# STUDIES OF METAL LIGAND STABILITY CONSTANT OF HYDROXY SUBSTITUTED CHALCONE COMPLEX IN 70% DIOXANE SOLVENT MEDIA PH METRICALLY

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**A B S T R A C T**

**The complex formation between Cu(II) Ni (II) & Co (II) metal ions and, 1-(5-bromo-2-hydroxyphenyl)-3-phenylprop-2-en-1-one (L$_1$) and , 1-(5-bromo-2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (L$_2$) Chalcones have have been studied at 0.1 M ionic strength (26± 0.1$^0$C) in 70% Dioxane-water mixture by Bjerrum method as adopted by Calvin Wilson.It is observed that Cu (II),Ni (II) and Co (II) metal ions form 1:1 and 1:2 complexes with ligands (L$_1$ & L$_2$). The data obtained were used to estimate and compare the value of proton- ligand stability constant (pK) and metal- ligand stability constant ( log k) .The effect of substituent was studied from estimated data (pk &log k)**

**Keywords: Substituted chalcone, Dioxane – water mixture, stability constant. Bjerrum method, Irving- Rossotti's equation**

## 1. Introduction

Considerable research work has been done in the past, on the study of complexes [1, 2]. Pund et al. have studied the interactions of La(III) and Nd(III) metal ions with 1-(4-hydroxy-6-methyl pyrimidino)-3-phenylthiocarbamide [(L$_1$), HMPPT)] and 1-(4-hydroxy-6-methyl pyrimidino)-3-methylthio carbamide [(L$_2$), HMPMT)] at 0.1 M ionic strength in 70 % Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson [3] Thakur et al have been studied The interaction between Th(III), Sm(III), Nd(III) and Pr(III) Metal Ions And 2-Mercapto-4-(4'-Aminophenyl)-6-(2'-Hydroxy-5'-Bromophenyl) Pyrimidine [M4AHBP] (L$_1$) and 2-Mercapto-4-(2'-Chlorophenyl)-6-(2'-Hydroxy-5'-Bromophenyl) Pyrimidine [M2CHBP] (L$_2$)[4].

Thorat et al have been studied the complex formation between Pr(III) & Sm(III) metal ions and 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(3-nitrophenyl)isoxazoline L1, 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(4-chlorophenyl) isoxazoline L2, 3-(2-hydroxy-3-nitro- 5-methylphenyl)-5-(2-furyl) isoxazoline L3[5]. The stepwise stability constant values of glycine with Mn(II) using pH measurements in 50%DMF- 50%Water and 70%DMF-30%Water medium have been studied by Vijayarohini et al [6]. Tayade et al have been studied the interactions of Cu(II), Cd(II) and Cr(III) metal ions with 5- phenylthiocarbamido-1-naphthol(L2) and 5-p-clorophenylthiocarbamido-1-naphthol (L3)[7]. Patil et al have been studied the interaction of Cu(II), Ni(II) and Co(II) metal ions with 2-hydroxy -5-bromo-N- (Phenyl)chalconeimines (L1) and 2-hydroxy -5-Bromo – N- (O- nitro phenyl ,Chalconeimine (L2) [8].Tayade et al have been studied effect of metal ion Fe(III) on the properties of complexes of substituted imidazolinone in 70% (DMF+water) mixture at 298K [9]. The complex formation between Pb2+ and Ag+ metal cations with 15-crown-5 (15C5), 1, 4, 8, 11-tetrathiacyclotetradecane (TTCTD) and 1, 7-diaza-12-crown-4 (DA12C4) macrocyclic ligands in an (acetonitrile) – MeOH (methanol) binary solvent mixtures using conductometric method was studied by Kazemi et al [10].

## 2. Experimental methodology

### 2.1 Material and Methods

All chemicals used are of AR grade. The ligands ($L_1$) & ($L_2$) were synthesized in the laboratory by reported protocol. The stock solutions of the ligand was prepared by dissolving required amount of ligand in a of 70% (Dioxane + water) mixture.

### 2.2 General procedure

Types of Titrations

i) Free acid $HNO_3$ (0.01 M)

ii) Free acid $HNO_3$ (0.01 M) and ligand ($20 \times 10^{-4}$ M)

iii) Free acid $HNO_3$ (0.01 M) and ligand ($20 \times 10^{-4}$) and metal ion ($4 \times 10^{-4}$ M) against standard 0.1N NaOH solution.

The ionic strength of all the solutions was maintained constant 1M by adding appropriate amount of $KNO_3$ solution. All the titrations were carried out in 70% (Dioxane+water) mixture and the reading were recorded for each 0.1 ml addition. The graph of volume of alkali added (NaOH) against pH were plotted. The ligands involved in the present work may be considered as a monobasic acid having only one dissociable H+ ion from phenolic -OH group and it can therefore, be represented as HL. The dissociating equillibria can be shown as.
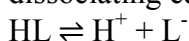
$$HL \rightleftharpoons H^+ + L^-$$

By the law of mass action, we have,

$$K = [HL] / ([H^+] [L^-]) \qquad (1)$$

Where, the quantities in bracket denote the activities of the species at equilibrium.

## 3. Result and Discussion

### 3.1 Calculation of Proton-Ligand Stability Constant ($n_A$)

The plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant (representing the replacement of H+ ions from functionalgroup of ligand with respect to pH value). The horizontal difference ($V_2-V_1$) was measured accurately between the titration curves of free acid and acid + ligand. It was used to calculate the formation number n at various pH values and fixed ionic strength $\mu = 0.1$ M using Irving and Rossotti's equation [1, 2].

$$\bar{n}_A = \gamma - \frac{(E_0+N) (V_2-V_1)}{(V_0 + V_1) TL^0} \qquad (2)$$

Where, $V^0$ is the initial volume of the solution. $E^0$ and $T_L{}^0$ are initial concentrations of the mineral acid and ligand respectively. $V_1$ and $V_2$ are the volumes of alkali of normality N during the acid and ligand titration at given pH. $\gamma$ is the replaceable proton from the ligand. The data of $n_A$ obtained at various pH along with the horizontal difference for some representative systems are represented in Table 1. The metal ligand Ligand formation number (n) is estimated by Irving- Rossotti's equation.

$$\bar{n} = \frac{(E_0+N) (V_3-V_2)}{(V_0 + V_2) Tm^0} \qquad (3)$$

Where, the notations have the same meaning as given in earlier equation. The horizontal difference ($V_3-V_2$) between the metal complex (A+M+L) and reagent (A+L) curve is used to evaluate the value of n using Irving Rossotti's equation.

**Table 1 Proton ligand stability constant (pK)**

| Ligand | System | pK | |
|--------|--------|------|------|
| | | Half integral method | Point wise method |
| $L_1$ | 1-(5-bromo-2-hydroxyphenyl)-3-phenylprop-2-en-1-one | 10.8027 | 7.7813 |
| $L_2$ | 1-(5-bromo-2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one | 8.5921 | 7.2422 |

**Table 2: Metal-ligand stability constant (log K)**

| System | $LogK_1$ | $LogK_2$ | $\Delta LogK$ | $LogK_1/LogK_2$ |
|---|---|---|---|---|
| Cu(II)+$L_1$ | 9.8618 | 8.3949 | 1.4669 | 1.0601 |
| Ni(II)+ $L_1$ | 9.2723 | 8.4476 | 0.8247 | 1.0976 |
| Co(II)+ $L_1$ | 9.1668 | 8.1472 | 1.0196 | 1.1251 |
| Cu(II)+$L_2$ | 4.5755 | 2.2960 | 2.2795 | 1.9928 |
| Ni(II)+ $L_2$ | 4.1757 | 2.2968 | 1.8789 | 1.8180 |
| Co(II)+ $L_2$ | 5.7712 | 3.4947 | 2.2765 | 1.6514 |

**Conclusion**

From the titration curves, it is observed that the departure between acid + ligand (A+L) curve and acid + ligand + metal (A+L+M) curve for all systems started from pH 3.6 this indicated the commencement of complex formation. Also change in colour from yellow to orange in the pH range from 3.9 to 8.6 during titration showed the complex formation between metal and ligand.

The order of pK values of ligands is found to be pK of ligand ($L_1$) greater than pK ligand ($L_2$). The lower pK values of ligand ($L_2$) because ($L_2$) has electron realizing −Br group to phenyl ring which decrease the activity of ligand ($L_2$) to form more stable complex. From the table 2, it is observed that the difference between log $K_1$ and log $K_2$ values are not sufficiently large that indicates the simultaneous formation of complex between metal ion and ligand. The values of log $K_1$ and log $K_2$ (table 2) for Cu(II)–$L_1$, Ni (II)-$L_1$, Co (II)-$L_1$ complexes are comparatively higher than Cu (II)–$L_2$, Ni (II)-$L_2$ and Co (II)- $L_2$. It indicates that Cu (II), Co (II), Ni (II) forms more stable complexe with ligand ($L_1$) than complexes with ligand ($L_2$). The higher value of ratio (log $K_1$ / log $K_2$) for Co (II)-$L_1$ and Cu (II)-$L_2$, Ni (II)-$L_2$, Co (II)-$L_2$ ligand ($L_1$ and $L_2$) complexes indicate the more stepwise complex formation as compare to Cu (II)-$L_1$ and Ni (II)-$L_1$ complex.

**Acknowledgement**

**Reference**

[1] F.H.C. Rossotti and H. Rossotti : *The determination of stability constants*, McGraw Hill Book Co.

[2] A. E. Martell and M. Calvin : *Chemistry of metal chelate compounds*, Prentie Hall, Inc. Englad, Cliffs, N. J.**1962**.

[3] Pund D. A, Bhagwatkar R. A, Tayade D. T, Rathod D. B. 2010**.** Studies on interaction between La (iii), and Nd(iii) metal ions and 1-(4-hydroxy-6-methyl pyrimidino)-3-substituted thicarbamide at 0.1 m ionic strength pH metrically,Rasayan J. Chem.,2(3), 246-249.

[4] Thakur.S.D, Mahajan. D.T, Munot.K.P, Deshmukh.R.D, Tihile.M.S.2011. Metal-ligand stability constants of Th(III), Sm(III), Nd(III) and Pr(III) metal ion complexes with 2-mercapto-4-substituted phenyl-6-substituted phenyl pyrimidines at 0.1 M ionic strength pH metrically, *Der Pharma Chemica,* 3 (6): 382-389.

[5] Thorat S.A, Thakur S.D. 2015. Metal ligand stability constant of substituted 3, 5-diaryl isoxazolines complexes in 70% dioxane solvent media, *J. Curr. Chem. Pharm. Sc,* 5(2), 67-74.

[6] Vijayarohini.S, Swamidoss C, Kavitha. G, Alwar.B, 2014. The effect of different concentrations of DMF-$H_2O$ on the proton ligand dissociation constant (pk) and the stability constant of mn-glycine complex, *International Journal of Pharmaceutical Science Invention,*3(7) 46-49.

[7] Tayade. D.T, Wadekar. A.B. 2015. To study the stability of complexes of substituted thiocarbamidonaphthols with different transition metal ions in 70% mixed solvent media,*International J.Applied Research,*1(13) 640-642.

[8] Patil N.R, Thakur S.D.2015. Studies on interaction between cu(ii), ni(ii) and co(ii) metal ions and hydroxy-substituted chalconeimines, at 0.1 M ionic strenghth

pH metrically, *International Journal of Recent Scientific Research,*6(5) 4032-4034.

[9] Tayade.R.R, Shrirao.A.S, Jagtap. V.S, Chaudhari. P.P, Chaudhari.K.G, Wadekar. M.P. 2015. Stability constant determination of substituted imidazolinone drugs pH-metrically, *International Journal of Chemical and Physical Sciences,*4, 23-29.

[10] Kazemi.M.S, Shamshirgaran.B. 2016. Determination of the stoichiometry, stability constant of complexes formation and thermodynamic parameters between 15-Crown-5, 1, 4, 8, 11- tetrathiacyclotetradecane and 1, 7-diaza-12-crown-4 macrocyclic ligands in acetonitrile – methanol binary solvent mixtures