



PHYSICO-CHEMICAL STUDY OF FORMATION CONSTANT OF SOME TRANSITION METAL COMPLEXES WITH SCHIFF'S BASE LIGAND DERIVED FROM 2-ACETYLTHIOPHENE AND 2- HYDRAZINOBENZOIC ACID.

Bimlesh Kumar Yadav

Teacher,

Department of chemistry,

+2 High School, Chakka Pirri, Darbhanga, Bihar 846001(India)

Abstract: We study the synthesis of Schiff's base ligand 2-Thiophenyl Ethanal Phenyl hydrazone 2-Carboxylic acid and their metal complexes of divalent Cobalt, Nickel, Copper, Zinc and Cadmium.

Analytical study of metal salts were done by Half-integral method, Mid-point calculation method and straight line plot method. pH metric titration were carried out with the help of digital pH meter and stability constant of complexes of metal Co, Ni, Cu, Zn and Cd with ligand Synthesized were computed by Irving-Rossotti method modified by Calvin-Bjerrum.

The stability constant values of given metal were found to be in the order Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II).

This result is in arrangement with the natural order proposed by Irving -William.

Key Words: Divalent Cobalt, Nickel, Copper, Zinc and Cadmium, complex compounds of divalent metal, stability constant, Schiff's bases, Thermodynamic parameters, Irving-Rossotti titration technique, protonation constant.

I. INTRODUCTION

Schiff's base ligands and corresponding metal complexes have received much attention in recent years due to their wide uses as dyes, pigments, catalysts, intermediates in organic synthesis, polymer stabilizers and due to their broad range of biological activities, including anti-fungal, anti-bacterial, anti-malarial, anti-proliferative, anti-inflammatory, anti-viral and anti-pyretic properties^[1-4].

Schiff bases are named after Hugo Schiff (1834-1915), a German chemist. He discovered Schiff bases in 1864^[5] and other imines and was responsible for research into aldehydes and had the schiff test named after him. Fuschine was studied by Schiff as a schiff reagent in 1866 which was apparently used during the last decades of the 19th century for industrial dyes.

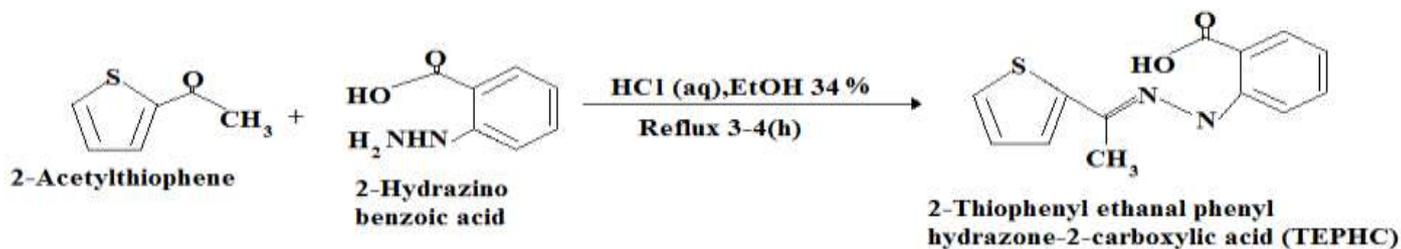
A well-known Schiff base ligand is a salen type^[6] with a bi-functional and tetra-dentate ligand. Several asymmetric salen-type Schiff bases were reported by R. Atkins^[7] in 1985. This paper deals the synthesis and study of stability constant of bi-valent transition metal complexes i.e. Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with novel Schiff base ligand TEPHC.

II. EXPERIMENTAL

Nitrate salts of divalent Co, Ni, Cu, Zn and Cd all were E. Merck. All other chemicals used were Anal R grade and used without further purification. Elemental analysis of metal salts were done by volumetric and gravimetric methods. All titration were carried out in the aqueous dioxane medium in the ratio 3:2(v/v). Dioxane was purified by standard method.

III. SYNTHESIS OF LIGAND (TEPHC)

TEPHC was synthesised by condensation reaction of 2-acetylthiophene and 2-hydrazino benzoic acid with ethyl esterification. The reaction mixture was refluxed in water bath for 3-hours and the precipitate were filtered and washed several times and recrystallized with absolute alcohol. The yield of product was very pure.



The pH metric titration curve of acid, acid + TEPHC and acid + TEPHC + metal ion solution were done at constant ionic strength 0.4(M) KNO_3 solution at $303 \pm 1\text{K}$ in inert atmosphere. The same process of titration was repeated for all the five metal (Co, Ni, Cu, Zn and Cd) ions. The colour change and appearance of turbidity at particular pH were recorded simultaneously. The variation in pH of solutions with each addition of alkali was recorded in Table 4.

IV. RESULT

Volume of all these reaction mixtures was made up to 25mL using 40% (v/v) aqueous- dioxane added separately in each set of the below reaction mixtures before making up the volume 25mL. The reaction mixtures for the pH metric titration of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of ligand 2-Thiophenyl ethanal phenyl hydrazone-2-carboxylic acid (TEPHC). The reaction mixtures in each set, solution(i), solution(ii) and solution(iii) were titrated individually against standard 0.4(N) NaOH.

Solution (i) : 1.00 mL 0.1(N) HNO_3 + 5 mL 0.1(M) KNO_3 + 19 mL aqueous dioxane.

Solution (ii): 1.00 mL 0.1(N) HNO_3 + 5 mL 0.1(M) KNO_3 + 17 mL aqueous dioxane + 2mL 0.0005(M) ligand (TEPHC) solution.

Solution (iii) : 1.00 mL 0.1(N) HNO_3 + 5 mL 0.1(M) KNO_3 + 16 mL aqueous dioxane + 2 mL 0.0005(M) ligand (TEPHC) solution + 1 mL metal salt solution.

[M(II) = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).]

Titration curves

pH-metric titration of acid, acid + ligand and acid + ligand + Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes against standard NaOH solution was carried out at a constant ionic strength 0.1(M) KNO_3 and at different temperatures ($293 \pm 1\text{K}$, $303 \pm 1\text{K}$ and $313 \pm 1\text{K}$) in aqueous -dioxane 40% (v/v) and titration curves obtained by plotting the pH values against the volume of alkali added to prepared solution (i), solution (ii) and solution (iii) to attain the same pH values are referred to a acid curve, ligand (TEPHC) curve and complex curve respectively. Figure 4.1, exhibit the titration curves of the M(II) -Co(II), Ni(II), Cu(II), Zn(II) and Cd (II) complexes with ligand TEPHC.

Each figure has the following seven curves (a) to(g).

Curve (a) : HNO_3

Curve (b) : HNO_3 + Ligand (TEPHC)

Curve (c) : HNO_3 + Ligand (TEPHC) + Co(II)

Curve (d) : HNO_3 + Ligand (TEPHC) + Ni(II)

Curve (e) : HNO_3 + Ligand (TEPHC) + Cu(II)

Curve (f) : HNO_3 + Ligand (TEPHC) + Zn(II)

Curve (g) : HNO_3 + Ligand (TEPHC) + Cd(II)

Table 4.1(a), pH metric titration results of the M(II) -Co(II), Ni(II), Cu(II), Zn(II) and Cd (II) complexes at $293 \pm 1\text{K}$ temperatures in aqueous-dioxane medium.

Ligand : TEPHC $\mu = 0.1$ (M) KNO_3

Vol. Of KOH (mL)	pH						
	Acid	Ligand	Metal				
			Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
0.00	3.50	3.50	3.50	3.50	3.50	3.50	3.50
0.15	3.60	3.50	3.60	3.60	3.60	3.60	3.40
0.30	4.50	3.55	3.70	3.70	3.70	3.30	3.20
0.45	8.50	4.10	4.30	4.20	4.00	3.75	3.30
0.60	10.00	5.00	4.50	4.50	4.50	4.00	3.80
0.75	10.50	8.50	5.00	5.00	5.00	4.50	4.00
0.90	10.80	9.50	6.50	6.30	6.20	5.50	4.50
1.05	11.00	10.00	7.00	6.50	6.30	6.00	5.00
1.20	11.25	10.25	8.00	8.00	8.00	6.50	5.20
1.35	11.40	10.50	9.00	9.00	9.00	7.00	5.50
1.50	11.50	10.60	9.50	9.50	9.50	7.50	6.00
1.65			10.00		10.00		
1.80			10.50				
1.95							

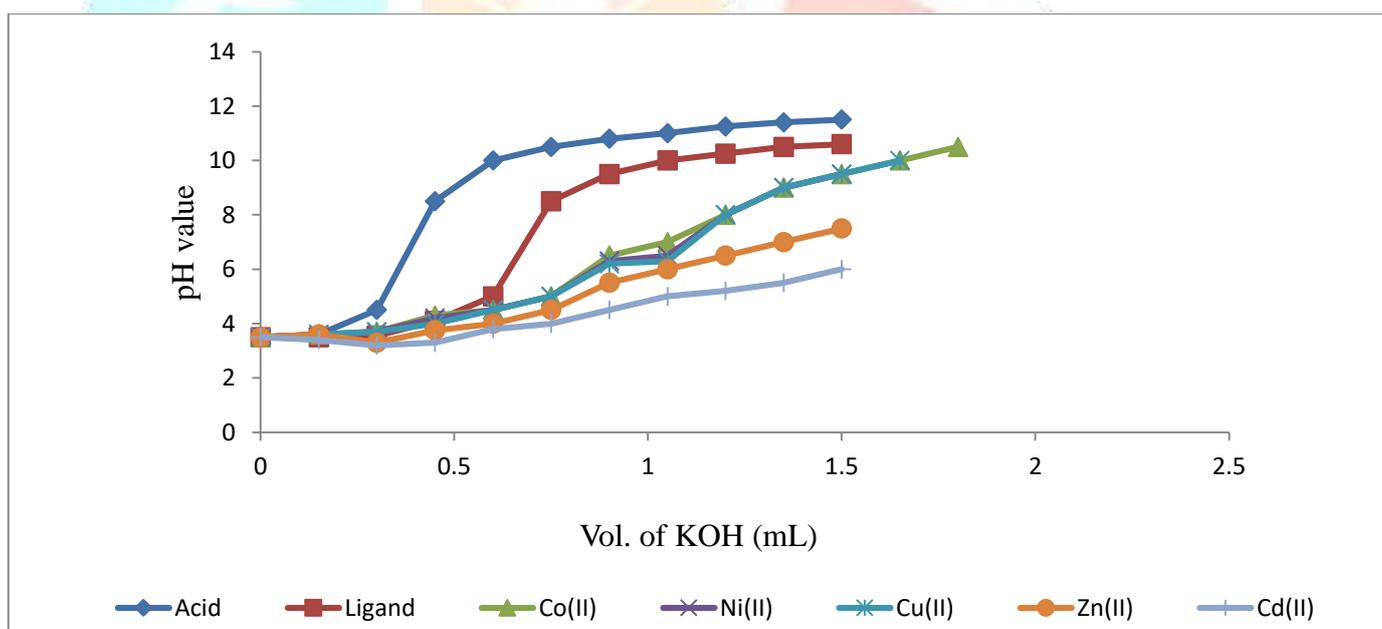


Figure 4.1 (a). pH metric titration curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at $293\pm 1K$ temperatures in aqueous- dioxane medium.

Figure 4.1(a) exhibits the titration curves in aqueous-dioxane medium at temperature $293\pm 1K$. It is observed from figure 4.1(a) ($293\pm 1K$) that the acid titration curve starts from pH 3.50 and extends to pH 11.50 while the ligand (TEPHC) curve is observed on the left side of the acid curve from pH 3.50 to 10.60. Shift of the ligand (TEPHC) curve at a lower pH with respect to the acid curve for the same value of alkali is probably due to acidic properties of the ligand (TEPHC) which has the tendency to accept a proton from the strongly acidic medium. At pH 3.55, the acid and ligand (TEPHC) curves converge and ligand (TEPHC) curve then starts diverging from the acid curve at pH 5.00. The divergence of ligand (TEPHC) curve from the acid curve indicates the protonation of the ligand (TEPHC) at that pH range. Only one inflection point is observed at pH range 4.50 to 10.60 in the titration curve of the ligand (TEPHC), showing that aqueous dioxane accepted only one proton at these pH ranges. Addition of the metal ion to the free ligand (TEPHC) solution results in shifting the buffer region of the ligand (TEPHC) to a lower pH value as observed in the complex curves having Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions, respectively. This observation suggests that complex formation proceeds by releasing protons from the base. A large decrease in pH for the metal titration curves relative to the ligand (TEPHC) curve might be attributed to strong metal-ligand (TEPHC) interaction. The metal-ligand (TEPHC) curves are well separated from the ligand (TEPHC) curve as shown by the figures. The Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complex

curves start diverging from the ligand (TEPHC) curve at pH 3.50, 3.50, 3.70, 3.60, and 3.50, respectively, showing that the respective metal-ligand (TEPHC) complexation started at these pH values.

Table 4.1 (b). pH metric titration result of M(II)-Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) complexes at 303±1K temperatures in aqueous-dioxane medium.

Ligand : TEPHC $\mu= 0.1$ (M) KNO₃

Vol. of KOH (mL)	pH						
	Acid	Ligand	Metal				
			Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
0.00	3.50	3.50	3.50	3.50	3.50	3.50	3.50
0.15	3.65	3.60	3.55	3.50	3.50	3.50	3.40
0.30	4.55	3.70	3.65	3.65	3.60	3.55	3.55
0.45	8.55	4.30	4.25	4.15	3.95	3.70	3.65
0.60	10.05	4.55	4.45	4.40	4.35	4.05	3.75
0.75	10.55	7.95	4.95	4.90	4.75	4.45	3.90
0.90	10.85	9.00	6.45	6.25	6.15	5.55	4.45
1.05	11.05	9.50	6.95	6.45	6.25	6.05	4.95
1.20	11.30	10.20	7.95	7.90	7.90	6.45	5.15
1.35	11.45	10.45	8.95	8.90	7.95	7.05	5.45
1.50	11.55	10.70	9.45	9.40	9.35	7.55	5.95
1.65			9.95		9.40		
1.80			10.45				
1.95							

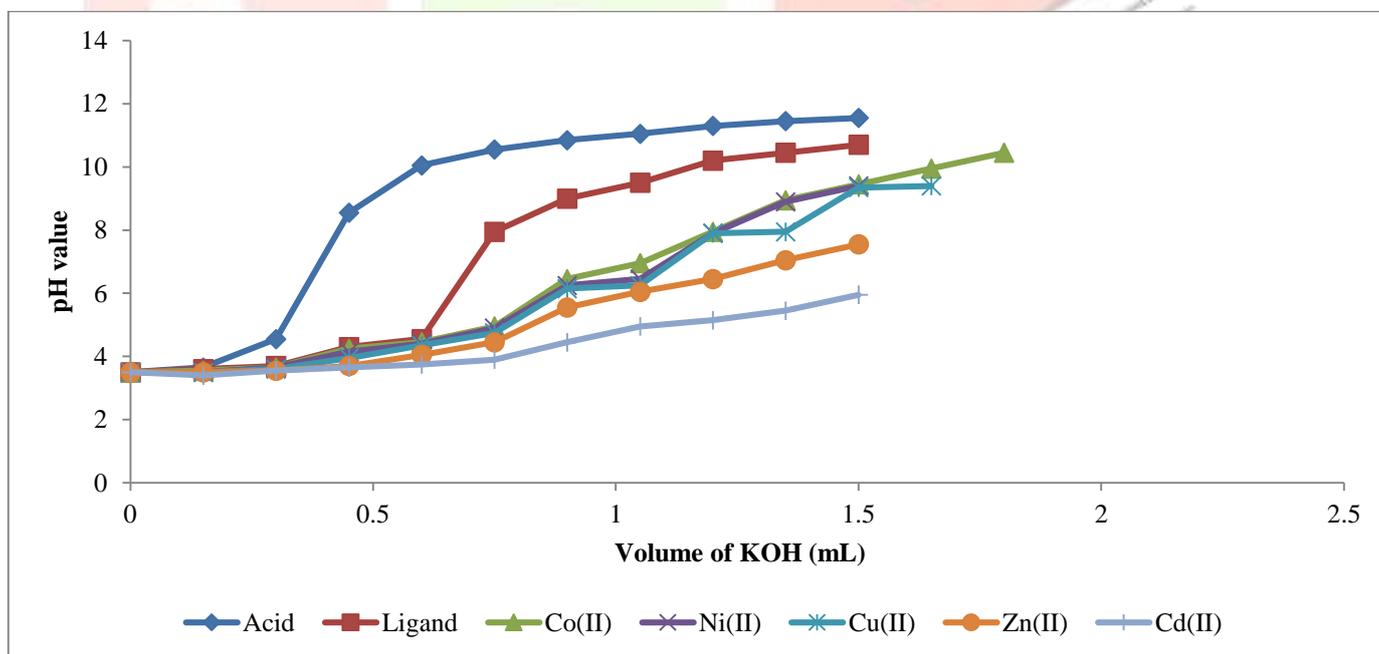


Figure 4.1 (b). pH metric titration curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 303±1K temperatures in aqueous- dioxane medium.

Figure 4.1 (b) exhibits the titration curves in aqueous-dioxane medium at temperature 303±1K. It is observed from figure 4.1(b) (303±1K) that the acid curve starts from pH 3.50 and extends to pH 11.55 while the ligand (TEPHC) curve is observed on the left side of the acid curve from pH 3.50 to 10.70. Shift of the ligand (TEPHC) curve at a lower pH with respect to the acid curve for the same which has the tendency to accept a proton from the strongly acidic medium. At pH 3.60, the acid and ligand (TEPHC) curves converge and the ligand (TEPHC) curve then starts diverging from the acid curve at pH 4.55. The divergence of the ligand (TEPHC)

curve from the acid curve indicates the protonation of the ligand (TEPHC) at that pH range. Only one inflection point is observed at pH ranges 4.50 to 10.70 in the titration curve of the ligand (TEPHC), showing that aqueous dioxane accepted only one proton at these pH ranges. Addition of metal ion to the free ligand (TEPHC) solution results in shifting the buffer region of the ligand (TEPHC) to a lower pH value as observed in the complex curves having Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions respectively. This observation suggests that complex formation proceeds by releasing protons from the base. A large decrease in pH for the metal titration curves relative to ligand (TEPHC) curve might be attributed to strong metal-ligand (TEPHC) interaction. The metal-ligand (TEPHC) curves are well separated from ligand (TEPHC) curve as shown by the figures. The Co(II), Ni(II), Cu(II) Zn(II) and Cd(II) complex curves start diverging from the ligand (TEPHC) curve at pH 3.50, 3.55, 3.65, 4.25, and 4.00, respectively, showing that the respective metal-ligand (TEPHC) complexation started at these pH values.

Table 4.1 (c). pH metric titration result of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 313±1K temperatures in aqueous- dioxane medium.

Ligand : TEPHC $\mu= 0.1$ (M) KNO_3

Vol. of KOH (mL)	pH						
	Acid	Ligand	Metal				
			Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
0.00	3.50	3.50	3.50	3.50	3.50	3.50	3.50
0.15	3.60	3.55	3.50	3.50	3.45	3.45	3.45
0.30	4.50	3.65	3.60	3.60	3.50	3.45	3.45
0.45	8.50	4.25	4.20	4.10	3.90	3.65	3.55
0.60	10.00	4.50	4.40	4.35	4.30	4.00	3.70
0.75	10.50	7.90	4.90	4.85	4.85	4.40	3.90
0.90	10.80	8.95	6.40	6.20	6.10	5.50	4.40
1.05	11.00	9.90	6.90	6.40	6.20	6.00	4.90
1.20	11.25	10.15	7.90	7.85	7.80	6.40	5.10
1.35	11.40	10.40	8.90	8.85	7.90	7.00	5.40
1.50	11.50	10.65	9.40	9.35	9.30	7.50	5.90
1.65	11.60		9.90		9.35		
1.80			10.40				
1.95							

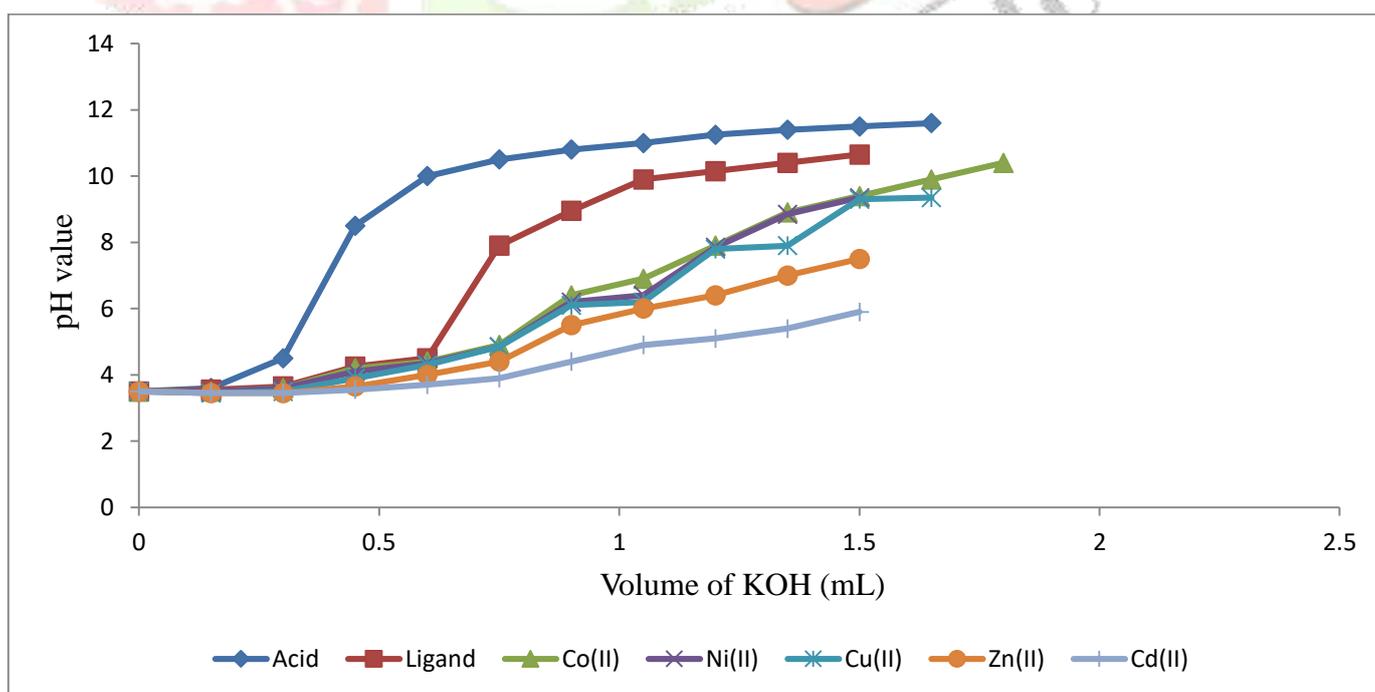


Figure 4.1 (c). pH metric titration curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 313±1K temperatures in aqueous- dioxane medium.

Figure 4.1 (c) exhibits the titration curves in aqueous-dioxane medium at temperature $313\pm 1\text{K}$. It is observed from figure 4.1 (c) ($313\pm 1\text{K}$) that the acid titration curve starts from pH 3.50 and extends to pH 11.60 while the ligand (TEPHC) curve is observed on the left side of the acid curve from pH 3.60 to 10.65. Shift of the ligand (TEPHC) curve at a higher pH with respect to the acid curve for the same volume of alkali is probably due to the acidic properties of the ligand (TEPHC) which has the tendency to accept a proton from the strongly acidic medium. At pH 3.55, the acid and ligand (TEPHC) curves converge and the ligand (TEPHC) curve then starts diverging from the acid curve at pH 4.00. The divergence of the ligand (TEPHC) curve from the acid curve indicates the protonation of the ligand (TEPHC) at that pH range. Only one inflection point is observed at pH ranges 4.50 to 10.00 in the titration curve of the ligand (TEPHC), showing that aqueous dioxane accepted only one proton at these pH ranges. Addition of metal ion to the free ligand (TEPHC) solution results in shifting the buffer region of the ligand (TEPHC) to a lower pH value as observed in the complex curves having Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions, respectively. This observation suggests that complex formation proceeds by releasing proton(s) from the base. A large decrease in pH for the metal titration curves relative to the ligand (TEPHC) curve might be attributed to strong metal – ligand (TEPHC) interaction. The metal – ligand (TEPHC) curves are well separated from the ligand (TEPHC) curve as shown by the figures. The titration was continued till the reaction mixture turned turbid. The turbidity is due to the formation of hydroxo complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions which started at pH 3.55, 4.55, 5.55, 5.00 and 4.50 respectively. It was not possible to extend the investigation beyond these pH, since the formation of hydroxo complex species is likely to disturb the postulated metal – ligand (TEPHC) equilibrium. The titration curves at $303\pm 1\text{K}$ and $313\pm 1\text{K}$ show similar pattern though the pH ranges at which the protonation of the ligand (TEPHC), the metal – ligand (TEPHC) complexation and metal-hydroxo formation occurred, are different.

Table 4.2(a). Value of $\bar{n}A$ of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at $293\pm 1\text{K}$ temperatures in aqueous-dioxane medium.

T= $293\pm 1\text{K}$

pH	$\bar{n}A$				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
6.40	1.01	0.94	0.87	0.84	0.80
6.70	0.98	0.94	0.87	0.83	0.79
7.10	0.97	0.95	0.86	0.82	0.78
7.20	0.96	0.96	0.85	0.82	0.77
7.45	0.95	0.96	0.85	0.82	0.75
7.70	0.95	0.92	0.84	0.81	0.73
8.10	0.95	0.92	0.83	0.81	0.72
8.45	0.95	0.91	0.81	0.80	0.71
9.10	0.94	0.89	0.74	0.72	0.70
9.10	0.91	0.81	0.71	0.71	0.79
9.20	0.86	0.71	0.44	0.61	0.51
9.50	0.74	0.61	0.31	0.41	0.31
10.10	0.61	0.41		0.31	
10.15	0.34	0.31			

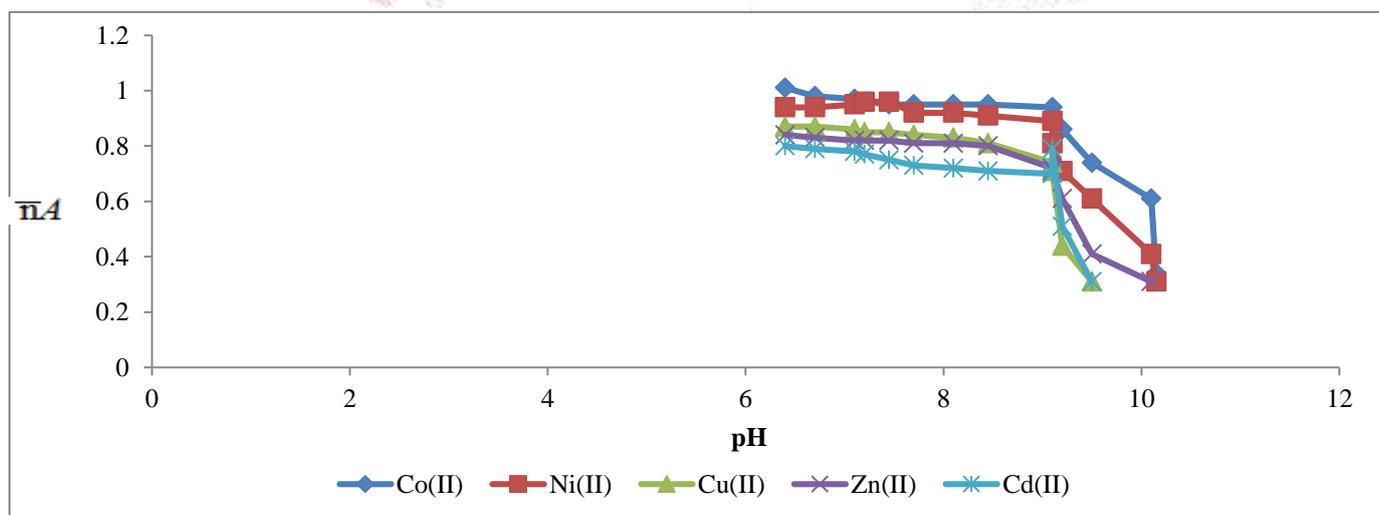


Figure 4.2 (a). Formation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at $293\pm 1\text{K}$ temperatures in aqueous-dioxane medium.

Table 4.2 (b). Value of \bar{n}_A of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at $303\pm 1\text{K}$ temperatures in aqueous-dioxane medium.T= $303\pm 1\text{K}$

pH	\bar{n}_A				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
6.40	1.00	0.98	0.87	0.81	0.80
6.70	0.98	0.95	0.87	0.80	0.75
6.10	0.97	0.94	0.86	0.79	0.70
7.45	0.96	0.93	0.85	0.78	0.65
7.70	0.95	0.91	0.84	0.77	0.60
8.10	0.94	0.90	0.83	0.76	0.55
8.45	0.92	0.88	0.80	0.75	0.50
9.10	0.91	0.87	0.74	0.72	0.45
9.10	0.91	0.85	0.70	0.70	0.40
9.20	0.90	0.80	0.44	0.68	0.35
9.50	0.86	0.70	0.30	0.61	0.30
10.10	0.74	0.60	0.26	0.40	0.25
10.25	0.61	0.40		0.30	
	0.30	0.30			1.01

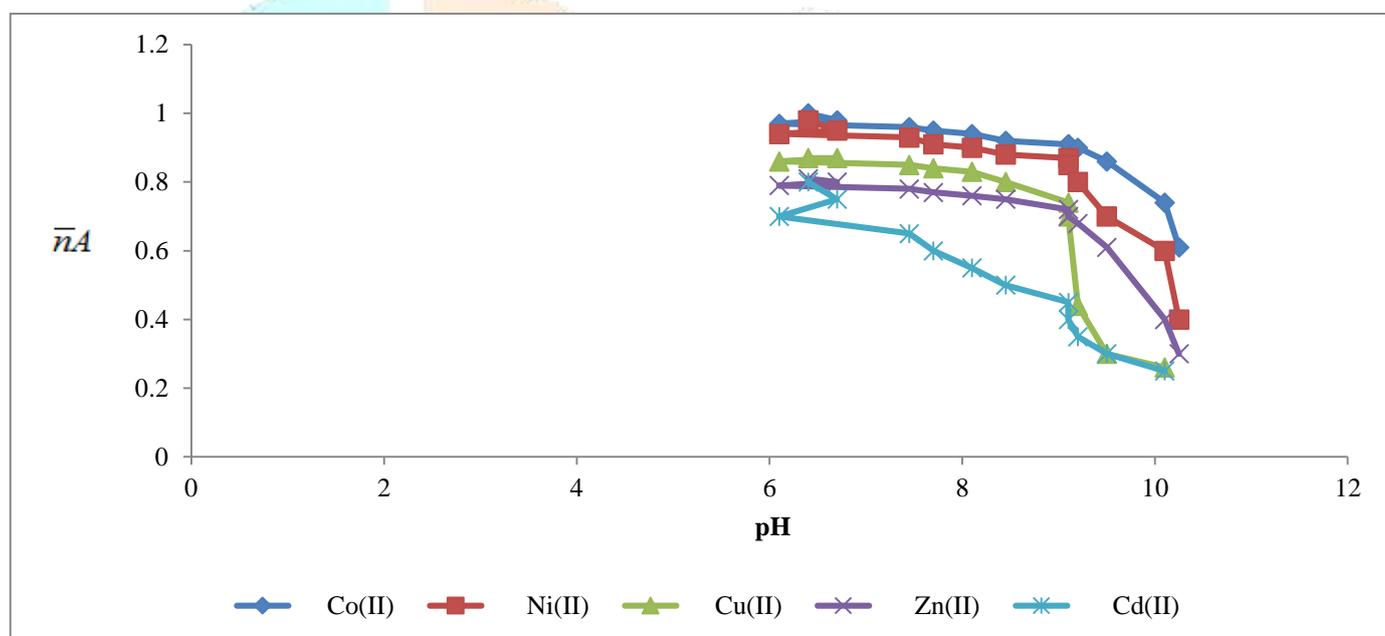
**Figure 4.2 (b).** Formation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at $303\pm 1\text{K}$ temperatures in aqueous- dioxane medium.

Table 4.2 (c). Value of $\bar{n}A$ of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 313±1K temperatures in aqueous-dioxane medium.

T=313±1K

pH	$\bar{n}A$				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
6.40	1.00	0.98	0.87	0.81	0.80
6.60	0.97	0.95	0.86	0.80	0.73
6.10	0.97	0.93	0.85	0.79	0.70
7.40	0.96	0.92	0.84	0.78	0.66
7.65	0.95	0.91	0.83	0.77	0.62
8.10	0.93	0.90	0.82	0.76	0.54
8.40	0.92	0.89	0.81	0.75	0.51
9.00	0.91	0.86	0.75	0.72	0.46
9.10	0.90	0.85	0.72	0.70	0.40
9.15	0.85	0.82	0.44	0.68	0.35
9.45	0.83	0.72	0.30	0.81	0.30
10.95	0.72	0.63	0.26	0.40	0.25
10.25	0.61	0.41		0.30	
	0.30	0.30			1.01

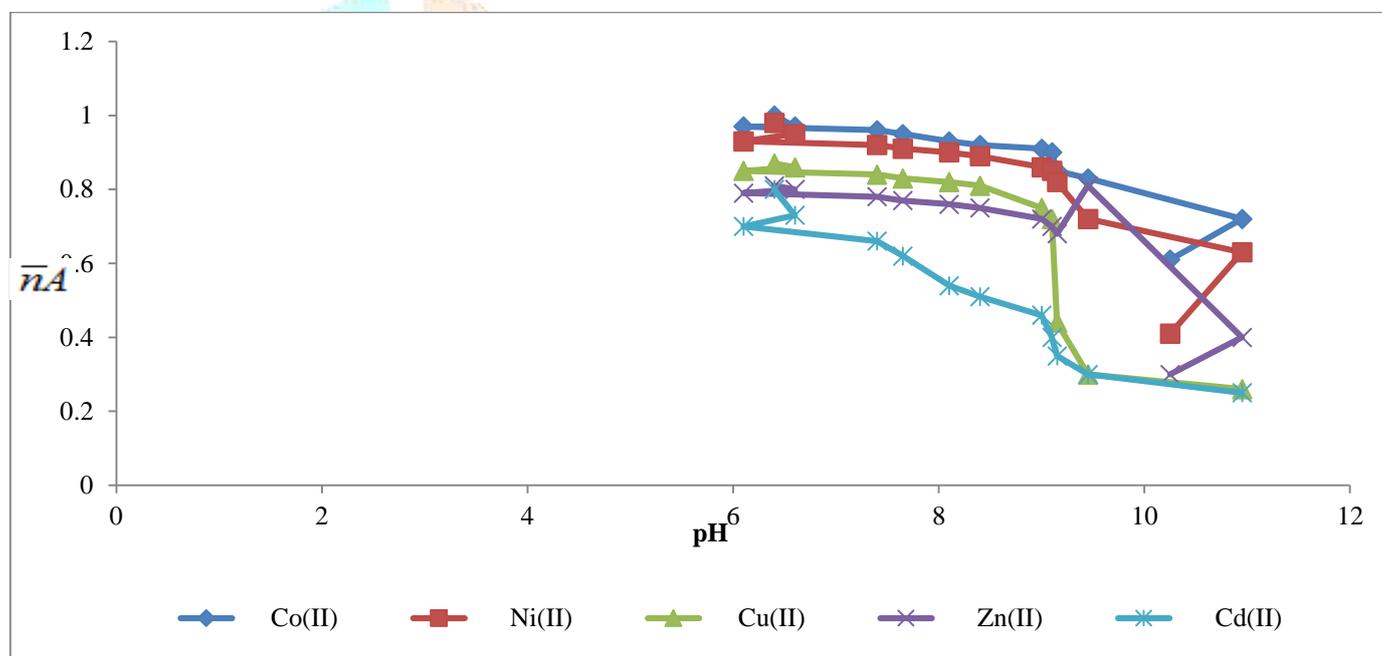


Figure 4.2 (c). Formation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 313±1K temperatures in aqueous-dioxane medium.

Table 4.3(a). Protonation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 293±1K temperatures in aqueous- dioxane medium.

pL	$Log \frac{2-\bar{n}A}{\bar{n}A-1}$				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
7.45	1.00	0.84	0.84	0.65	0.74
7.70	0.97	0.85	0.95	0.69	0.75
8.05	0.98	0.83	0.84	0.70	0.80
8.20	0.96	0.81	0.85	0.71	0.76
8.45	0.95	0.82	0.89	0.70	0.71
8.70	0.94	0.83	0.90	0.65	0.69
8.95	0.91	0.80	0.91	0.60	0.65
9.20	0.91	0.81	0.89	0.51	0.52
9.45	0.90	0.78	0.87	0.45	0.50
9.70	0.90	0.80	0.85	0.40	0.46
9.80	0.85	0.74	0.83	0.39	0.44
10.05	0.75	0.73	0.80	0.35	0.35
10.20	0.70	0.72	0.75	0.30	0.36
10.45	0.65	0.70	0.65	0.25	0.32
10.70	0.45	0.65	0.60	0.20	0.30
10.95	0.35	0.50	0.55	0.20	0.25
11.20	0.30	0.35	0.50	0.15	0.20

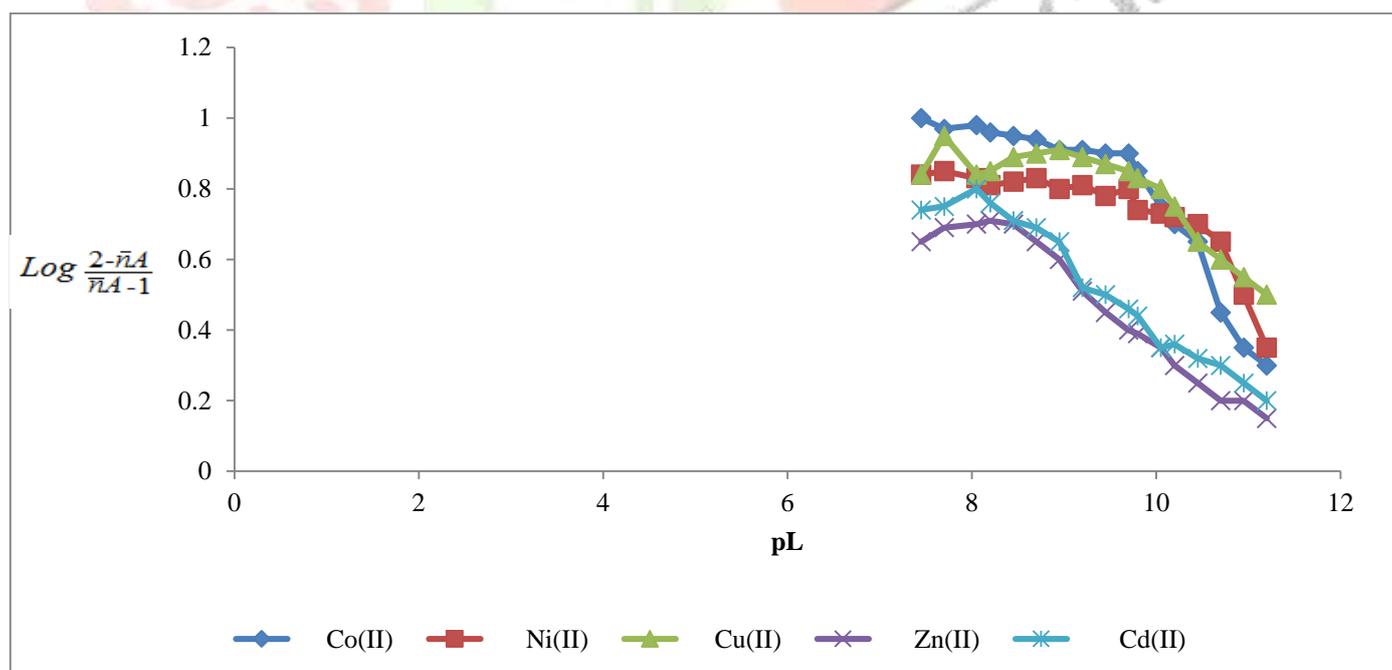
**Figure 4.3(a).** Protonation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 293±1K temperatures in aqueous- dioxane medium.

Table 4.3(b). Protonation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 303±1K temperatures in aqueous- dioxane medium.

pL	$Log \frac{2 - \bar{n}A}{\bar{n}A - 1}$				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
7.45	0.85	0.79	0.94	0.68	0.75
7.65	0.860	0.78	0.94	0.70	0.77
8.00	0.84	0.77	0.95	0.75	0.80
8.20	0.87	0.76	0.94	0.74	0.79
8.40	0.86	0.75	0.94	0.72	0.75
8.65	0.85	0.74	0.92	0.68	0.72
8.90	0.84	0.70	0.90	0.65	0.70
9.15	0.83	0.68	0.86	0.60	0.67
9.40	0.82	0.65	0.83	0.58	0.65
9.65	0.87	0.62	0.80	0.53	0.61
9.75	0.72	0.57	0.75	0.50	0.57
10.00	0.65	0.50	0.70	0.45	0.52
10.15	0.50	0.45	0.58	0.40	0.46
10.90			0.50		0.41
11.05			0.41		0.35

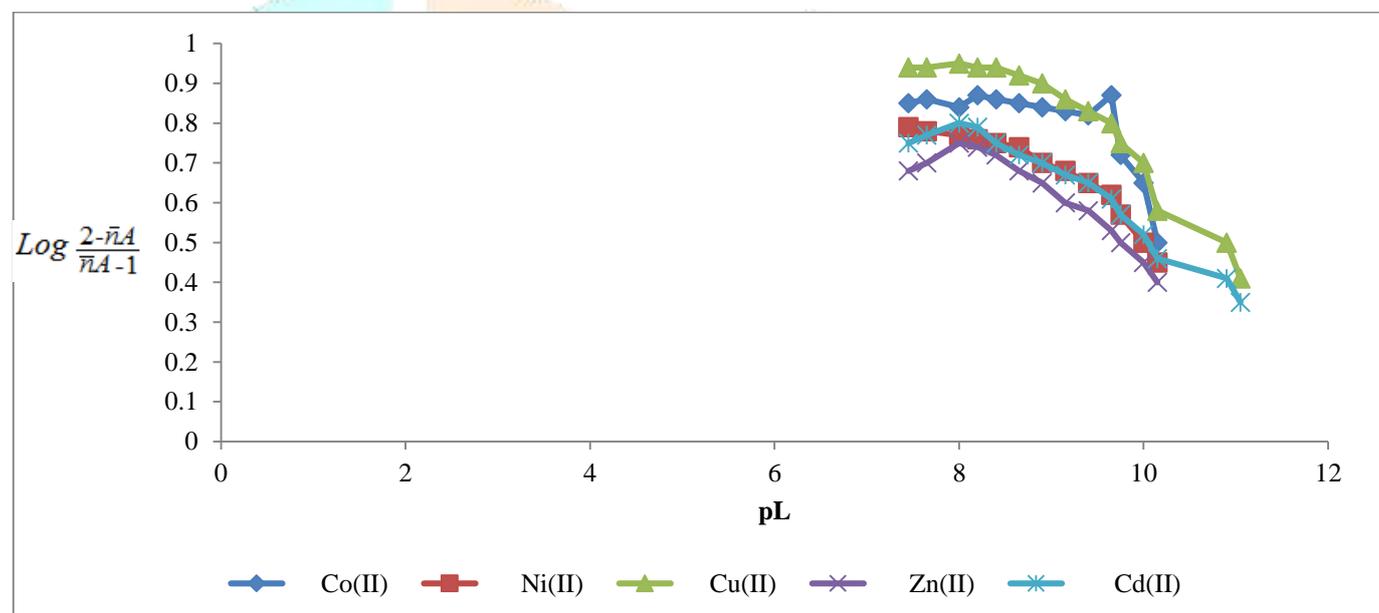
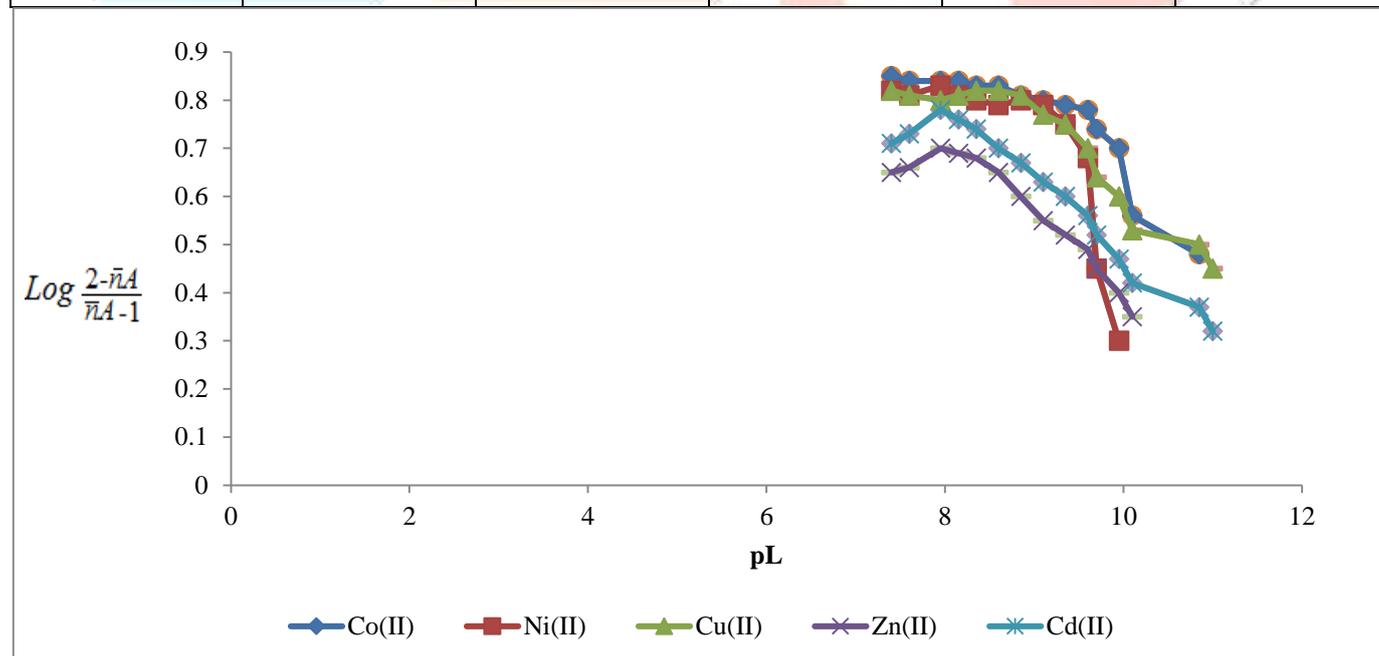


Figure 4.3(b). Protonation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 303±1K temperatures in aqueous- dioxane medium.

Table 4.3(c). Protonation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 313±1K temperatures in aqueous- dioxane medium.

pL	$Log \frac{2-\bar{n}A}{\bar{n}A-1}$				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
7.40	0.85	0.82	0.82	0.65	0.71
7.60	0.84	0.81	0.81	0.66	0.73
7.95	0.84	0.83	0.80	0.70	0.78
8.15	0.84	0.81	0.81	0.69	0.76
8.35	0.83	0.80	0.82	0.68	0.74
8.60	0.83	0.79	0.82	0.65	0.70
8.85	0.81	0.80	0.81	0.60	0.67
9.10	0.80	0.79	0.77	0.55	0.63
9.35	0.79	0.75	0.75	0.52	0.60
9.60	0.78	0.68	0.70	0.49	0.56
9.70	0.74	0.45	0.64	0.45	0.52
9.95	0.70	0.30	0.60	0.40	0.47
10.10	0.56		0.53	0.35	0.42
10.85	0.48		0.50		0.37
11.00			0.45		0.32

**Figure 4.3(c).** Protonation curves of M(II)-Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at 313±1K temperatures in aqueous- dioxane medium.

4.3. Proton-ligand stability constant

The protonation curves of TEPHC at three different temperatures (293±1K, 303±1K and 313±1K) in aqueous-dioxane, TEPHC are obtained by plotting $\bar{n}A$, the average number of proton attached per ligand (TEPHC) vs pL.

The figures show that the protonation curves extend from 0.2 to 1.0 on the $\bar{n}A$ scale showing that only one proton was dissociated from the ligand (TEPHC) in aqueous dioxane. The dissociation constants ($log K^H$) of the ligand (TEPHC) at different temperatures was evaluated from the curves using Bjerrum's half integral method [8].

4.4. Metal-ligand (TEPHC) stability constant

The average number of ligand (TEPHC) attached per metal ion, \bar{n}_A and the free ligand (TEPHC) exponent, pL are calculated by using the expression given by Irving and Rossotti. The metal-ligand (TEPHC) formation curves at different temperatures obtained by plotting the values of \bar{n}_A against pL and are shown in Figures 4.4(a), 4.4(b) and 4.4(c).

Table 4.4(a). Metal-ligand formation curve of TEPHC-complex curve in aqueous dioxane medium at 293±1K.

pL	$Log \frac{2-\bar{n}_A}{\bar{n}_A-1}$					
	Ligand	Metal				
		Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
5.27	0.85	0.94	0.63	0.57	0.68	0.75
5.30	0.70	0.65	0.50	0.50	0.55	0.65
5.33	0.56	0.54	0.32	0.35	0.42	0.60
5.40	0.50	0.30	0.22	0.26	0.34	0.50
5.65	0.40	0.18	0.20	0.20	0.25	0.45
5.80	0.35	0.10	0.15	0.10	0.16	0.40
6.24				0.05	0.10	0.38
6.28					0.05	0.35

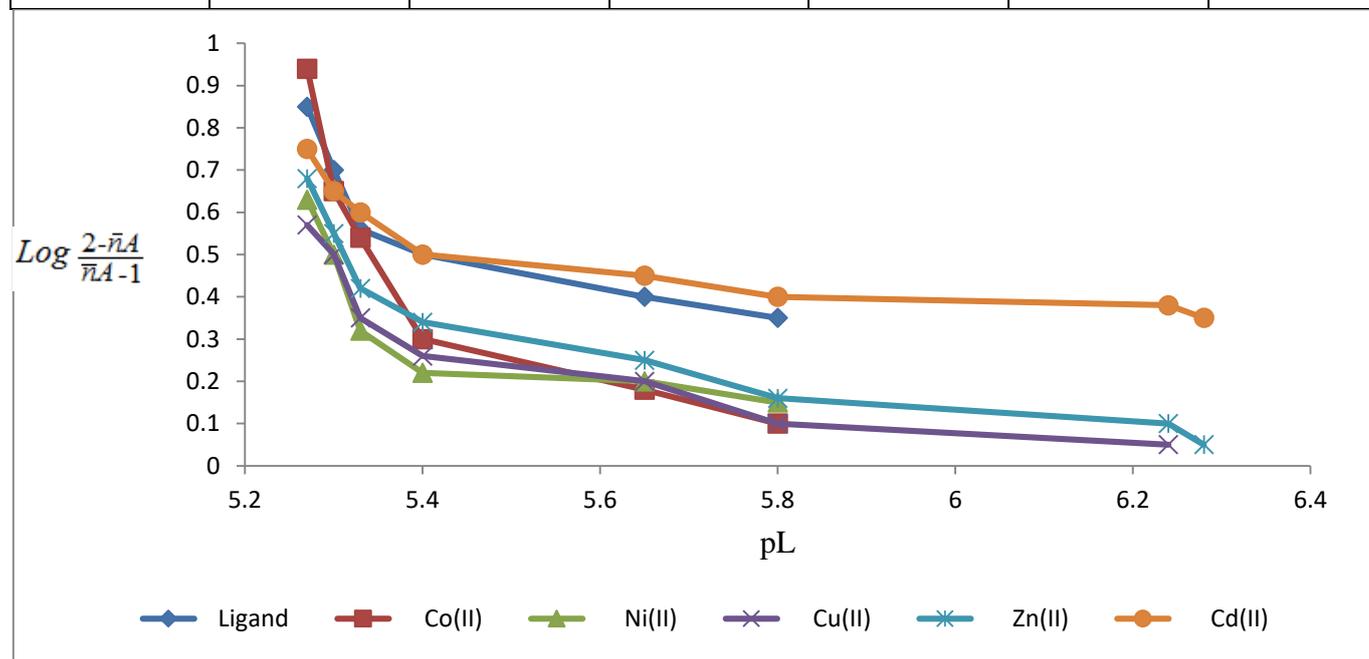


Figure 4.4(a). Metal-ligand formation curve of TEPHC-complex curve in aqueous dioxane medium at 293±1K.

Table 4.4(b). Metal-ligand formation curve of TEPHC-complex curve in aqueous dioxane medium at 303±1K.

pL	$Log \frac{2-\bar{n}_A}{\bar{n}_A-1}$					
	Ligand	Metal				
		Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
5.26	0.86	0.93	0.64	0.56	0.69	0.89
5.31	0.71	0.64	0.49	0.49	0.56	0.64
5.34	0.57	0.53	0.31	0.34	0.43	0.54
5.41	0.51	0.29	0.23	0.25	0.35	0.46
5.66	0.40	0.17	0.19	0.19	0.26	0.39
5.81	0.36	0.09	0.16	0.09	0.17	0.37
6.25				0.01	0.09	0.34
6.26					0.03	0.39

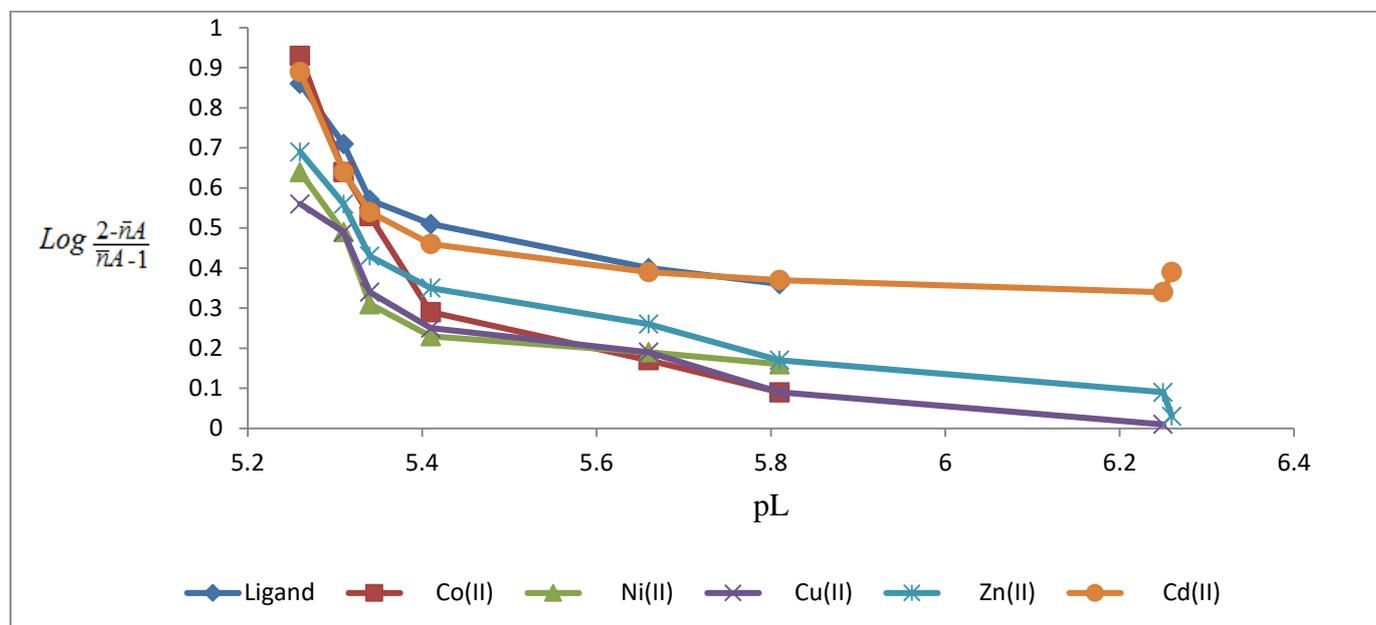


Figure 4.4(b). Metal-ligand formation curve of TEPHC-complex curve in aqueous dioxane medium at 303±1K.

Table 4.4(c). Metal-ligand formation curve of TEPHC-complex curve in aqueous dioxane medium at 313±1K.

pL	$Log \frac{2-\bar{n}A}{\bar{n}A-1}$					
	Ligand	Metal				
		Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
5.24	0.87	0.95	0.62	0.54	0.70	0.91
5.29	0.72	0.66	0.47	0.47	0.57	0.66
5.32	0.58	0.55	0.29	0.32	0.44	0.56
5.39	0.52	0.31	0.21	0.23	0.36	0.48
5.64	0.41	0.19	0.17	0.17	0.27	0.41
5.78	0.37	0.11	0.14	0.07	0.16	0.39
5.83				0.01	0.10	0.36
6.26					0.04	0.41

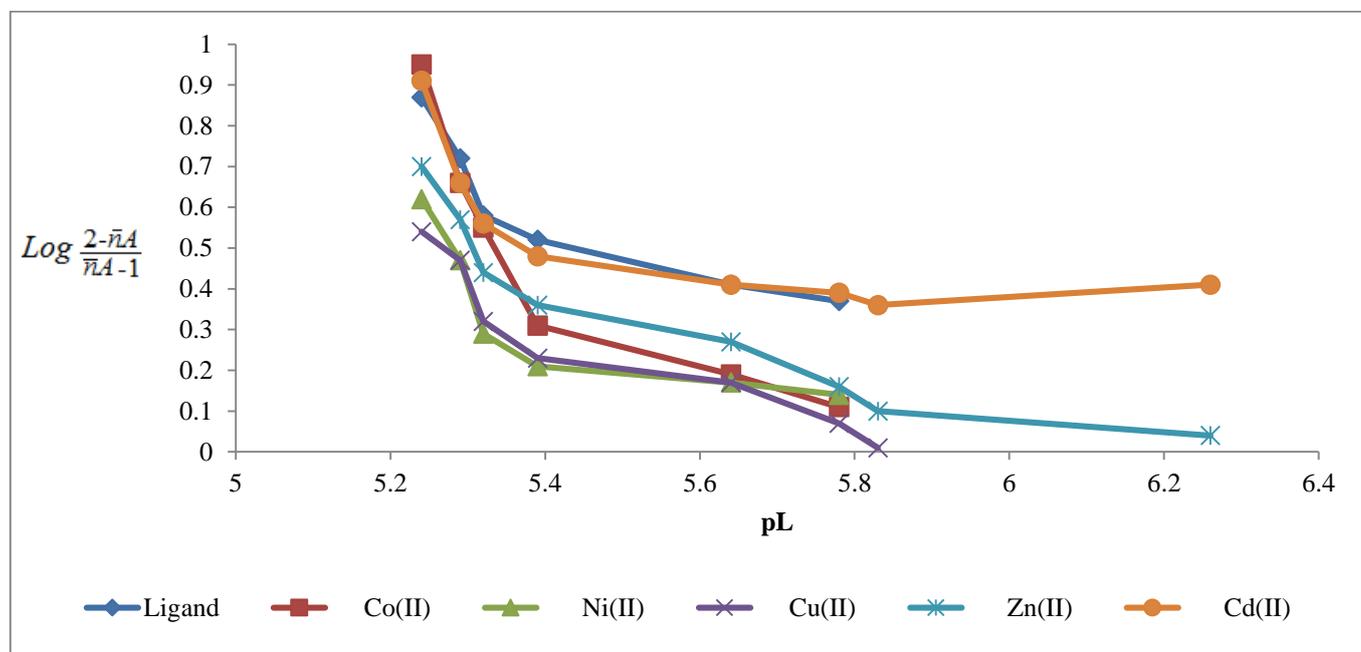


Figure 4.4(c). Metal-ligand formation curve of TEPHC-complex curve in aqueous dioxane medium at 313±1K.

An analysis of the metal – ligand (TEPHC) formation curves at various temperatures indicates that the ligand (TEPHC) formed complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions at different pH ranges. However, the values of \bar{n} ($0.1 < \bar{n} < 1.5$) for all the complexes at different temperatures in aqueous dioxane media, would suggest that TEPHC formed only 1:1 metal-ligand (TEPHC) complexes with the metal ions. It has been observed from the figures that the maximum value of $\bar{n}A$ obtained for all complexes is 1.04. The stability constant of the complexes in aqueous-dioxane, evaluated from the formation curves employing Bjerrum's half integral method and are also included in Table 4.2(a), 4.2(b) and 4.2(c). The table shows that at all temperatures, there is a gradual decrease in $\log K^M$ value from Co(II) < Ni(II) < Cu(II) < Zn(II) < Cd(II) where the trend follows: Cu(II) < Ni(II) < Co(II) < Zn(II) < Cd(II).

A gradual decrease in the stability constants of the complexes in aqueous-dioxane media with an increase in temperature is also observed showing that the complexation reactions were exothermic in nature and hence favourable at lower temperature. This behaviour might also be ascribed to the thermal hydrolysis of the metal complexes^[9].

At a constant temperature, the stability constants of the complexes in aqueous-dioxane, fall in the Irving-Williams order^[10]. The values of stability constants of the Cu(II) complex are higher than those of Ni(II) and Cd(II) complexes. The extra stabilization of the Cu(II) complex could be attributed to the unique electronic configuration on Cu²⁺ and the Jahn-Teller effect^[11].

4.5. Thermodynamic parameters

The thermodynamic parameters associated with the protonation and complexation at ionic strength 0.1 (M) KNO₃ are also studied. The change in free energy (ΔG) is calculated from the formation constant values ($\log K$) at various temperatures using the temperature coefficients and Gibb's Helmholtz equation^[12]. The change in enthalpy (ΔH) for the protonation and complexation reactions of the ligand (TEPHC) in aqueous-dioxane media is evaluated from the slope of the plots and these values are used for calculating the ΔS values associated with above reactions. The thermodynamic parameters thus obtained for the protonation and complexation reactions of 40% (v/v) aqueous-dioxane.

Formula for the calculation of ΔG , ΔH and ΔS :

$$1. \Delta G^\circ = \Delta H^\circ - T\Delta S \quad (1)$$

$$\Delta G^\circ = -RT \ln K$$

$$2. \Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T} \quad (2)$$

Table 4.5 : Value of Log K of stability constant computed by three methods.

Temperature	Log K						
	Method	Ligand	Metal				
			Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
293±1K	a	10.90	10.60	10.30	9.90	9.75	8.65
	b	10.80	10.50	10.20	9.80	9.65	8.55
	c	10.70	10.40	10.10	9.70	9.55	8.45
303±1K	a	10.10	9.90	9.70	9.50	9.40	8.40
	b	10.00	9.80	9.60	9.40	9.30	8.30
	c	9.90	9.70	9.50	9.30	9.20	8.20
313±1K	a	9.60	9.50	9.40	9.10	9.15	8.10
	b	9.50	9.45	9.30	9.15	9.10	8.00
	c	9.40	9.30	9.20	9.05	8.90	7.90

Table 4.6 : Stepwise stability constant value

Temperature	Log K					
	Ligand	Metal				
		Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
293±1K	10.80	10.50	10.20	9.80	9.60	8.55
303±1K	10.00	9.80	9.60	9.40	9.30	8.50
313±1K	9.50	9.50	9.30	9.15	9.05	8.00

Table 4.7. Protonation constant ($\log K^H$) of TEPHC and stability constants ($\log K^M$) of 1:1 M(II)-chelates at different temperatures in 40%(v/v) aqueous-dioxane.

Medium	Temperature	$\log K^H$	$\log K^M$				
			Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
Aqueous-dioxane	293±1K	11.18±0.01	5.65±0.10	5.55±0.10	5.45±0.10	5.89±0.01	9.09±0.01
	303±1K	11.01±0.01	5.22±0.08	5.20±0.08	5.15±0.08	5.47±0.07	8.82±0.07
	313±1K	10.71±0.02	5.18±0.02	5.15±0.02	5.10±0.02	5.34±0.02	7.79±0.06

Table 4.8. Thermodynamic parameters of 1:1 M(II)- Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) chelates at different temperatures in 40% (v/v) aqueous-dioxane.

Medium	M(II)-complexes	$-\Delta G^*$ ($\text{kJ}\cdot\text{mol}^{-1}$)			$-\Delta H^*$ ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS^* ($\text{J}\cdot\text{deg}^{-1}\cdot\text{mol}^{-1}$)
		293±1K	303±1K	313±1K		
40% (v/v) Aqueous-dioxane	Co(II)	30.31±0.03	30.35±0.04	31.40±0.01	30.33±0.02	20.30±0.03
	Ni(II)	30.70±0.02	31.82±0.02	30.89±0.01	30.48±0.09	21.87±0.03
	Cu(II)	30.47±0.04	30.83±0.02	46.24±0.01	30.60±0.02	22.57±0.02
	Zn(II)	29.32±0.02	29.39±0.07	29.40±0.02	30.70±0.01	25.35±0.02
	Cd(II)	32.09±0.06	30.62±0.05	30.80±0.03	30.85±0.10	24.90±0.04

As shown by the tables, the ΔG values were negative for both the protonation and complexation reactions suggesting that all these reactions were spontaneous. It is also observed that these values have no sharp behavior with temperature, indicating the independent nature of the reactions with respect to temperature [13].

For the protonation of TEPHC, negative ΔH and positive ΔS values in aqueous-dioxane indicate that protonation of the ligand (TEPHC) was both enthalpy and entropy driven in these media.

A decrease in $\log K$ values with an increase in temperature and the negative values of ΔH for both protonation and complexation reactions would also suggest the importance of enthalpy rather than the entropy factor in both processes.

V. CONCLUSION

Schiff base TEPHC was prepared and their potentiometric study with complex of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions. The order of stability of metal complexes is found as Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II).

VI. ACKNOWLEDGEMENT

I am thankful to the principal of MLSM College, Darbhanga for providing necessary facilities in Chemistry lab to complete my paper.

REFERENCES

- [1]. R. Hernández-Molina and A. Mederos, *Comprehensive Coordination Chemistry II* 2003, Elsevier Ltd, 2003, 411
- [2]. P. Anand, V.M. Patil, V.K. Sharma, R.L. Khosa and N. Masand. *International Journal of Drug Design and Discovery*, 2012, **3**, 851
- [3]. K.C. Gupta, A. Kumar Sutar and C. C. Lin, *Coord. Chem. Rev.*, 2009, **253**, 1926
- [4]. K.C. Gupta and A.K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420
- [5]. H. Schiff, *Justus Liebig's Annalen der Chemie*, 1864, **131**, 118
- [6]. P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Justus Liebig's Annalen der Chemie*, 1933, **503**, 84
- [7]. R. Atkins, G. Brewer, E. Kokot, G.M. Mockler and E. Sinn, *Inorg. Chem*, 1985, **24**, 84
- [8]. J. Bjerrum. *Metal ammine formation in aqueous solution*. P. Haase and Son: Copenhagen. (1941).
- [9]. H. M. Irving and H. S. Rossotti. The calculation of formation curves of metal complexes from pH-titration curves in mixed solvents. *J. Chem. Soc.*, 2904-2910 (1954).
- [10]. H. M. Irving and R. J. P. Williams. The stability of transition-metal complexes. *J. Chem. Soc.*, 3192-3210 (1953).
- [11]. D. F. Shriver and P. W. Atkins. *Inorganic Chemistry*. 3rd edn. University Press: Oxford. 235-236 (1999).
- [12]. H. M. Erbary, H. A. Shehata, Ez El, M. A. F. Arab, A. A. Mohamed and M. M. Emar. Thermodynamics of amino acid ionization in aqueous solutions using pH-titration. *J. Indian Chem. Soc.*, 73, 25-29 (1996).
- [13]. K. B. Yatsimirskii and V. P. Vasil Ev. *Instability constants of complex compound*. Pergamon Press: Oxford, (1960).

