GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

STUDIES THE INFLUENCE OF IONIC STRENGTHS OF Cu (II) AND Ni (II) METAL IONS COMPLEX WITH HYDROXY SUBSTITUTED CHALCONE BY pH METRIC TECHNIQUE

Mohd. Wajid Shaikh Mohd. Waris[*1] & S.D.Thakur[2]
[*1]Research Student, Department of Chemistry, Bar.R.D.I.K & N.K.D Collage, Badnera, Amravati-444604. Maharashtra India
[2]Assistant Professor, Department of Chemistry, Bar.R.D.I.K & N.K.D Collage, Badnera, Amravati-444604. Maharashtra India

ABSTRACT

The interaction of Cu (II) and Ni (II) metal ion complex with 1-(5-bromo-2-hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one chalcone (L_3) has been studied at 0.02 to 0.1 mol.dm^{-3} ionic strength at $(30 \pm 0.1)^0$C in 70% dioxane-water mixture pH - metrically. The values of Pk [Proton - Ligand stability constant] and log k [Metal - Ligand stability constant]. are utilised to estimate the thermodynamic stability constant at zero ionic strength and to know the exact nature of complexation equilibria. Pk/log k values are found to be increasing with decreasing the values of ionic strengths. KNO_3 was used to maintain the ionic strength of solution.

Keywords: Ionic strength, Substituted hydroxy chalcone, Dioxane-water.

I. INTRODUCTION

Sumer *et al.,* studies of Influence of Ionic strength of medium on the complexation equilbria of substituted hydroxy 1-3-propanodiones with Cr (III) & La (III) metal ions PH metrically [1] Quazi syed have studied Influence of Ionic strengths of Cu (II) metal ion complex with Rubeanic acid by pH – metrically [2].Sonar A.N studied the effect of ionic strength of medium on the thermodynamic parameters of etodolac with Cu (II), Zn (II) complexes [3]. Farrokh *et al,* have been studied Ionic strength dependence of formation constant, complexation of glycine with dioxouranium (IV) ion [4]. Mandakmone *et al.,* have studied the stability constants of UO2 (II) Complexes with some substituted Coumanins at 0.1 m ionic strength potentiometrically & spectrophotometrically [5]. Meshram *et al.,* have studied stability constants of Pr[III] complexes with substituted pynazoline [6]. P. Agrawal and Narwade M. L. *et al.* have determined metal ligand stability constant at 0.1 M ionic strength [7]. Palaskar *et al* have studied the effect of ionic strength and dielectric constant of cu (II)-3-nitrophthalic acid potentiometricaly at various ionic strengths [8]. Kumar et al have been studied transition metal ion Co (II), Cu (II), Ni (II) and Zn (II) complexes, Speciation of binary complexes of Ca (II), Mg (II) and Zn (II) with L-glutamic acid in DMSO-water Mixtures [9]. Naik et al studied stability constants of Co (II), Sr(II), Pr(II) complexes with substituted azoles at various ionic strength. The influence of ionic strengths on complex equilibria of substituted pyrazoles with Sm(III) and Pr(III) [10]

II.   METHOD & MATERIAL

All chemicals used are of AR grade. The ligands (L_3) 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. Equip-tronics digital pH meter model EQ – 614 (accuracy ± 0.02 units) was used for measuring the PH of solution. Metal solution was prepared in double distilled water. Ligand solution is prepared in 70% ethanol - water [v/v] solution nitric acid, sodium hydroxide & nitrate used were of A.R. Grade. The titration was conducted in an inert atmosphere of nitrogen. The ionic strength of the solution was maintained constant by adding an appropriate amount of 1 M KNO_3 solution. The values were recorded by pH meter.

13

III. RESULT & DISCUSSION

Cu (II) and Ni (II) metal ions complex with 1-(5-bromo-2-hydroxypenta-2,4-dien-1-one chalcone may be considered as a mono basic acid having one replaced H+ ion from phenolic -OH group and can be represented as

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

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 nA were calculated by Irving and Rossotti expression

$$nA = \gamma - \frac{(E_0+N)(V_2-V_1)}{(V_0+V_1)TL^0} \qquad (1)$$

where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.15 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 values of (V_2-V_1): 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 of ligands were calculated by alzebraic method point wise calculation and also, estimated from formation curves nA Vs pH (hal integral method) by noting pH at which nA = 0.5 Metal-ligand stability constants (log k) were determined by the half integral method by plotting n Vs pL. The experimental n values determined using expression

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

Where N, E_0, V_o 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^0M (4 x 10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture. The pk values of ligand and log K values of Cu(II) and Ni(II) metal ion complexes with 1-(5-bromo-2-hydroxypenta-2,4-dien-1-one chalcone at various ionic strength were calculated by Irving and Rossotti's method are set out in (table 1 & 2). It could be observed that pk and log k values are found to decrease with increasing ionic strength that in accordance with Debye-Huckel theory. The pK / log K values were employed the calculate the thermodynamic constants with the help of Bronsted equation.

$$Log\ K = log\ K^0 + A.\ \Delta z^2.\ \sqrt{\mu} \qquad (3)$$
And
$$pK = pK^0 - A.\ \Delta z^2.\ \sqrt{\mu} \qquad (4)$$

Where 'A' is the Debye-Huckel constant, Δz^2 is difference in the square of the charges of product and reactant ions and K0 formation constant at zero ionic strength. The system has been studied at, 0.02, 0.04, 0.06, 0.08 and 0.10 mol.dm^{-3} ionic strengths by varying the concentration of sodium perchlorate. In addition to sodium perchlorate, the titrating system contained ions from perchloric acid, metal nitrate and sodium hydroxide. The total ionic strength (μ) of the medium is calculated by following expression.

$$\mu = 1/2\ \Sigma\ C_iZ_i^2 \qquad (5)$$

Where C_i and Z_i are the concentration and valency of metal ions respectively. The values of pK, log K_1, and log K_2 were plotted against $\sqrt{\mu}$, which gave straight lines. The magnitude of Δz^2 and slopes were calculated from graphs. (Table 1,2) The data obtained of pK and log K could be used to know the mechanism of complexation equilibria. The expected and observed values for Δz^2 for the corresponding dissociation and association reaction equilibria are given (Table 3, 4). It is observed that slope values (observed) of pK and log K are less than the expected values. Those values do not give conclusive evidence regarding the magnitude of charge of reacting spacies except the information that these are oppositely charged.

The discrepancy may be due to the limited applicability of Bronsted equation. The plots of pK / log K Vs [$\sqrt{\mu}/(1+\sqrt{\mu})$] and [$\sqrt{\mu}/ (1+ \sqrt{\mu})$ - 0.3 $\sqrt{\mu}$] are also plotted and are straight line and slope values were determined. It showed that modified Debye-Huckel equation also did not show much improvement in the slope values. This may be due to the fact that value for closest distance approach 'a' is fixed (3.33 A^0). The discrepancy between observed and expected slope values was through of to be due to the concentration and not activity terms used in the equation of stability constants.

Thermodynamics stability constants (pK^0/log K^0)
The thermodynamic stability constants (p K^0 & log K^0) are calculated at zero ionic strength from various   plots Table 5. It can be seen from table 4 that the agreement of the thermodynamic constants (pK^0 & log K^0) obtained from various plots for a particular system are approximately same.

Table 1. Proton-ligand stability constant (pk) of ligands [L$_3$] at various ionic strengths (μ) in 70 % dioxane-water

μ	$\sqrt{\mu}$	$\dfrac{\sqrt{\mu}}{(1+\sqrt{\mu})}$	$\dfrac{\sqrt{\mu}}{(1+\sqrt{\mu})} - 0.3\sqrt{\mu}$	pK
0.10	0.3162	0.2402	0.1453	6.4506
0.08	0.2828	0.2204	0.1355	6.5826
0.06	0.2449	0.1967	0.1232	7.0100
0.04	0.2000	0.1666	0.1066	8.0576
0.02	0.1414	0.1236	0.0814	9.2064

Table 2. Metal-ligand stability constant (log k) of various system at various ionic strengths (μ) in 70 % dioxane-water

System	μ	$\sqrt{\mu}$	$\dfrac{\sqrt{\mu}}{(1+\sqrt{\mu})}$	$\dfrac{\sqrt{\mu}}{(1+\sqrt{\mu})} - 0.3\sqrt{\mu}$	log K_1	log K_2	log k_1-log K_2
Cu(II)-L$_3$	0.10	0.3162	0.2402	0.1453	5.5879	3.2457	2.3422
	0.08	0.2828	0.2204	0.1355	9.71	3.4925	6.2175
	0.06	0.2449	0.1967	0.1232	10.145	7.6206	2.5244
	0.04	0.2000	0.1666	0.1066	10.345	8.0155	2.3295
	0.02	0.1414	0.1236	0.0814	10.589	9.2295	1.3595
Ni(II)-L$_3$	0.10	0.3162	0.2402	0.1453	5.1019	2.945	2.1569
	0.08	0.2828	0.2204	0.1355	8.9275	6.6479	2.2796
	0.06	0.2449	0.1967	0.1232	8.9502	7.2269	1.7233
	0.04	0.2000	0.1666	0.1066	9.2347	7.7728	1.4619
	0.02	0.1414	0.1236	0.0814	10.0587	9.3842	0.6745

Table 3. Slopes and Δz^2 values from the plots of pk / log k Vs $\sqrt{\mu}$

System	pk Vs Δz^2		log K_1 Vs $\sqrt{\mu}$		log K_2 Vs $\sqrt{\mu}$	
	-Slope	Δz^2	-Slope	Δz^2	-Slope	Δz^2
L$_3$	16.51	-31.9899	---	---	----	---
Cu(II) L$_3$	----	----	22.72	- 44.0224	37.14	- 71.9627
Ni(II) L$_3$	-----	----	22.28	- 43.1699	31.25	- 60.5502

Table 4. The different possible reactions and observed and expected values of $\Delta z2$ for corresponding dissociation or association equilibria of various systems

System	Constant	Reaction Equilibria	Δz^2	
			Expected	observed
L_3	pK	$HL \rightleftharpoons H^+ + L^-$	2.0	-31.9899
Cu(II) L_3	$LogK_1$	$L^- + Cu^{2+} \rightleftharpoons (CuL)^{1+}$	-4.0	-44.0224
	$Logk_2$	$(CuL)^{1+} L^- \rightleftharpoons (CuL_2)$	-2.0	-71.9627
Ni(II) L_3	$LogK_1$	$L^- + Ni^{2+} \rightleftharpoons (NiL)^{1+}$	-4.0	-43.1699
	$Logk_2$	$(NiL)^{1+} L^- \rightleftharpoons (NiL_2)$	-2.0	-60.5502

Table 5: Thermodynamic dissociation constants at zero ionic strength (pK0 and log K0)

System	Plots	log K° / pK°
(L_3)	pK Vs $\sqrt{\mu}$	11.37
	pK Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	12.18
	pK Vs $[\sqrt{\mu}/(1+\sqrt{\mu})] - 0.3\sqrt{\mu}$	12.85
Cu(II)-(L_3)	log K_1 Vs $\sqrt{\mu}$	14.66
	log K_1 Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	15.52
	log K_1 Vs $[\sqrt{\mu}/(1+\sqrt{\mu})] - 0.3\sqrt{\mu}$	16.19
	log K_2 Vs $\sqrt{\mu}$	15.12
	log K_2 Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	16.74
	log K_2 Vs $[\sqrt{\mu}/(1+\sqrt{\mu})] - 0.3\sqrt{\mu}$	18.05
Ni(II)-(L_3)	log K_1 Vs $\sqrt{\mu}$	13.73
	log K_1 Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	14.63
	log K_1 Vs $[\sqrt{\mu}/(1+\sqrt{\mu}] - 0.3\sqrt{\mu}$	15.34
	log K_2 Vs $\sqrt{\mu}$	14.20
	log K_2 Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	15.54
	log K_2 Vs $[\sqrt{\mu}/(1+\sqrt{\mu})] - 0.3\sqrt{\mu}$	16.61

IV.   ACKNOWLEDGEMENTS

REFERENCES

1. S.D.Thakur,D.T.Mahajan,K.P.Munot, R.D.Deshmukh,M.S.Tihile,V.H.Masand,Der Pharma Chemica, 2011, 3 (6), pp.165-173.
2. Q.S. Azharuddin, Journal of Applied Chemistry, 2012, 1(6) pp. 14-16.
3. A.N. Sonar, International Journal of Applied and Pure Science and Agriculture, 2016, 2 (4) pp. 176-179.
4. F. Garib ,S. Ali, J. Farbod, J. phys. & theo. Chem.I.A.U.Iran, 2005, 2 (1) pp. 27-32.
5. A. V. Mandakmare, M. L. Narwade, Acta Ciencia Indica, 1994, 20, (1), pp. 30.
6. Y. K. Meshram, Orient J. Chem, 2000 16(1), pp. 173-176.]
7. P. Agrawal , M.L.Narwade, Acta Ciencia Indica, 2003, XXIXC (2) 121.
8. Palaskar, N. G. and Samyak, J. of Chem, 26-29 March 1998.
9. B.A.Kumar,S.Raju,K.B.Naik,B.B.V.Sailaja ,G. N. Rao, Der Pharma Chemica, 2011, 3 (5), pp. 155-167.
10. A.B. Naik, M.L.Narwade, Russian J. Co-ord Chem; 2009, Vol. 35, No. 12, pp. 932-937.