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Synthesis and characterization of N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline and potentiometric study on stability of its complexes with transition elements

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ABSTRACT

2-hydroxy-1-napthalydene ***(1)*** *on condensation with 2-ethoxyanilline* ***(2)*** *gives Schiff base N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline (****3****). Formation of Schiff base 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 Schiff base N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline was studied by the potentiometric technique at 27±0.1 ^{0}C in 60%(v/v) Dioxane - water medium at 0.1M (NaClO4) ionic strength. The stability constants of these binary complexes of N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline with transition elements were evaluated and Order of stability constant found as Cu>Zn>Ni >CO>Mn.*

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

INTRODUCTION

The development of bioinorganic chemistry field has received interest in Schiff bases and their metal complexes due to their novel structural features, intensive spectral and magnetic properties. Schiff bases play vital role in organic synthesis, 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 [1-6]. During such complexes, Schiff base acts as organic ligands. These complexes had very wide application in various fields like food industry dyes industry analytical chemistry [7] catalysis [8-9] and biological studies [10]. Schiff base ligands show number of sites of bonding that lead to the higher coordination polyhedra and also cause greater kinetic and thermodynamic stability. The compact nature polydentate Schiff bases make them more effective in attaining higher coordination structure. The possibility of complexation of bi, tri and tetra dentate Schiff base ligand was shown by various workers [11-12]. 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 [13-14].

The widespread occurrence and use 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 [15-16].

In the present study bi-dentate Schiff base having O-N potential sites has been successfully synthesized by condensation of 2-hydroxy-1-napthalydene with 2-ethoxyanilline. In view of the importance of Schiff base and transition elements in medicine, in the present investigation the synthesis, characterization stability constant of Mn(II), CO(II), Ni(II), Cu(II) and Zn(II) complexes of N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline (3) have been described.

MATERIALS AND METHODS

Experimental:
(A) Synthesis of Schiff base: Take equimolar mixture of 2-hydroxy-1-napthaldehyde (0.1 mol) and 2-ethoxyanilline (0.1 mol) in appropriate volume of ethanol,charged 2-3 drops of glacial acetic acid at room temperature. Then raised temperature of reaction mass up to reflux, reaction mass reflux for 3-4 hrs under continuous stirring 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 through G1 sintered filtration assembly and recrystallized by alcohol.

(B) Potentiometric determination of Stability constant: The Calvin-Bjerrum titration technique has been used in the present study. The experimental procedure involved potentiometric titration of solutions of

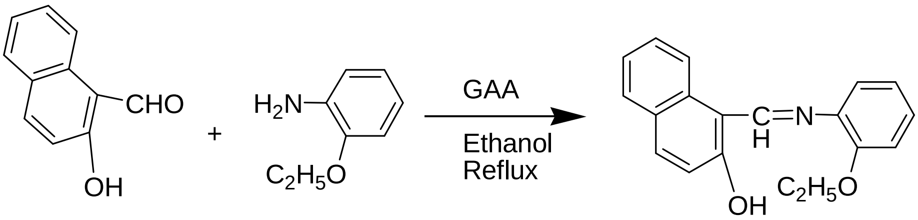
i) Free $HClO_4$, (A)
ii) Free $HClO_4$ + Ligand (A+L) and
iii) Free $HClO_4$ + Ligand + Metal ion (A+L+M)

Against standard NaOH solution in 60% (v/v) Dioxane – water medium and 0.1M ($NaClO_4$) 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 burrate. 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 Schiff base and potentiometric determination are of A.R. grade such as 2-ethoxyanilline, Glacial acetic acid, ethanol, Ethyl acetate, Hexane, $HClO_4$, $NaClO_4$, and NaOH etc.

RESULTS AND DISCUSSION

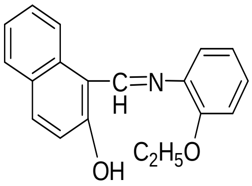
Schiff base of the present investigation are prepared as per scheme-I:



Scheme I: synthesis of Schiff base

Above synthesized Schiff base confirmed by TLC, MP, IR and C, H, N analysis, the data obtained is represented in tabular form in **Table-1.**

Table.1: Characterization data of Schiff base

Organic ligand structure	Mol. Wt	M.P.	Elemental analysis			IR spectra in cm^{-1}
			Element	Found	Calculated	
 M.F. $C_{19}H_{17}NO_2$	291.12	122^0C	C	78.43	78.25	3450-3215 (phenolic-OH), 3105, 3000, 2895 (Ar-CH), 1570-1575 (C=N), 1500-1600 (Ar C=C), 1380 (C-N), 1285-1295 (C-O).
			H	5.71	5.84	
			N	4.67	4.81	

In the solution study, the organic ligand N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline 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.

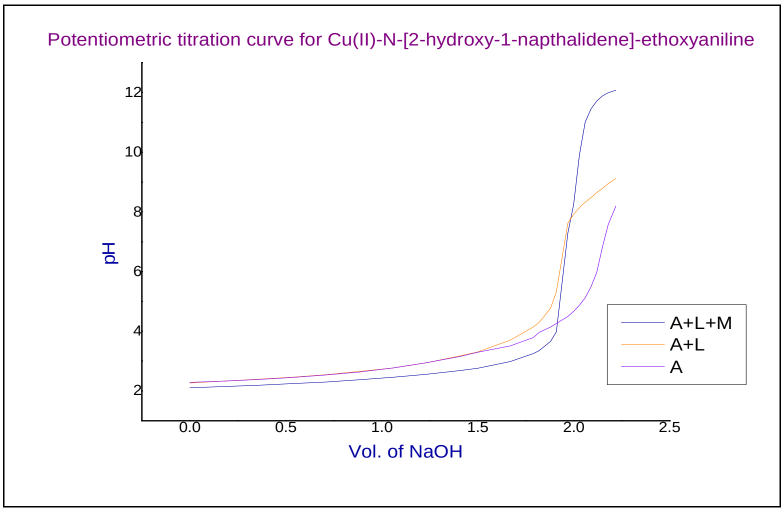


Fig.1: Potentiometric titration curve for Acid, Acid + Ligand and Acid + Ligand + Metal

Theory behind estimation of stability constant is given by Calvin-Bjerrum (18-19). The equilibria involved in the formation of binary complexes may be represented as

$$M + L \rightleftharpoons ML \qquad \text{(i)}$$

Where M: metal and L: Ligand.
Applying the law mass action

$$K = \frac{[ML]}{[M]\,[L]} \qquad \text{(ii)}$$

Where k: equilibrium constant.
The stepwise formation of a complex ML_N can be described by the following set of equilibrium constants.

$$K1 = \frac{[ML]}{[M]\,[L]} \qquad \text{(iii)}$$

$$K2 = \frac{[ML]}{[M]\,[L]} \qquad \text{(iv)}$$

The general method for determining the stepwise stability constant for complexes containing simple non-chelating ligands was first described by Bjerrum. 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.

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

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

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

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 $\log K_1$ and values ranging from 1.2 to 1.8 indicate $\log K_2$. Pointwise as well as half-integral methods is used to find out $\log K_1$ and $\log K_2$ of the complex see fig.2.

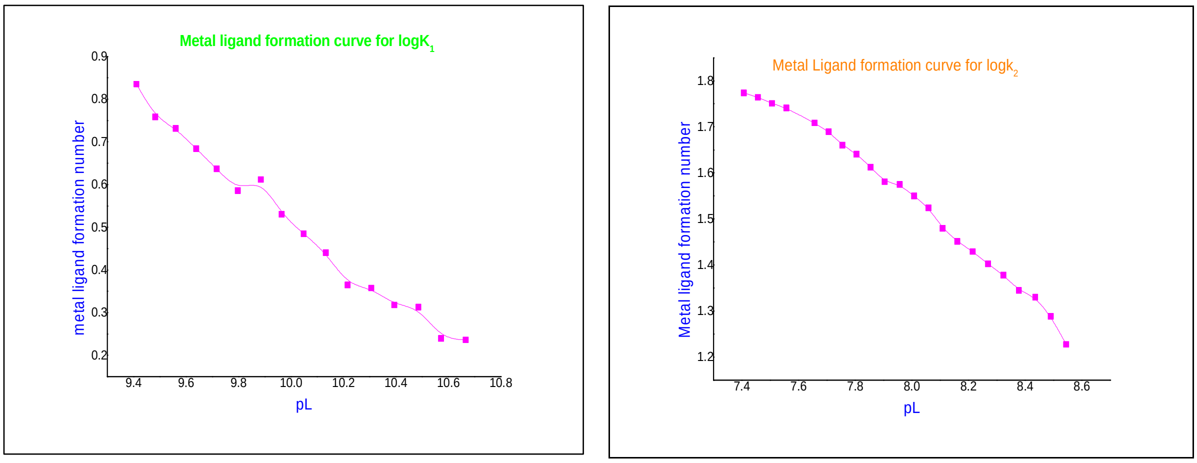


Fig.2: Metal Ligand formation curve for logk$_1$ and logk$_2$

The pK$_1^H$ (10.0431) and pK$_2^H$ (8.0575) 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$_1$, logK$_2$ 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$_1$	4.99	5.97	6.38	10.02	6.21
logK$_2$	3.82	Ppt	5.11	8.08	5.79
Logβ	8.81	5.57	11.49	18.10	12.00

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

CONCLUSION

Schiff base **(3)** has been successfully and conveniently synthesized, which play the role of organic ligand in the complex formation of N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline with transition elements. The present work describes the effect of Schiff base on the stability of the complexes. N-[2-hydroxy-1-napthalydene]-2-ethoxyanilline and its complexes with transition elements may have interesting biological activity.

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