Metal-ligand stability constants of Co (II), Ni (II) and Cu (II) metal ion complexes with N-(5-methyl-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone) ethylenediamine at 0.1 M ionic strength pH metrically

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ABSTRACT

The interaction of Co(II), Ni(II) and Cu(II) metal ions with N-(5-methyl-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone) ethylenediamine have been studied at 0.1M ionic strength in 70% Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Co(II), Ni(II) and Cu(II) metal ions form 1:1 complexes with ligand (L). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constant (logK), from estimated data (pK and log K),

Keywords: Unsymmetrical, Schiff base ligand, Bjerrum method, metal-ligand stability constant.

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INTRODUCTION

Salen type Schiff bases derived from the reaction of salicyladehyde with primary amine are straightforward to prepare, electron donors with easily-tunable electronic and steric effect thus being versatile [1, 2]. Schiff base complexes incorporating phenolic group as chelating moieties in the ligand are considered as models for executing important biological reactions [3, 4]. Schiff base ligands containing donor atoms like N, O show broad biological activity and one of special interest because of the variety of ways in which they are bonded to metal ions [5]. The interaction of metal ions with biologically active compounds may enhance their activities [6]. The studies in metal-ligand complexes in solution would be interesting which throw a light on the mode of storage and transport of metal ion in biological kingdom. The relation between stability and basicity of the ligands is indicated by the formation constant and free enery change value. Bulkier group increases the basicity of ligands as well as stability [7, 8].

Protonation constant of salicylidence (N-benzoyl) glycyl hydrazone and its coordination behavior towards some bivalent metal ions have been studied at different temperature in aqueous dioxane medium [9]. The interaction of Cu(II), Cr(III), Nd(III) and Pr(III) metal ions with substituted hydroxy chalcones at 0.1 M ionic strength in 70% dioxane-water mixture have been studies by Bjerrum method [10].

In the present paper, we describe the interaction between Co(II), Ni(II), and Cu(II) metal ions and N-(5-methyl-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone) ethylenediamine (L) at 0.1 M ionic strength in 70% dioxane-water mixture at (30 ± 0.1) by Bjerrum pH metric method as adopted by Calvin and Wilson [11-15].

EXPERIMENTAL SECTION

All chemicals used were of analytical grade. The unsymmetrical Schiff base ligand N-(5-methyl-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone) ethylenediamine (L) (Fig.1) was prepared according to the reported method [16] and its purity was checked by IR, NMR and m.p. techniques before used.

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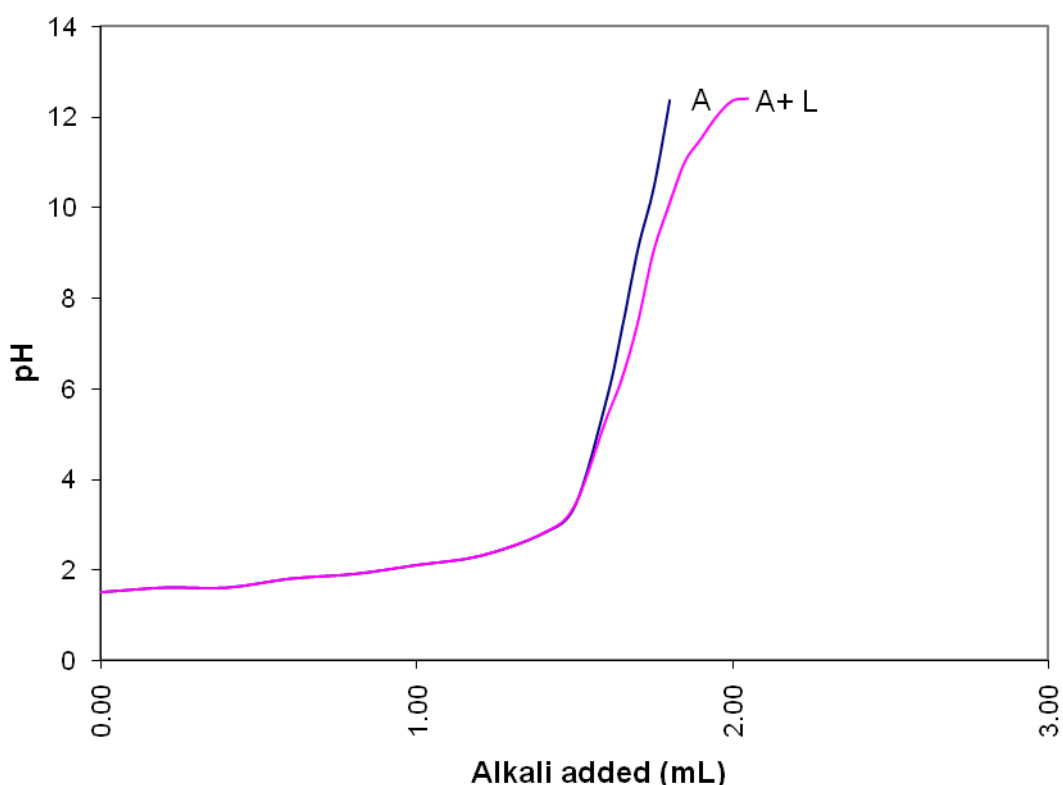**Fig. 1: N-(5-methyl-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone) ethylenediamine**
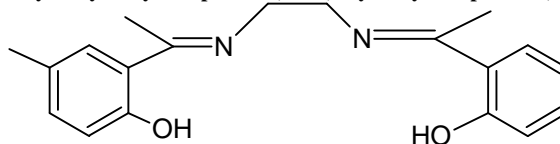
The solution of ligand was prepared in purified 70% dioxane-water mixture and standardized by pH metric technique. Systronic microprocessor based instrument with accuracy in 0.01 unit with glass and saturated calomel electrode was used for titrations. It was calibrated by buffer solution of pH 7.00 and 9.20 at 28 ± 0.1 ^{0}C before processing the titration.

Titrations were carried out in an inert atmosphere by a constant flow of nitrogen gas. The experimental procedure involved the titration of

i) Free acid HNO_3 (0.01 M)
ii) Free acid HNO_3 (0.01 M) and the ligand (20 x 10^{-4} M)
iii) Free acid HNO_3 (0.01 M), ligand (20 x 10^{-4} M) and metal ion (4 x 10^{-4} M) against standard NaOH solution. The ionic strength of all the solutions was maintained constant (0.1 M) by adding appropriate amount of 1M KNO_3 solution.

All the titrations were carried out in 70% dioxane-water mixture. The graph of volume of alkali NaOH against pH was plotted (Fig. 2)

Fig. 2: pH against volume of NaOH at M = 0.1 M at (30 ± 0.1) ^{0}C

RESULTS AND DISCUSSION

The extent of deviation may be the dissociation of –OH group. The N-(5-methyl-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone)ethylenediamine may be considered as a dibasic acid having two replaceable H+ ion from phenolic –OH group and can be represented as

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$$H_2L \rightleftharpoons 2H^+ + L^{--}$$
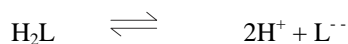
The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A + L) and acid + ligand + metal ion curve (A + L + M)] between volumes of NaOH against pH.

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Table 1).

$$n_A = \gamma - \frac{(E_0 + N)(V_2 - V_1)}{(V_0 + V_1)T_L{}^0} \quad ----- (1)$$

where γ denotes the number of dissociable proton. N is the concentration of sodium hydroxide (0.2 mol.dm^{-3}), $(V_2 - V_1)$ is the measure of displacement of the ligand curve relative to acid curve, Where V_2 and V_1 are the volume of alkali added to reach the same pH reading to get accurate value of $(V_2 - V_1)$: the titration curves were drawn on an enlarged scale. E^0 and $T_L{}^0$ are the resultant concentration of nitric acid and concentration of ligand respectively. V_0 is the initial volume of reaction mixture (50 cm^3). Proton-ligand stability constant pK value (Table 1) of ligand was calculated by algebraic method point wise calculation and also estimated from formation curve (Fig. 3) n_A vs. pH (half integral method) by noting pH at which $n_A = 0.5$ [Bjerrum 1957] (Table 2).

Fig. 3: Formation curves of n_A against pH at M = 0.1 M at (30 ± 0.1) ^{0}C
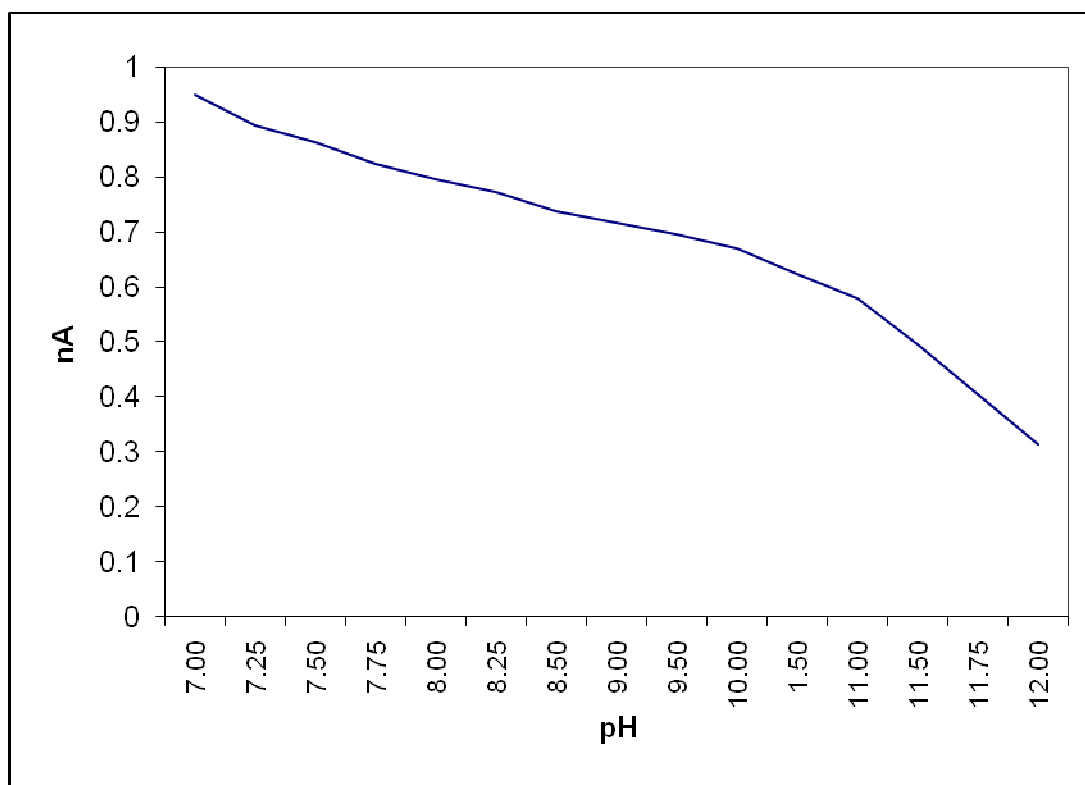
Metal-ligand stability constant (log K) were determined by the half integral method by plotting n vs. pL. The experimental n values determined using expression.

$$n = \frac{(E_0 + N)(V_3 - V_2)}{(V_0 + V_2)Tm^0} \quad -------- (2)$$

Where N, E_0, V_0 and V_2 have same significance as in equation (1), V_3 is the volume of NaOH added in the metal ion titration to attain the given pH reading and $T_M{}^0$ (4 x 10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture.

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Table 1 Proton-ligand stability constant (pK)

System	pK	
	Half Integral method	Point wise Calculation
N-(5-methyl-2-hydroxyacetophenone)-N'-(2-hydroxyacetophenone) ethylenediamine (L)	11.25	11.40

Table 2 Metal -ligand stability constant (log K)

System	Log K_1	Log K_2	Log K_1 – Log K_2	log K_1/ log K_2
Co (II) - L	6.233	5.555	0.678	1.122
Ni (II) – L	6.257	5.565	0.692	1.124
Cu (II) – L	6.216	5.315	0.901	1.170

CONCLUSION

From the titration curve, it is observed that the (acid + ligand) curve and (acid + ligand + metal) curve for all system of ligand started from pH = 2.70 and of ligand to started from pH = 4.0, this indicates the commencement of complex formation. The change in yellow color in pH range from 2.25 to 7.50 during the titration showed the complex formation between metal and ligand.

Proton-Ligand stability constnat (pK)-
It is observed from titration curve (Fig. 1) that the ligand curve start deviating from free acid (HNO_3) curves at pH > 2.70. The extent of deviations may be the dissociation of -OH group completely.

Metal-ligand stability constant (log K) -
The difference between log K_1 and log K_2 values indicates the formation of complex between metal ion and ligand. The ratio of (Log K_1/Log K_2) indicates that the complex formed between Co (II), Ni (II) and Cu (II) metal ion and ligand are more stable.

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