International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.15, pp 204-212, 2017

Study of proton-ligand and metal-ligand stability constants of Cu (II) and Mn (II) complexes with chlorosubstituted pyrazoles and isozoles in 80% DMF-water solvent using pH-meter

P. S. Nandurkar[1]*, M. M. Rathore[2]

[1]Goverment Vidarbha Institutes of Science and humanities, Amaravati.
[2]Vidyabharti Mahavidyalaya Amaravati.

Abstract : The hydrogen-ion activity in water-based solutions, its acidity or alkalinity expressed as pH scientifically is measured on the pH meter. pH meter instrument is also used to find out stability of complexes through titrations. Stability constant is equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to from the complex. The proposed study deals with the proton-ligand stability constant and metal-ligand stability constant of chlorosubstituted pyrazoles and isoxazoles by Calvin Bjerrum titration on pH meter.
Key Words : pH- meter, chlorosubstituted pyrazole, chlorosubstituted isoxazole, Calvin Bjerrum titration.

Introduction:

The determination pH of a solution, we can employ number of methods like potentiometric, conductometric, cryscopic but for the purpose of titrations, we can directly use the pH meter. The pH-metric is an automatic instrument of measuring the pH of a solution. There are number of pH- meters, involving different principles, but most of the chemists use only the direct reading type pH meter. The hydrogen-ion activity in water-based solutions, its acidity or alkalinity expressed as pH scientifically is measured on the pH meter. The combined glass electrode is used in the pH meter. The glass electrode is the most widely used hydrogen ion responsive electrode and its use depends on the fact that when a glass membrane is immersed in a solution, a potential is developed which is a linear function of the solution[1].

pH meter instrument is also used to find out stability of complexes through titrations. Stability constant is equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to from the complex. Ramteke[2] *et al* determined stability constants of 4-(2-chlorophenyl)-3-(3-furanoyl-5-(2-hydroxyphenyl)pyrazole with Cu(II), Ni(II), Co(II) and Nd(III) metal ions in 70% dioxane-water mixture. Pethe[3] *et al* reported the interaction of 3-(4'-bromophenyl)-4-benzoyl-5-(2-hydroxyphenyl)pyrazole and 3-(4'-chlorophenyl)-4-benzoyl-5-(2-hydroxyphenyl)pyrazole with Co(II) and Ni(II) by pH metrically.

The proposed study deals with the proton-ligand stability constant and metal-ligand stability constant of chlorosubstituted pyrazoles and isoxazoles by Calvin Bjerrum titration on pH meter.

Materials and Methods:

Proton-ligand stability constants and metal-ligand stability constants studied on three ligands which are:

1. (3-(3,5-Dichloro-2-hydroxyphenyl)-1-phenyl-5-(1-phenylprop-1-en-2-yl)-1*H*-pyrazol-4 yl)(phenyl)methanone. (**ligand BC3**)

2. (3-(3, 5-Dichloro-2-hydroxyphenyl)-5-(1-phenylprop-1-en-2-yl) isoxazole-4-yl)(phenyl) methanone. (**ligand BC4**)

The ligands (BC3, FP3 and BC4) were completely dissolved in 80% DMF-water mixture. This is useful in pH metric titrations because all equilibrium processes that take place in water containing solvent-mixtures sensitively. The two metals selected for metal-ligand stability constants were: Cu (II) and Mn (II).

The Calvin-Bjerrum titration method was used to calculate proton-ligand stability constant and metal-ligand stability constant. The titration data were used to draw the graphs. Three kinds of titrations were performed against volume of NaOH. The ligands (BC3 and BC4) were separately titrated with metal complexes. These titrations were:

(a) Acid titration.
(b) Acid + Ligand titration.
(c) Acid + Ligand + Metal titration.

The titration procedures are:

(a) Acid titration: 5 ml HNO_3 (0.1M) + 5 ml KNO_3 (0.1M) + 35ml DMF + 5 ml water.
(b) Acid + Ligand titration: 5 ml HNO_3 (0.1M) + 5 ml KNO_3 (0.1M) + 10 ml ligand (in DMF-water 80%) + 25ml DMF + 5 ml water.
(c) Acid + Ligand + metal titration: 5 ml HNO_3 (0.1M) + 5 ml KNO_3 (0.1M) + 10 ml ligand (in DMF-water 80%) + 25ml DMF + 2 ml metal ion solution + 3 ml water.

Here 0.1 M HNO_3 acids were used for the preparation of a stock solution. The exact normality was calculated by titrating against standard sodium hydroxide solution. 0.1 M KNO_3 solution which was prepared from carbonates free double distilled water. Ionic strength of sodium hydroxide is kept constant as 0.1 M by addition of potassium nitrate solution.

The titration curves were prepared by plotting pH of solution and volume of NaOH added as shown in tables 1 to 4 and in graphs 1 to 4.The dissociation of OH^- is clearly indicated by the titration (acid + ligand) curves deviated from acid curves at pH 4.86 and continued up to pH 12.67 (Graphs 1 to 4).

Calculation of proton-ligand formation number ($\bar{n}_A$):

The proton-ligand formation numbers $\bar{n}_A$ were calculated from acid titration. The $\bar{n}_A$ values (proton-ligand formation numbers) were calculated by Irving Rossoti's expression curve (A) acid and acid + ligand titration curves (A+L).

The difference ($V_2 – V_1$) between the volumes (A+L) and (A) was measured accurately. The values of V_1 and ($V_2 – V_1$) were used in the calculations which are represented in tables 3.7 to 3.9.

$$\bar{n}_A = \gamma - \frac{(V_2 - V_1)(N + \varepsilon_0)}{(V_0 + V_1)T^0_L}$$

Where, γ = Number of replaceable hydrogen atoms per ligand molecule,
V_0 = Total initial volume of the solution
V_1 and V_2 are the volumes of alkali required during the acid and ligand titration at the given pH.
N = Normality of NaOH used for titration

ε_0 and $T^0{}_L$ are the initial concentrations of free acids and the ligands

pH Metric Titration Data:

3.3.2.1 Titration data of ligand (BC3) with Cu (II):

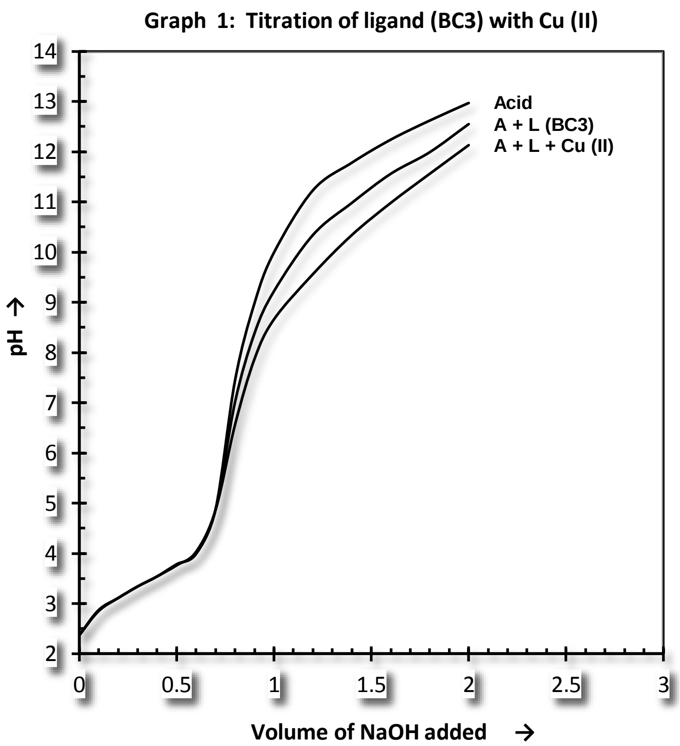
System: Ligand (BC3) with Cu (II), Medium: 80% (DMF: water), N = 0.2 N (NaOH)
Temperature = 25^0C, Ionic strength (μ) = 0.1 M KNO_3, ε_0 = 0.002 M HNO_3
$T^0{}_m$ = 0.0004 M

Table 1: Titration data of ligand (BC3) with Cu (II)

Vol. of NaOH added	Acid	A+L(BC3)	A+ L+ Cu (II)
0	2.37	2.37	2.37
0.1	2.87	2.87	2.85
0.2	3.11	3.11	3.11
0.3	3.34	3.34	3.34
0.4	3.54	3.54	3.54
0.5	3.78	3.78	3.76
0.6	3.99	3.99	4.03
0.7	4.87	4.87	4.86
0.8	7.44	7.01	6.56
0.9	8.98	8.38	7.87
1.0	9.99	9.22	8.66
1.2	11.23	10.34	9.56
1.4	11.78	10.98	10.34
1.6	12.24	11.56	10.98
1.8	12.62	11.99	11.56
2.0	12.97	12.55	12.13

Table No. 2 Titration data of ligand (BC3) with Mn (II)

Vol. of NaOH added	Acid	(A+L+BC3)	A+L+Mn(II)
0	2.37	2.37	2.37
0.1	2.87	2.87	2.86
0.2	3.11	3.11	3.1
0.3	3.34	3.34	3.34
0.4	3.54	3.54	3.54
0.5	3.78	3.78	3.75
0.6	3.99	3.99	3.98
0.7	4.87	4.87	4.89
0.8	7.44	7.01	6.45
0.9	8.98	8.38	7.56
1.0	9.99	9.22	8.45
1.2	11.23	10.34	10.01
1.4	11.78	10.98	10.56
1.6	12.24	11.56	10.98
1.8	12.62	11.99	11.34
2.0	12.97	12.55	12.08



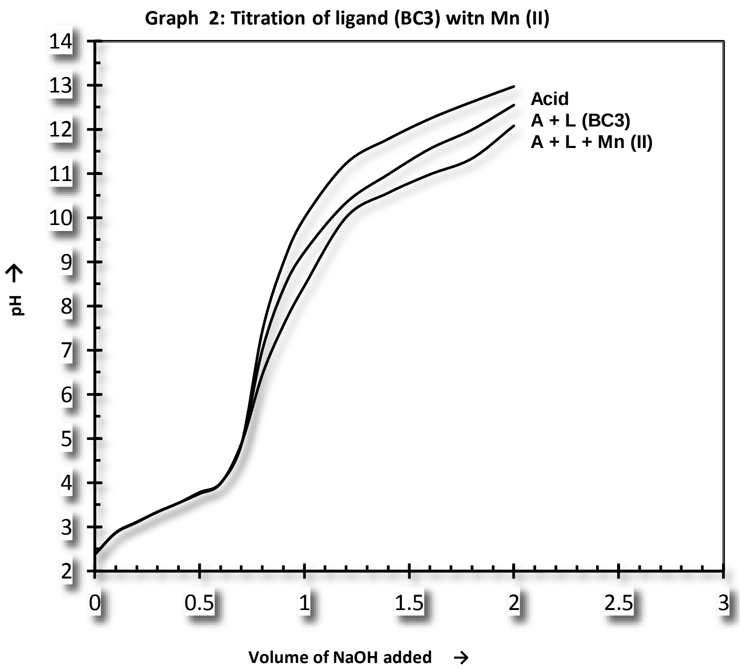


Table 3: Titration data of ligand BC4 with Cu (II)

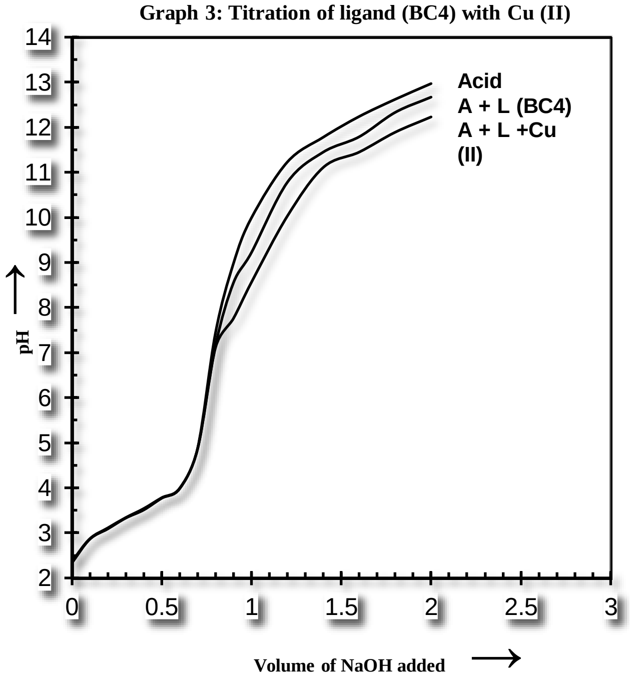
Vol. of NaOH added	Acid	A+L(BC3)	A+ L+ Cu (II)
0	2.37	2.34	2.34
0.1	2.87	2.86	2.86
0.2	3.11	3.09	3.09
0.3	3.34	3.33	3.33
0.4	3.54	3.51	3.51
0.5	3.78	3.77	3.77

0.6	3.99	3.98	3.98
0.7	4.87	4.86	4.86
0.8	7.44	7.16	7.11
0.9	8.98	8.55	7.76
1.0	9.99	9.22	8.56
1.2	11.23	10.78	10.03
1.4	11.78	11.45	11.11
1.6	12.24	11.79	11.45
1.8	12.62	12.33	11.89
2.0	12.97	12.67	12.23

Table 4: Titration data of ligand BC4 with Mn (II)

Vol. of NaOH added	Acid	A+ L (BC4)	A+ L+ Mn (II)
0	2.37	2.34	2.33
0.1	2.87	2.86	2.87
0.2	3.11	3.09	3.08
0.3	3.34	3.33	3.32
0.4	3.54	3.51	3.5
0.5	3.78	3.77	3.76
0.6	3.99	3.98	3.97
0.7	4.87	4.86	4.84
0.8	7.44	7.16	6.87
0.9	8.98	8.55	7.67
1.0	9.99	9.22	8.67
1.2	11.23	10.78	10.21
1.4	11.78	11.45	11.11
1.6	12.24	11.79	11.32
1.8	12.62	12.33	11.67
2.0	12.97	12.67	12.07

Graph 3: Titration of ligand (BC4) with Cu (II)



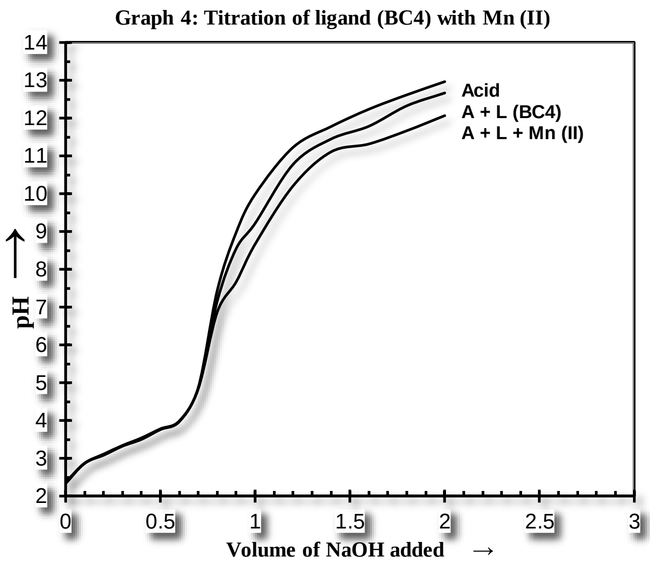


Table 1.1: Metal Complex Titration data:

Ligands	Metal ions	pH at Commencement of Hydrolysis (deviation of A + L curve from A acid curve)	pH at Commencement of Hydrolysis (deviation of A + L + M curve from A + L curve)
BC3	Cu (II)	7.01	6.56
	Mn (II)	7.01	6.45
BC4	Cu (II)	7.16	7.11
	Mn (II)	7.16	6.87

The departure of metal complex titration curve from reagent titration curve is seen at around pH 7. The pH of hydrolysis for all the metal ions under investigation was around pH = **7 to 7.6.**

The Pattern of Titration Curves:

The acids + ligand titration curves (A+L) are deviated from acid titration curves (A) for all systems at pH (4.87 for BC3), (4.86 for BC4) and continuously increased deviation up to pH (12.55 in BC3) and (12.67 in BC4). These kinds of deviations show the dissociation of -OH group of ligands. The present investigation consider the ligand (BC3 and BC4) having only one dissociable H^+ ion from -OH group.

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

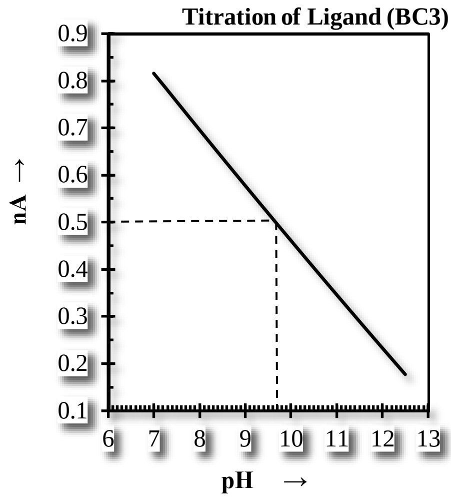
H = Acids, L = Ligand.

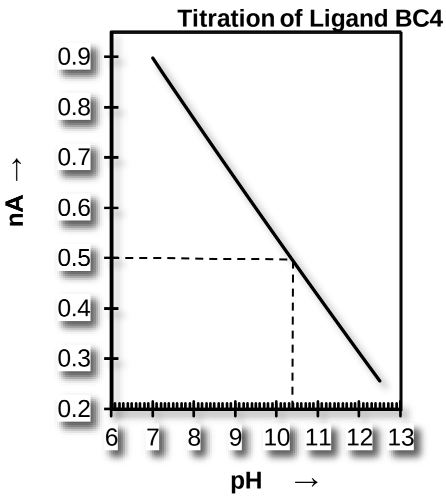
The (0.2 N) NaOH is used in the pH metric titration. The difference (V_2 and V_1) is estimated from the plot between the volume of NaOH and pH of the solution.

Calculation of proton-ligand formation number ($\bar{n}_A$):

$$\bar{n}_A = \gamma - \frac{(V_2 - V_1)(N + \varepsilon_0)}{(V_0 + V_1)T^0_L}$$

The values of $\bar{n}_A$ (average number of protons) were calculated along with the values of (V_2 - V_1) at various pH are presented in following graphs:





Graph 1. Titration of ligand (BC3)

Graph 2. Titration of ligand (BC3)

Proton-ligand stability constant:

There are many methods for calculating pK_1 and pK_2 values. Here we have used the half integral method for determination of pK_1 values. Naik[14] *et al* and Patil[38] used half integral method and calculated pK_1 and pK_2 values. The pK values were initially calculated from formation curves $\bar{n}_A$ versus pH. The values of pH were $\bar{n}_A$ = 0.5 correspond to the value of pK_1 for one dissociable group.

Table 1.1.1 Proton-ligand stability constant of BC3, and BC4 systems

Systems	**proton-ligand stability constant (pK) by half integral method**
BC3	9.7
BC4	10.4

Determination of metal-ligand stability constants:

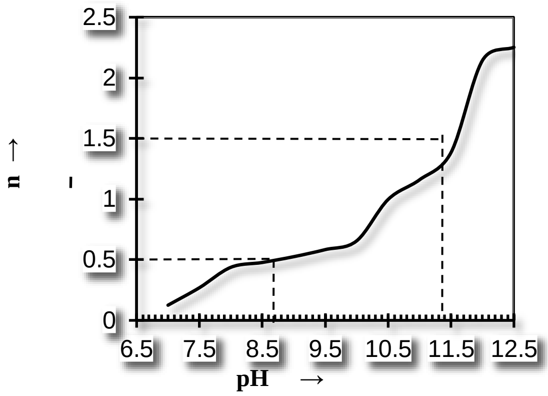
The stability constant of metal complex can be calculated by following $\bar{n}$ equation. $\bar{n}$ is defined as the average number of ligands bounds per metal atom and it can be calculated from the formula,

$$\bar{n} = \frac{(V_3 - V_2)(N + \varepsilon_0)}{(V_0 + V_2)\, \bar{n}_A\, T^0_M}$$

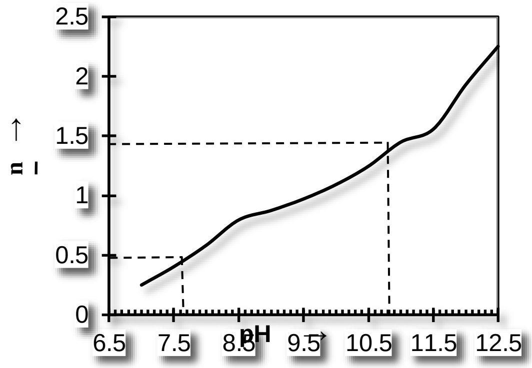
The value of $\bar{n}$ is corresponding pH value.

$$pL = \log\left[\frac{\left[H^+\right]}{K_L\left(T^0_L - T^0_M\left(\bar{n}\right)\right)}\right]$$

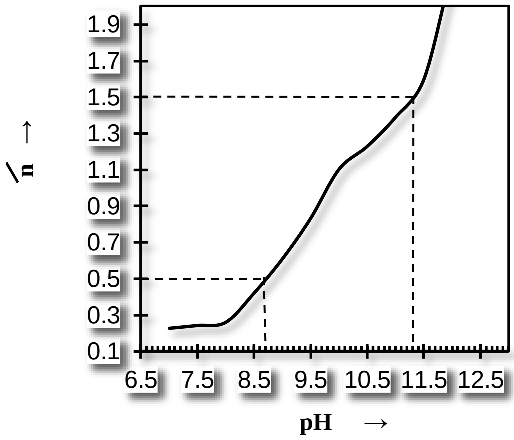
The plots of variation of $\bar{n}$ with pH that is metal-ligand formation curves are given in the graphs 3 to 6.



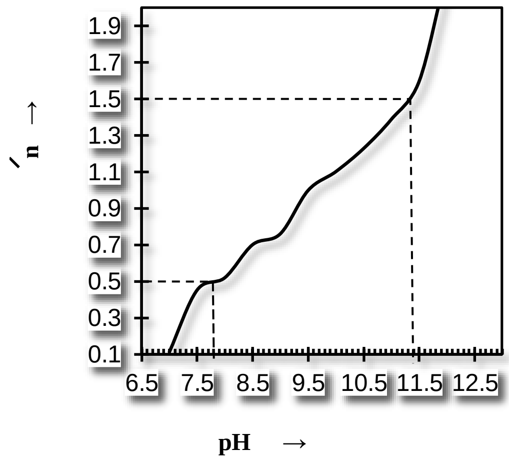
Graph 3. Ligand (BC3) with Cu (II)



Graph 4. Ligand (BC3) with Mn (II)



Graph 5. Ligand (BC4) with Cu (II)



Graph 6. Ligand (BC4) with Mn (II)

The pK values were calculated from formation curves of $\bar{n}$ versus pH. The value of pH was $\bar{n}$ = 0.5 which corresponds to the value of $\log K_1$ and the value of pH was $\bar{n}$ = 1.5 which corresponds to the value of $\log K_2$. The values of $\log K_1$ and $\log K_2$ of the complexes with metal ions were calculated by using half integral method:

Table 1.2 Metal-ligand stability constant $\log K_1$ and $\log K_2$ by half integral method

System	log K_1	log K_2	log K_1/ log K_2
Ligand (BC3) with Cu (II)	3.644	0.9546	2.689
Ligand (BC3) with Mn (II)	4.644	1.154	3.49
Ligand (BC4) with Cu (II)	4.443	1.953	2.49
Ligand (BC4) with Mn (II)	5.343	1.853	3.49

Result and discussion:

The proton-ligand stability constants (pK_1values) for substituted ligands were found to be 9.7 and 10.4 in BC3 and BC4 systems respectively. This is due to phenolic –OH group dissociating at 9.5 and above it in aqueous medium. The metal ligand stability constants log K1 and log K2 shows low stability at higher pH for 1:2 complexes as compare to 1:1 complex. Half cell configurations have more stability. From this tabulated data, it is observed that large difference between $\log K_1$ and $\log K_2$ values exhibits stepwise complex formation.

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