



POTENTIOMETRIC STUDIES OF Cu(II) COMPLEXES WITH SOME SCHIFF BASES

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ABSTRACT

The present paper represents the systematic solution study of complex formation of Cu (II) ion with Schiff bases synthesized from substituted hydroxybenzaldehyde- $L_1 = \{4-[(3, 5\text{-diiodo-2-hydroxyphenyl)methylidene]amino\}-1, 5\text{-dimethyl-2-phenyl-1, 2-dihydro-3H-pyrazolone}$; $L_2 = \{4-[(2\text{-hydroxyphenyl) methylidene]amino\}-1, 5\text{-dimethyl-2-phenyl-1, 2-dihydro-3H-pyrazol-3-one}$ and $L_3 = \{4-[(5\text{-iodo-2-hydroxy-3-nitrophenyl)methylidene]amino\}-1,5\text{-dimethyl-2-phenyl-1, 2-dihydro-3H-pyrazol-3-one}$ have been studied at $30 \pm 0.1^\circ\text{C}$ and 0.1 M ionic strength in 60% (v/v) ethanol-water medium. The stability constant of these complexes indicates the formation of 1 : 1 and 1 : 2 complexes with all the Schiff bases.

Key words: Schiff bases, Stability constant, Binary complexes.

INTRODUCTION

Complexation studies are very important from the point of view of analytical and biochemical researches. This study has received the attention of many researchers¹⁻³. The extent to which a ligand binds to a metal ion is expressed in terms of stability constants^{4,5}. Their determination by potentiometric study at $30 \pm 0.1^\circ\text{C}$ and 0.1M ionic strength in 60% (v/v) ethanol-water medium has been reported here. The general method for determining the stepwise stability constant for complexes containing simple non-chelating ligands was first described by Bjerrum.

EXPERIMENTAL

All the chemicals, substituted hydroxybenzaldehyde, 4-aminoantipyrine, 2-amino-

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pyridine, NaOH, ethanol, transition metal salts, perchloric acid, sodium perchlorate, etc. were of analytical grade. The concentration of metal ions in the solution was determined by standard procedure⁶⁻⁸.

Schiff bases were prepared by condensation reaction of substituted hydroxybenzaldehyde and 2-aminopyridine and 4-aminoantipyrine and characterized by I. R. spectra.

The stability constant of these Schiff bases were determined by Irving and Rossotti⁹ technique. The following three sets of the solution were prepared –

(a) 2 mL free HClO₄ (0.5M)

(b) Mixt. (a) + 10 mL 0.01M ligand.

(c) Mixt. (b) + 2 mL 0.01M metal ion solution and titrated against 0.2M NaOH solution and total volume of solution was made 50 mL.

RESULTS AND DISCUSSION

Proton ligand stability constant

The acid + ligand curves deviate from acid curve from pH = 8.38 indicating deprotonation of phenolic -OH group in this pH range (Fig. 1).

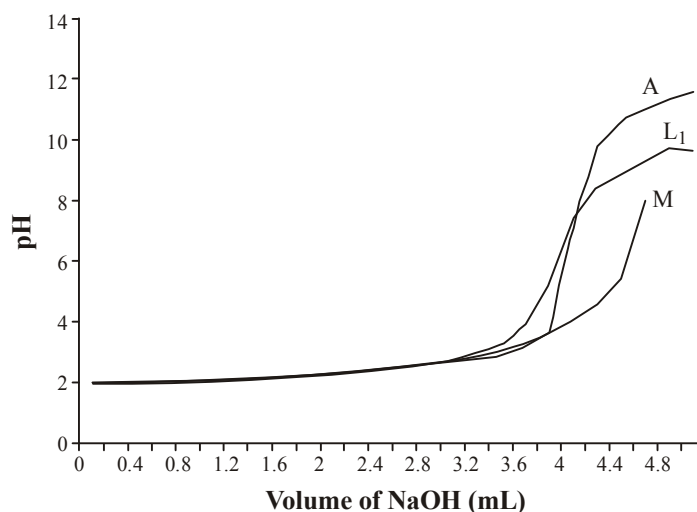


Fig. 1: Potentiometric curve for A + L₁ + M

The values of \bar{n}_A for various pH were calculated and found to be 0.2-0.8 indicating the presence of only one pK for each ligand. pK values calculated by point wise calculations and half integral methods were found to be in good agreement as shown in Table 1. The trends of pK values of Schiff bases are $L_3 > L_2 > L_1$.

Metal ligand stability constant

The displacement of metal titration curve along volume axis (Fig. 1) indicates the formation of complex species and lie in pH range, where hydrolysis is not expected. The probability of formation of polynuclear complex was ruled out as the metal concentration was very low.

Table 1: Proton ligand and metal-ligand stability constants in 60% (v/v) ethanol-water medium at $30 \pm 0.1^\circ\text{C}$

| Ligands | pK | Stability constant | Ni | Cu | Zn |
|----------------|---------|--------------------|---------|---------|---------|
| L ₁ | 9.02864 | Log K ₁ | 11.2567 | 11.4496 | 11.3924 |
| | | Log K ₂ | 10.3574 | 10.7096 | 10.7425 |
| | | Log β | 21.6141 | 22.1592 | 22.1349 |
| L ₂ | 9.59922 | Log K ₁ | 10.6426 | 10.7050 | 10.8262 |
| | | Log K ₂ | 10.0126 | 10.7031 | 10.6356 |
| | | Log β | 20.6552 | 21.4081 | 21.5618 |
| L ₃ | 9.78964 | Log K ₁ | 10.2921 | 11.3112 | 11.3041 |
| | | Log K ₂ | 10.1526 | 10.4197 | 10.3612 |
| | | Log β | 20.4447 | 21.7309 | 21.7653 |

Effect of ligand basicity

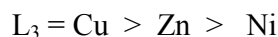
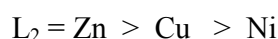
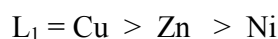
The effect of ligand basicity and metal ion on the stability has also been examined. The relation $\log K = a \cdot \text{pK} + b$ was tested, since the ligands used in the present work form a close series i.e. they have identical binding sites and hence, the plot of $\log K$ vs. pK is expected to be linear. The validity of the linear relationship has been examined to case of transition metal complexes of substituted ligands by plotting pK vs. $\log \beta$. Since the

difference between $\log K_1$ and $\log K_2$ is very small, the linear relationship indicates identical binding sites in the ligand.

One would expect that a larger difference between $\log K_1$ and $\log K_2$ values is due to possible steric hindrance to the linking of second ligand to metal ion and a smaller difference is due to the trans structure. The ratio of $\log K_1 / \log K_2$ is small in all cases. Separation factors between the first and second formation constants are well within the expected range and absence of high values implies that there is little or no steric hindrance to addition of second ligand.

Effect of metal ion

The stability constant of bivalent metal ion complexes derived from similar type of ligands generally follow the Irving-Williams order. It is clear that the ligands follow the following order of stability in their complexes –



The stability of metal complexes of ligand L_2 is similar to the Swami¹⁰ and ligand L_1 and L_3 show similar stability of metal complexes to Kalara et al.¹¹

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