



## Synthesis, characterization and potentiometric study on stability of N-[2-hydroxy-1-naphthylidene]-2-methylaniline complexes with transition elements

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### ABSTRACT

Organic ligand N-[2-hydroxy-1-naphthylidene]-2-methylaniline (**3**) was obtained by the condensation of 2-hydroxy-1-naphthylidene (**1**) with 2-methylaniline (**2**). Formation of Schiff base (**3**) confirmed by TLC, M.P., IR and C,H,N analysis. Further formation of complexes of transition elements like Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with organic ligand N-[2-hydroxy-1-naphthylidene]-2-methylaniline was studied by the potentiometric technique at 27±0.1°C in 60%(v/v) Dioxane - water medium at 0.1M (NaClO<sub>4</sub>) ionic strength. The stability constants of N-[2-hydroxy-1-naphthylidene]-2-methylaniline with transition elements were evaluated and Order of stability constant found as Cu > Co > Zn > Ni > Mn.

**Keywords:** Schiff base, Transition elements, Potentiometric technique and Stability constant.

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### INTRODUCTION

In the field of bioinorganic chemistry development of Schiff bases as organic ligands and their metal complexes have received interest due to their novel structural features, intensive spectral and magnetic properties. In organic synthesis, Schiff bases play vital role, as they readily form stable complexes with transition elements, since it has been recognized that many of these complexes may serve as models for biologically important species [1-5]. During such complexes, Schiff base acts as organic ligands. These binary complexes had various applications in various fields like catalysis [6], analytical chemistry [7] and biological studies. Due to the number of sites of bonding in organic ligands (Schiff base), complexes lead to the higher coordination polyhedra and also cause greater kinetic and thermodynamic stability. To achieve higher coordination structure, compact nature of polydentate Schiff bases plays the key role. The possibility of complexation of bi, tri and tetra dentate organic ligand (Schiff base) was shown by various workers [8]. The metal complexes with bi, tri and tetra dentate Schiff bases having O-N, O-S, and O-N-S as potential sites were reported [9]. Presence of transition elements in biological systems is a result of its ability to chemically interact with organic and inorganic substances. This has initiated widespread examination and discussion of transition elements in medicine and biology. Cu – containing superoxide is the best example of anti-inflammatory agent.

In the present work synthesis of bi-dentate Schiff base having O-N potential sites has been successfully carried out by condensation of 2-hydroxy-1-naphthylidene with 2-methylaniline. In view of the vital role of organic ligand and

transition elements in medicine, in the present investigation the synthesis, characterization and potentiometric study on stability of Mn(II), CO(II), Ni(II), Cu(II) and Zn(II) complexes of N-[2-hydroxy-1-naphthaldene]-2-methylaniline (3) have been discussed.

### EXPERIMENTAL SECTION

**Synthesis of Schiff base:** Take equimolar mixture of 2-hydroxy-1-naphthaldehyde (0.1 mol) and 2-methylaniline (0.1 mol) in ethanol, charged 2-3 drops of glacial acetic acid at room temperature. Then reflux for 3-4 hrs and progress of reaction check on TLC using Ethyl acetate : Hexane (5:5) as solvents. After completion of reaction, reaction mixture cool at room temperature and poured on ice-cold water. The precipitate product was filtered out and recrystallized by alcohol.

**Potentiometric determination of Stability constant:** Calvin-Bjerrum titration technique has been used for the determination of stability constants. The experimental procedure involved potentiometric titration of solutions of

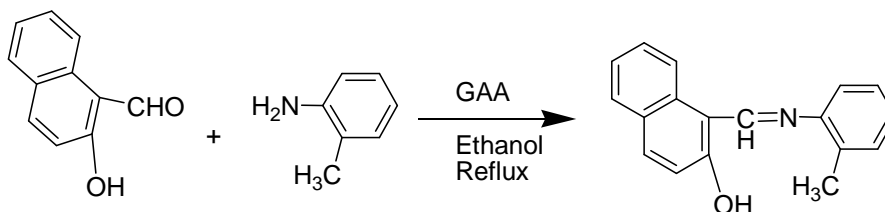
- i) Free  $\text{HClO}_4$ , (A)
- ii) Free  $\text{HClO}_4$  + Ligand (A+L) and
- iii) Free  $\text{HClO}_4$  + Ligand + Metal ion (A+L+M)

Against standard NaOH solution in 60% (v/v) Dioxane – water medium and 0.1M ( $\text{NaClO}_4$ ) ionic strength. The titrations were carried out in a 150ml corning glass beaker. Nitrogen gas slowly bubbled through the solution to remove dissolved oxygen and carbon dioxide. The gas was continuously bubbled after each addition of alkali from the burette. pH meter reading were noted only after the gas bubbling was completely stopped. At the point where pH meter reading rise suddenly the rate of gas bubbling was increased so as to get quickly the steady readings.

All the chemicals used for the synthesis of organic ligand and potentiometric determination are of A.R. grade such as methylaniline, Glacial acetic acid, ethanol, Ethyl acetate, Hexane,  $\text{HClO}_4$ ,  $\text{NaClO}_4$ , and NaOH etc.

### RESULTS AND DISCUSSION

Schiff base as organic ligand of the present investigation are prepared as per scheme-I:



**Scheme I: synthesis of Schiff base**

The TLC, MP, IR and C, H, N analysis data of synthesized compound confirm the formation of organic ligand N-[2-hydroxy-1-naphthaldene]-2-methylaniline and *Hres*. Mass spectra confirmed the molecular mass of the synthesized derivatives.

**N-[2-hydroxy-1-naphthaldene]-2-methylaniline:** White needles (EtOH) (this compound was prepared by the reaction 2-hydroxy-1-naphthaldehyde and methylaniline in the presence of GAA. It was obtained as a white solid); Mol wt.: 261; M.P; 118–120<sup>0</sup>C; IR (KBr)  $\nu_{\text{max}}$ : 3410-3315 (ph-OH), 1570-1575 (C=N), 1380 (C-N), 1285-1295 (C-O) $\text{cm}^{-1}$ . HRESIMS m/e (pos): 261.1154[M<sup>+</sup>] for M.F.  $\text{C}_{18}\text{H}_{15}\text{NO}$ , elemental analysis: C: 82.92, H: 5.80, N: 5.15 (found) and C: 82.65, H: 5.72, N: 5.36 (Calculated).

In the solution study, the organic ligand N-[2-hydroxy-1-naphthaldene]-2-methylaniline insoluble in water therefore we used 60% Dioxane: water mixture which shows appreciable solubility for the ligand. Hence solution study was possible.

The potentiometric titration curve obtained for acid, acid+ligand, acid+ligand+metal is shown in fig.1 from the graph stability constant for proton ligand and metal ligand equilibria has been evaluated.

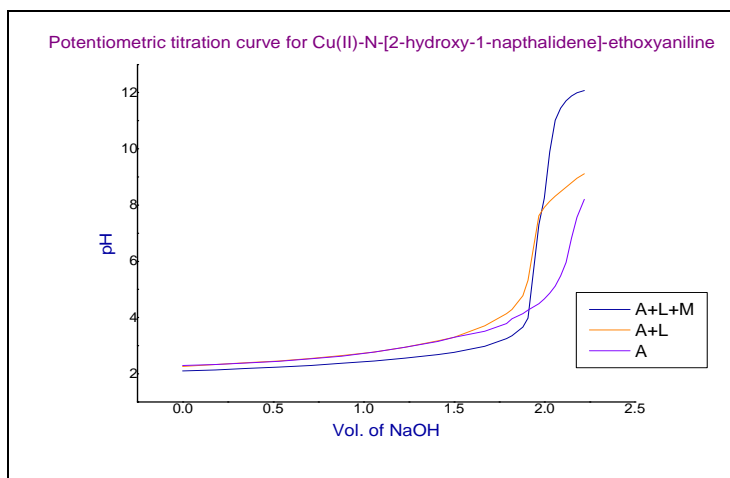


Fig.1: Potentiometric titration curve for Acid, Acid + Ligand and Acid + Ligand + Metal

Theory behind estimation of stability constant is given by Calvin-Bjerrum [10]. The equilibria involved in the formation of binary complexes may be represented as



Where M: metal and L: Ligand.

Applying the law mass action

$$K = \frac{[ML]}{[M][L]} \quad (ii)$$

Where k: equilibrium constant.

The stepwise formation of a complex  $ML_N$  can be described by the following set of equilibrium constants.

$$K_1 = \frac{[ML]}{[M][L]} \quad (iii)$$

$$K_2 = \frac{[ML]}{[M][L]} \quad (iv)$$

The general method for determining the stepwise stability constant for complexes containing simple non-chelating ligands was first described by Bjerrum[11-12]. He introduced the concept of degree of formation or ligand number  $\bar{n}$ , which he defined as the average number of ligands bound per metal ion present in different forms, i.e.

$$\bar{n} = \frac{\sum_{i=0}^N i[ML_i]}{\sum_{i=0}^N [ML_i]} \quad (v)$$

A similar function for the proton - ligand complexes is given by

$$\bar{n}_A = \frac{\sum_{i=0}^j i\beta_i^H [H]^i}{\sum_{i=0}^j \beta_i^H [H]^i}, (\beta_0^H = 1) \quad (vi)$$

Where  $\bar{n}_A$  is the mean number of protons bound per non-complex bound ligand molecule.

The protonation constants  $\bar{n}$  has been calculated and plotted against logK values. The values corresponding to  $\bar{n}$  ranging from 0.2 to 0.8 indicates logK<sub>1</sub> and values ranging from 1.2 to 1.8 indicate logK<sub>2</sub>. Pointwise as well as half-integral methods is used to find out logK<sub>1</sub> and logK<sub>2</sub> of the complex see fig.2.

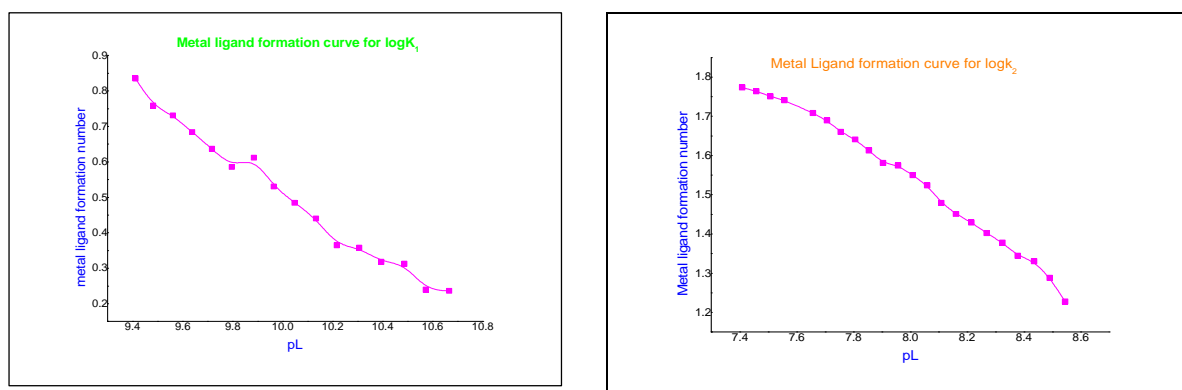


Fig.2: Metal Ligand formation curve for logk<sub>1</sub> and logk<sub>2</sub>

The  $pK_1^H$  and  $pK_2^H$  values of Schiff base which represent the deprotonation of NH group at azomethine nitrogen atom and phenolic –OH group respectively. These values shows that the substituents in the phenyl ring of the amine component of Schiff base influence the electron density at the azomethine nitrogen and also affect the deprotonation of phenolic –OH group. The stepwise stability constant logK<sub>1</sub>, logK<sub>2</sub> and overall stability constant (logβ) is given Table.2

Table.2 : stability constant					
Log	Mn(II)	CO(II)	Ni(II)	Cu(II)	Zn(II)
logK <sub>1</sub>	4.61	5.76	5.77	9.02	5.34
logK <sub>2</sub>	3.76	4.67	4.48	7.33	4.97
Logβ	8.37	10.4	10.25	16.35	10.31

N-[2-hydroxy-1-naphthylidene]-2-methylaniline follows order of stability constants of their bivalent metal complexes in present investigation as Cu > Co > Zn > Ni > Mn.

## CONCLUSION

In the present investigation N-[2-hydroxy-1-naphthylidene]-2-methylaniline (**3**) has been successfully and conveniently synthesized, which play the role of organic ligand in the complex formation with transition elements. Potentiometric study on stability of organic ligands complexes with transition elements follows order of stability constants is Cu > Co > Zn > Ni > Mn.

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