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STUDIES OF PROTON AND METAL-LIGAND STABILITY CONSTANTS OF Cu(II),Ni(II),Co(II) COMPLEXES OF SUBSTITUTED SCHIFF'S BASES

Dr. A. D. Khambre[1], Dr.M.L.Narwade[2]

[1]*Department of Chemistry, Mahatma Fule College Of Science And Arts, Patur, Dist-Akola, (India)*

[2]*Department of Chemistry, Vidyabharati Mahavidyalay, Amravati, Dist.-Amravati, (India)*

ABSTRACT

The Interaction of Cu(II),Ni(II),Co(II) metal ions with

(i) 2'-Hydroxy,3'-Bromo,5'-Chloro-4-methoxy-N[orthonitrophenyl]chalcon imine(L1)

(ii) 2'-Hydroxy,5'-Chloro,4-methoxy-N[orthonitrophenyl]chalcone imine.(L2)

(iii) 4-(2-Hydroxy,3-Bromo,5-Chloro Phenyl)-6-(4-Anisyl Phenyl)-2-Imino-6-H,2,3-dihydro 1,3-thiazine (L3) have been studied at 0.1M Ionic strength.It is observed that, Cu(II),Ni(II),Co(II) metal ions form 1:1 and 1:2 complexes with L_1,L_2 and L_3.

The substituted Schiff's bases show formation of simultaneous complexes.The order of proton-ligand stability constant is as $pKL_2>pKL_3>pKL_1$. The data obtained for pK and logK are used i)To see the effect of substituents,ii) To check the validity of logk = a.pK + b.Here proton-ligand & metal-ligand stability constants have been studied pH-metrically by Calvin-Bjerrum titration technique.

Keywords: Metal Ions(Cu(II), Ni(II), Co(II)), Ligand (Substituted Pyrazoles), Solvent (1,4 – Dioxane) etc.

I. INTRODUCTION

Schiff;s Bases and their derivatives are biologically *important* compound having antibacterial[1-2],antitumour[3],antimicrobial[4] properties. Shelke *et al*[5] have investigated the interaction between UO_2(II) and Cu(II) with dicarboxylic acids in dioxane-water mixture. Narwade *et al*[6] have studied the equilibrium constants of Cu(II) complexes with some substituted chalcones at 0.1M ionic strength pH metrically. Sawalakhe and Narwade[6] have studied stability constants of Cu(II) complexes with some substituted chalcones at 0.1M ionic strength. Rajput[7] has studied proton-ligand stability constants with some chloro substituted pyrazolines, isoxazolines, pyrazoles and isoxazoles.Deshmukh[8] has studied proton –ligands stability constants with dichlrosubstituted pyrazolines, is oxazolines, pyrazoles and isoxazoles. Banerjee *et al*[9] have synthesized number of mixed ligands of alkaline earth metal complexes with a view to understand the bio-inorganic chemistry of metal ions.

Raghuwanshi *et al*[10] have studied stability constants of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture spectrophotometrically. Mandakmare *et al*[11] have studied the interaction between UO_2(II) and substituted coumarins at 0.1M ionic strength potentiometrically and spectrophotometrically.

Recently Palaskar[12] has studied the effect of ionic strength and dielectric constant of Cu(II) -3-nitrophthalic acid potentiometrically at 0.02,0.04,0.06,0.08 and 1.0M ionic strength in aqueous medium at 30°C. The present work deals with the study of complex formation between Cu(II),Ni(II),Co(II) with substituted Schiff's Bases and determination of proton-ligand and metal-ligand stability constants of some substituted Schiff's bases pH-metrically by Calvin- Bjerrum titration technique.

II. EXPERIMENTAL

Substituted Schiff's Bases ligands L_1,L_2 and L_3 were sythesized in the laboratory & their purity was checked by TLC on microscopic slides with silica gel-G layer thickness 0.3.The structure of L_1,L_2 and L_3 were confirmed by IR & NMR spectra.

2.1 Synthesis of Ligands

The solution of ligands were prepared in 1,4-dioxane. The solution of NaOH,HNO_3,KNO_3 & metal ions ($Cu(NO_3)_2$,$Ni(NO_3)_2$ & $Co(NO_3)_2$) were obtained from BDH grade chemicals.

The pH measurements were carried out with ELICO-LI-10 pH meter (accuracy ± 0.05 units) using glass electrode & calmel electrode at 28 ± 0.1^{O}C. The B values (pH meter reading in 70% dioxane-water mixture) were converted to pH values by applying the correction given by Van Viterts & Hass. pH meter was calibrated by standard buffer solution (pH 4.01,7.00 & 9.11).

Experimental procedure involves following three sets of titrations :

i)Free acid titration (HNO_3,1 x 10^{-2}M)

ii)Free acid + ligand titration (20 x 10^{-4})

iii)Free acid + ligand (20 x 10^{-4}M) + metal ion titration (4 x 10^{-4}M)

were carried out with standard NaOH solution (0.189 to 0.289) in presence of an inert atmosphere by bubbling a constant flow of nitrogen gas.

III. RESULTS AND DISCUSSION

The ligands are monobasic containing only one OH group; hence it's dissociation is represented as below.

$$HL \Leftrightarrow H^+ + L^-$$

The deviations between acid curves (acid + ligand curves) started at about pH 1.80 forL_2,for all the systems this deviation gradually increases up to pH 12.00,which shows the dissociation of –OH group of ligands.

3.1 Determination of Proton-Ligand Formation Numbers (nA)

The values of (nA) are estimated by using Irving and Rossotti experiments. Formation curves are prepared by plotting values of nA vs pH.

3.2 Calculations

The values of pK are calculated from fornation curves (i.e.half integral method). The pH at nA-=0.5 corresponds the proton-ligands stability constant (pK).The order of proton-ligand stability constant is pKL_2>pKL_3>pKL_1. The correct value is also calculated by pointwise calculation method. The pK values for L_1 to L_3 are given in Table-1.

The sudden increase in pK value of ligand is due to the presence of group attached to phenyl ring as electron withdrawing group. In case of ligand,the inductive effect of benzoyl group may be compensated due to the presence of electron releasing group that results in an increase in the pK value of ligand.

TABLE – 1 Determination of Proton Ligand Stability Constants (Pk)

Medium : 70% Dioxane-water **μ** =0.1M **T^0L** = 20 x 10^{-4}M

T^oM = 4 x 10^{-4}M **N** = 0.2N **V^O** = 50 ml

E^o = 1 x 10^{-2} M = 0.01M **Temp.** = 28 ± 0.01°C

System	Constants (pK)	
	Half integral method	**Pointwise calculation**
L_1	2.40	2.4022 ± 0.02
L_2	4.20	4.2147 ± 0.02
L_3	3.40	3.4197 ± 0.03

IV. DETERMINATION OF METAL LIGAND STABILITY CONSTANTS

The deviation between (acid + ligand) and (acid + ligand + metal) curves started from pH 1.60 & increased continuously up to pH 12. It shows the commencement of complex formation. Cu(II) forms pale green coloured complex,Ni(II) forms light yellow and Co(II) forms light orange(pink) coloured complexes.

Calculation Of n values and determination of $logK_1$ and Log K_2 values :-

The values of n,$LogK_1$ & $LogK_2$ is estimated by applying Irving-Rossotti expression shown in Table 2 & 3.

Determination of n – values

Table - 2

T^0_L = 20 x 10^{-4}M **E^0** = 1.00 x 10^{-2}M **V^0** = 50ml **T^0M** = 4 x 10^{-4}M

System – Cu(II)-L_3					System – Co(II)- L_3				
pH	**V_2**	**V_3**	**(V_3-V_2)**	**n**	**pH**	**V_2**	**V_3**	**(V_3-V_2)**	**n**
1.40	1.27	1.32	0.05	0.3473	1.60	1.48	1.55	0.07	0.4843
1.60	1.48	1.56	0.08	0.5534	1.80	1.68	1.80	0.12	0.8270
1.80	1.68	1.88	0.20	1.3783	2.00	1.88	2.10	0.22	1.5103
2.00	1.88	2.12	0.24	1.6476	2.20	2.03	2.35	0.32	2.1905
2.20	2.03	2.35	0.32	2.1905	---	----	----	----	----

The maximum value of n was obtained at about pH 2.20 for Cu(II)L_3 & Co(II)L_3 which shows that there is a formation of 1:1 & !:2 complexes simultaneously.

Determination of $LogK_1$ & $LogK_2$ Value

Table – 3,

Medium : 70% Dioxane-water **μ** = 0.1M **T^0L** = 20 x 10^{-4}M

T^oM = 4 x 10-^{4}M **N** = 0.2N **V^O** = 50 ml

E^o = 1 x 10^{-2} M = 0.01M **Temp.** = 28 ± 0.01

System	Metal ligand stability constants (log K)			
	Half Integral		Pointwise Calculation	
	Log K_1	Log K_2	$LogK_1$	$LogK_2$
Cu(II)-L_1 Complex	3.58	3.27	3.59	3.37
Ni(II)-L_1 Complex	3.74	3.36	3.75	3.44
Co(II)-L_1 Complex	3.65	2.46	3.80	2.57
Cu(II)-L_2 Complex	5.25	4.56	5.37	4.61
Ni(II)-L_2 Complex	5.35	4.16	5.42	4.03
Co(II)-L_2 Complex	5.45	4.46	5.64	4.51
Cu(II)–L_3 Complex	4.58	4.35	4.59	4.38
Ni(II)-L_3 Complex	4.38	4.05	4.59	3.01
Co(II)-L_3 Complex	4.45	4.26	4.70	4.40

V. CONCLUSION

Cu(II) is more stable and less reactive as compared to Ni(II) and Co(II). The difference between $LogK_1$and $LogK_2$ values is smaller in all systems .It seems therefore that both 1:1 & 1:2 complexes are formed simultaneously and not in a stepwise process.

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