | |
|---|---|---|
| Schiff base | Half Integral<br>7.36 | Point Wise Calculation<br>7.28 |

### *Metal-Ligand Stability Constant (Log k)*

Metal-ligand stability constant of metal chelates with Schiff base of (5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl)(phenyl) methanone and 4-amino antipyrine were determined by employing Calvin -Bjerrum pH- metric titration method as adopted by Irving and Rossotti (1953). The formation of chelate between metal ions with Schiff base of (5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl)(phenyl) methanone and 4-amino antipyrine were indicated by the significant separation starting from pH =2.5 for all complexes.

**Table 2: Determination of metal-ligand stability constant (log K) rare earth metals with Schiff base at 0.1 M ionic strength**

| System | Logk1 | Logk2 | Logk1 -Logk2 | Logk1 / Logk2 |
|---|---|---|---|---|
| Ni (II) -Ligand-1 | 5.75 | 3.08 | 2.67 | 1.866883 |
| Mg (II) -Ligand-1 | 5.71 | 2.91 | 2.8 | 1.962199 |
| Co (II) -Ligand-1 | 5.09 | 2.57 | 2.52 | 1.980545 |
| Cu (II) -Ligand-1 | 6.04 | 3.15 | 2.89 | 1.91746 |
| Zn (II) - Ligand-1 | 5.99 | 3.03 | 2.96 | 1.976898 |

The result shows the ratio of Logk**1** / Logk**2** is greater than one and positive in all cases. This indicates that there is little or no steric hindrance to the addition of secondary ligand molecule. The difference between logK**1** and logK**2** was more than 2.5 indicating the simultaneous formation of 1:1 and 1:2 complexes.

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