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PH METRIC STUDIES on FORMATION CONSTANTS OF THE COMPLEXES OF HALO SUBSTITUTED CHALCONEIMINE WITH SOME TRANSITION METAL ION 70% DIOXANE-WATER MIXTURE pH METRICALLY

K.P.Kakade[1], Dr.R.D.Deshmukh[2], Dr. S.D. Thakur[3] & Sarita P Kakade [4]
Bar.R.D.I.K & Ny K.D.College Badnera Rly 1,2,3
Government Vidarbha Institute of Science and Humanities ,Amravati [4]

ABSTRACT

The interaction of Cu(II), Ni(II) ,Co(II), Cr(II), Fe(III) metal ions with 2- hydroxyl phenyl n (m- chloro-p Fluro) chalconeimine **(CFB)** have been studied at 0.1 M ionic strength (26± 0.10 C) in 70% Dioxane- water mixture by Bjerrum method as adopted by Calvin Wilson. 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: *Halo substituted chalconeimine, Dioxane , stability constant.*

I. INTRODUCTION

Considerable research work has been done in the past, on the study of complexes [1-2]The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ions in biological kingdom. With the view to understand the bi-inorganic chemistry of metal ions, Banerjee *et al* [3] have synthesized a number of mixed-ligand alkaline earth metal complexes. Bjerrum's [4] dissertation has taken the initiative to develop the field. Metal complexation not only brings the reacting molecules together to give activated complex [5] but also polarized electrons from the ligand towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity of ligands as well as stability. The stability of complexes is determined by the nature of central metal atom and ligands. The stability of complexes is influenced by the most important characteristics like degree of oxidation, radius and electronic structure. Irving and Williams [6] had studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionisation potential of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Narwade *et al* [7] have investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids. Many workers [8-23] have reported thei results on metal-ligand stability constants. Bodkhe *et al* [24] have reported the metal-ligand stability constants of some diketones. Tekade *et al* [25] investigated stability constants of some substituted pyrazolines, isoxalline and diketone. Speciation of binary complexes of Ca (II), Mg (II) and Zn (II) with L-glutamic acid in DMSO water Mixtures has been studied [26]. Thakur et al [27-28] have studied the interactions of hydoxy-1-3-propandiones with Cr (III) and La (III) metal io and Metal-ligand stability constants of Th (III), Sm (III),and 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 . Narwade et al [29]have investigated the Metal-ligand Stability Constants of Cu (II) Complexes and Measurement of Viscosity, Refractivity Index with some substituted Pyrazoles and Diketones at 0.1M Strength. Shivaraj *et al* [30] have studied formation constants and thermodynamic parameters of bivalent metal ion complexes with 3-amino-5-ethyl isoxazole Schiff bases and N, N, N, O and O, O donor ligands in solution. Thakur et al [31-32] have studied the influence of dielectric constants of medium on the complex equilibria of substituted hydroxy-1, 3-propandiones with Cr (III) metal ions and Studies on Interaction Between Cu(II), Cr (II) and Ni (II) Metal Ions At 0.1 M Ionic Strength pmetrically. Recently Tayade *et al* [33] have studied the interactions between divalent transition metal ions and some substituted imidazolinone at 0.1 ionic strength p[H] metrically. In present work an attempt has been made to study the interaction between Cu (II), Ni (II) and Co (II) and substituted hydroxyl chalconeimines, at 0.1 M ionic strength, pH metrically in 70 % dioxane water mixture**.**

II.   EXPERIMENTAL SECTION

Material and Methods

The halosubstituted chalconeimine are synthesized by amination of chalcone with substituted amines ,this chalcone are synthesized by using general claisen Schmidt method . For evaluating the stability constant the very pure and analytical grade solvent and extra pure double distilled water is used.

The solutions of ligands were prepared in purified 70 % dioxane-water mixture and standardized by pH metric technique. Systronic micro processor based instrument with accuracy $\pm$ 0.01 units with glass and saturated calomel electrode as used for the titrations. It was calibrated by buffer solution of pH 7.00 and 9.20 at 28 $\pm$ 0.1^{0}C, before processing the titrations. Titrations were carried out in an inert atmosphere by bubbling a constant flow of nitrogen gar. The experimental procedure involved the titrations of:

1. Free acid $HClO_4$ (0.01 M)

2. Free acid $HClO_4$ (0.01 M) and ligand (20 x 10-4 M)

3. Free acid $HClO_4$ (0.01 M) and ligand (20 x 10-4) 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 NaClO4 solution. All the titrations were carried out in 70 % dioxane-water mixture and the reading were recorded for each 0.1 ml addition. The graphs of volume of alkali (NaOH) against pH were plotted . ligand + metal ion curve (A+L+M)] between volumes of NaOH against pH   . The proton-ligand formation number ñA were calculated by Irving and Rossotti expression (Table1)

$$\bar{n}A = \gamma - \frac{(E0+N)(V2-V1)}{(V0+V1)TL} \quad .....(1)$$

where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.145 mol.dm^{-3}), (V2-V1) is the measure of displacement of the ligand curve relative to acid curve, where V2 and V1 are the volume of alkali added to reach the same pH reading to get accurate values of (V2-V1) the titration curves were drawn on an enlarged scale E^0 and TL^0 are the resultant concentration of perchloric acid and concentration of Ligand, respectively. V^0 is the initial volume of reaction mixture (50 cm^3). Proton-Ligand stability constant pk values (Table 1) of ligand were calculated by algebraic method point wise calculation and also estimated from formation curves ñA Vs pH (Half integral method) by noting p^H at which nA = 0.5 [Bjerrum 1957]. Metal-Ligand stability constants (log k) (Table 2&3) were determined by the half integral method by plotting n Vs pL. The experimental n values determined using expression

$$n = \frac{(E0+N)(V3-V2)}{(V0+V2)Tm0} \quad ..... (2)$$

Where N, E0, Vo and V2 have same significance as in equation (1), V3 is the volume of NaOH added in the metal ion titration to attain the given pH reading and T^{0}M (4 x 10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture.

Determination of Proton – Ligand Stability Constant
(Pointwise Calculation)
System – CFB

pH	$\bar{n}_A$	$\dfrac{\bar{n}_A}{1-\bar{n}_A}$	pK	Mean Value of pK
7.4	0.517949	1.074469	7.431194	
7.5	0.51795	1.074474	7.531196	8.066517
7.6	0.514246	1.058655	7.624755	
7.7	0.51382	1.056851	7.724014	

7.8	0.509191	1.037452	7.815968	
8.5	0.502602	1.010462	8.50452	
8.6	0.501059	1.004245	8.60184	
8.7	0.501059	1.004245	8.70184	

Half Integral method value of pK is - 8.50452,
Pointwise value of pK is - 8.066517

Determination of n system with Fe(III)

pH	V_2(ml)	V_3(ml)	$V_3 - V_2$ (ml)	$\bar{n}$
3.1	2.9747	2.9825	0.0078	0.075537
3.5	3.1483	3.1847	0.0364	0.422322
3.9	3.198	3.2425	0.0445	0.503069
4.0	3.198	3.2475	0.0495	0.558374
4.1	3.2125	3.2675	0.055	0.620246
4.2	3.2269	3.2969	0.07	0.791249
4.7	3.2702	3.3378	0.0676	0.818958
4.9	3.2847	3.3569	0.0722	0.924472
5.0	3.2868	3.3691	0.0823	1.053672
5.5	3.3268	3.4057	0.0789	1.102178
5.6	3.3268	3.4057	0.0789	1.102178
5.7	3.3356	3.4165	0.0809	1.12993
5.8	3.3356	3.4202	0.0846	1.184122
5.9	3.3356	3.4296	0.094	1.315692
6.1	3.3356	3.4346	0.099	1.385675
6.3	3.348	3.4546	0.1066	1.491703
6.4	3.348	3.4564	0.1084	1.538672
6.5	3.3564	3.4691	0.1127	1.599456
6.7	3.3564	3.4835	0.1271	1.848142
6.9	3.3684	3.498	0.1296	1.891334
7.0	3.3684	3.5124	0.144	2.033443

Determination of n system with Ni(II)

pH	V_2(ml)	V_3(ml)	$V_3 - V_2$ (ml)	$\bar{n}$
3.4	3.1141	3.1314	0.0173	0.201149
3.7	3.1697	3.1891	0.0194	0.221529
3.8	3.1829	3.2036	0.0207	0.240703
4.1	3.2125	3.2469	0.0344	0.387936
4.2	3.2269	3.2613	0.0344	0.388842
4.3	3.2413	3.2758	0.0345	0.396135
4.4	3.2558	3.2902	0.0344	0.403916
4.5	3.2558	3.2947	0.0389	0.471391
4.6	3.2558	3.2947	0.0389	0.471518
4.7	3.2702	3.3127	0.0425	0.514877
4.9	3.2847	3.3335	0.0488	0.624851
5.1	3.2982	3.348	0.0498	0.640907
5.4	3.3268	3.3769	0.0501	0.686176
5.5	3.3268	3.3769	0.0501	0.699862
5.6	3.3268	3.3913	0.0645	0.90102
5.7	3.3356	3.4057	0.0701	0.979086
5.8	3.3356	3.4057	0.0701	0.98117
6.0	3.3356	3.4202	0.0846	1.184122
6.1	3.3356	3.4203	0.0847	1.185522
6.2	3.3356	3.4346	0.099	1.385675
6.4	3.348	3.4491	0.1011	1.435053
6.5	3.3564	3.4635	0.1071	1.51998
6.6	3.3564	3.4635	0.1071	1.557325
6.7	3.3564	3.4635	0.1071	1.557325
6.8	3.3624	3.478	0.1156	1.677476
7.0	3.3684	3.4924	0.124	1.751021
7.1	3.3684	3.5068	0.1384	1.954366

Determination of n system with co (II)

pH	V_2(ml)	V_3(ml)	$V_3 - V_2$ (ml)	$\bar{n}$
3.1	2.9747	2.9825	0.0078	0.075537

Determination of n system with Cr (II)

pH	V_2(ml)	V_3(ml)	$V_3 - V_2$ (ml)	$\bar{n}$
3.4	3.1141	3.1291	0.015	0.174407
3.5	3.1483	3.1806	0.0323	0.3747525

3.5	3.1483	3.1847	0.0364	0.422322	3.6	3.1697	3.2069	0.0372	0.4158677
3.9	3.198	3.2425	0.0445	0.503069	3.7	3.1897	3.2274	0.0377	0.4303351
4.0	3.198	3.2475	0.0495	0.558374	3.8	3.1829	3.2213	0.0384	0.4465214
4.1	3.2125	3.2675	0.055	0.620246	3.9	3.198	3.2398	0.0418	0.4725457
4.2	3.2269	3.2969	0.07	0.791249	4.0	3.198	3.2415	0.0435	0.4906923
4.7	3.2702	3.3378	0.0676	0.818958	4.1	3.2125	3.2587	0.0462	0.521007
4.9	3.2847	3.3569	0.0722	0.924472	4.2	3.2269	3.2791	0.0522	0.5900453
5.0	3.2868	3.3691	0.0823	1.053672	4.5	3.2558	3.318	0.0622	0.713997
5.5	3.3268	3.4057	0.0789	1.102178	4.7	3.2702	3.3324	0.0622	0.7535379
5.6	3.3268	3.4057	0.0789	1.102178	4.8	3.2847	3.3469	0.0622	0.7767631
5.7	3.3356	3.4165	0.0809	1.12993	4.9	3.2847	3.3469	0.0622	0.7964286
5.8	3.3356	3.4202	0.0846	1.184122	5.0	3.2868	3.3562	0.0694	0.8885158
5.9	3.3356	3.4296	0.094	1.315692	5.1	3.2982	3.3673	0.0691	0.8892911
6.1	3.3356	3.4346	0.099	1.385675	5.6	3.3268	3.3902	0.0634	0.8856537
6.3	3.348	3.4546	0.1066	1.491703	5.8	3.3356	3.4046	0.069	0.9657736
6.4	3.348	3.4564	0.1084	1.538672	6.0	3.3356	3.4191	0.0835	1.168726
6.5	3.3564	3.4691	0.1127	1.599456	6.3	3.348	3.4335	0.0855	1.1964413
6.7	3.3564	3.4835	0.1271	1.848142	6.4	3.348	3.4335	0.0855	1.2136203
6.9	3.3684	3.498	0.1296	1.891334	6.5	3.3564	3.448	0.0916	1.3000014
7.0	3.3684	3.5124	0.144	2.033443	6.6	3.3564	3.448	0.0916	1.3319418
					6.8	3.3624	3.4572	0.0948	1.3756466
					6.9	3.3684	3.468	0.0996	1.4535252
					7.6	3.3889	3.4868	0.0979	1.460207
					7.9	3.3986	3.4986	0.1	1.494777
					8.1	3.4015	3.5157	0.1142	1.6982608
					8.2	3.3998	3.5157	0.1159	1.7235963
					8.3	3.3998	3.5264	0.1266	1.8941265

Determination of n system with Cu (II)

pH	V_2(ml)	V_3(ml)	$V_3 - V_2$ (ml)	$\bar{n}$
3.5	3.1483	3.1669	0.0186	0.215802
3.8	3.1829	3.2108	0.0279	0.324426
4.0	3.198	3.2369	0.0389	0.438803
4.1	3.2125	3.2563	0.0438	0.493942
4.2	3.2269	3.2752	0.0483	0.545961
4.3	3.2413	3.2897	0.0484	0.555737
4.5	3.2558	3.3103	0.0545	0.660433
4.6	3.2558	3.3246	0.0688	0.833945
6.1	3.3356	3.398	0.0624	0.873395
6.2	3.3356	3.398	0.0624	0.873395
6.4	3.348	3.4124	0.0644	0.914119
6.5	3.3564	3.4269	0.0705	1.000547
6.6	3.3564	3.4269	0.0705	1.02513
6.7	3.3564	3.4296	0.0732	1.06439
6.8	3.3624	3.4399	0.0775	1.124606
6.9	3.3684	3.4416	0.0732	1.068253
7	3.3684	3.4453	0.0769	1.085915
7.2	3.3735	3.4557	0.0822	1.189358
7.4	3.3889	3.4702	0.0813	1.203944
7.5	3.3913	3.4896	0.0983	1.455625
7.9	3.4015	3.5014	0.0999	1.493201
8	3.3998	3.5037	0.1039	1.553038
8.1	3.4098	3.5198	0.11	1.635549

Metal-ligand stability constants (log K) of 2- hydroxyl phenyl n (m- chloro –p Fluro) chalconeimine with some transition metal are given below

system + metal	Metal Ligand Stability Constants	
	log K1	**log K2**
(CFB-K1)+Cu	point wise method= 7.605665 Half integer method=8.205777	point wise method = 3.71268 Half integer method=3.663349
(CFB-K1)+Co	point wise method =8.499595 Half integer method=8.408153	point wise method =5.449861 Half integer method=5.371158
(CFB-K1)+Ni	point wise method =7.899846 Half integer method=7.700254	point wise method =5.380337 Half integer method=5.149478
(CFB-K1)+Fe	point wise method =7.038661 Half integel method=5.33510	point wise method = 2.78485 Half integer method =2.70176

III. CONCLUSION

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid + ligand + metal) curve for all systems started from pH = 3.0 this indicated the commencement of complex formation. Also change in colour from redish yellow to brown in the pH range from 3.0 to 8.5 during titration showed the complex formation between metal and ligand.

IV. ACKNOWLEDGEMENT

REFERENCES
1. F.H.C. Rossotti and H. Rossotti : *The determination ofstability 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. A. K. Banerjee and T.V.R. Rao, *J. Indian Chem. Soc.***1968**, 63, 480.
4. J. Bjerrum: *Metal amine formation in aqueous solutions*,P. Hasse and Sons, Copenhagen **1941**.
5. A. T. Florence and D. Attwood : *Physical principle's of pharmacy*, Macmillan.London **1981**.
6. H. Irving and R.J.P. William : *J. Chem. Soc.* **1953**,3192.
7. M. L. Narwade, M.M. Chincholkar and Sathe S. W.: *J Indian Chem Soc.*, **1985**, 62,194.
8. M. L. Narwade and A. S. Wankhade, *J. Indian Chem. Soc.*, **1993**,70, 709.
9. P. D. Sawalakhe and M. L. Narwade, *J. Indian Chem. Soc.* **1995**,70, 25.
10. S. N. Poddar, K. Dey and N.G. Poddar, *Indian J. Chem.*,**1970**, 8, 364.