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Determination of Stability Constant of Transition Metal Complexes With Schiff's Base Ligands Derived From Hetrocyclic Aldehydes And Substituted Aromatic Amines

Dr. Prem Mohan Mishra

Dept. of Chemistry, MLSM College, Darbhanga, **INDIA**

Email: mishrapm6@gmail.com

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ABSTRACT

Ligands were synthesized by the simple condensation reaction of furan-2- carbaldehyde with 7- hydroxyl naphthalene-2- amine. Ligand was estimated for elements by standard methods. Nitrate salts of divalent metals cobalt, nickel, copper and zinc were estimated volumetrically as well as gravimetrically. pH metric titration were carried out with the help of digital pH meter. Stability constant of complexes of these metals with ligand synthesized were computed by Irving Rossoti technique modified by Calvin Bjerrum [1]. The stability constant values of metal complexes were found to be in the order Cu(II) > Ni (II) > Co (II) > Zn(II). The observed results are in agreement with the natural order proposed by Irving – William [2].

Keywords: Metal ions, Schiff's base Ligands, complex compounds, stability constant.

INTRODUCTION

In continuation of our previous work here we are going to report stability constants of divalent metal complexes with Schiff's base ligands. Co-ordination compounds of transition meals with Schiff's base ligands containing nitrogen, sulphur and other donor atoms are being synthesized in very good number. These complexes have varying properties and very much useful in various fields.

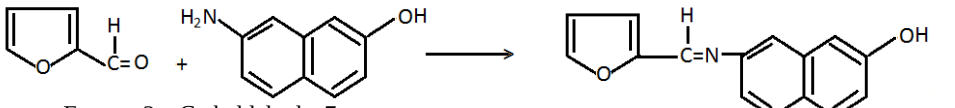
Schiff's base complexes are biologically [3] active and used in many fields. These complexes are used in catalysis [4], material science [5], Electrochemistry [6] and medicines [7]. It has been observed that metal complexes act as antitumor [8], antiviral [9], anti cancer [10] and many other anti bacterial agents [11]. A large number of tridentate Schiff's base ligands of Naphthyl amine and Furan – 2 – Carbaldehyde and their complexes have been synthesized [12]. Structures of these complexes were characterized and their properties investigated extensively.

Little is known about their stability in aqueous solution hence this title project was undertaken to investigate the stability constant of complexes of Co (II), Ni (II), Cu (II) and Zn (II) with 7' – hydroxynaphthyl – 2– hydroxyl furan – 2 - carbaldimine (HNFCI).

MATERIALS AND METHODS

Nitrate salts of all the divalent Co, Ni, Cu and Zn metals were of E. Merck grade. All other chemicals used were Anal R grade and used without purification. Dioxane was purified by standard methods [13] Elemental analysis of metals were done by volumetric as well as gravimetric methods [14]. Double distilled and deionized CO_2 free water was used throughout the experiment.

All titrations were done in aqueous – dioxane medium in the ratio 3: 2 (v/v). Schiff's base ligands were synthesized by the condensation of with 7 –Hydroxy naphthalene – 2 – amine 3 g of amine were mixed with aqueous solution of 1.2 g aldehyde. The mixture was boiled under reflux in the presence of glacial acetic acid for 2h. The solution was concentrated and cooled to 0^0 C. The product obtained was filtered, washed several times and recrystalised from ethanol. The yield of product (mol. mass, 237) was 2.15 g. The reaction is shown below



Furan – 2 – Carbaldehyde 7 – Hydroxyl naphthalene – 2 – amine

7' – Hydroxynaphthyl – 2 – hydroxyl Furan – 2 - carbaldimine

pH metric titrations were carried out keeping same strength of all the solutions (table 1) and same experimental conditions. These titrations were done at constant ionic strength of 0.10 (M) KNO_3 solutions at temperature 298 K within the limit of $\pm$ 1K. Titrations were carried out in a cell and glass electrode in a thermostat with the help of micro burette. pH metric titration of acid, acid + ligand and acid + ligand + metal ion solutions were done in an inert atmosphere of nitrogen. The same process of titration was repeated for all the four Co, Ni, Cu and Zn metal ions. The change in colour and appearance of turbidity at particular pH value were recorded simultaneously. The change in pH of the solutions with each addition of alkali was recorded in table 2.

Table 1. Concentration of solutions of metal ions, ligand, acid and salt

Metal ions	**V^0 in mL**	**Y**	**N^0**	**E^0**	**T^0_L**	**T^0_M**
Co (II)	100	1	1.0(M)	1.0 x 10^{-2}(M)	2.5 x 10^{-3} (M)	5.0 x 10^{-4}(M)
Ni (II)	100	1	1.0(M)	1.0 x 10^{-2}(M)	2.5 x 10^{-3} (M)	5.0 x 10^{-4}(M)
Cu (II)	100	1	1.0(M)	1.0 x 10^{-2}(M)	2.5 x 10^{-3} (M)	5.0 x 10^{-4}(M)
Zn (II)	100	1	1.0(M)	1.0 x 10^{-2}(M)	2.5 x 10^{-3} (M)	5.0 x 10^{-4}(M)

Table 2. Ligand HNFCI,Temp. 298 $\pm$ 1K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane medium (v/v) = 3:2

			pH – meter reading (B)			
Vol. of alkali added in mL	**H^+**	**H^++ L**	**H^+ +L + Co(II)**	**H^+ +L + Ni(II)**	**H^+ + L + Cu(II)**	**H^+ + L + Zn(II)**
0.0	2.02	2.36	2.32	2.32	2.34	2.34
0.1	2.12	2.44	2.44	2.45	2.45	2.44
0.2	2.34	2.58	2.56	2.56	2.54	2.56
0.3	2.54	2.87	2.84	2.85	2.85	2.82
0.4	2.96	3.32	3.32	3.30	3.32	3.45
0.5	3.10	3.52	3.54	3.50	3.52	3.50
0.6	3.36	3.74	3.72	3.72	3.74	3.75
0.7	3.82	4.12	4.14	4.10	4.13	4.12
0.8	4.64	4.78	4.76	4.76	4.82	4.78
0.9	10.16	7.44	6.12	6.12	6.54	6.62
1.0	11.80	10.56	7.44	7.46	8.26	8.16
1.1	12.05	11.31	8.00	7.92	8.62	8.32
1.2	12.06	12.02				

RESULTS AND DISCUSSION

A graph was plotted between pH [B] and volume of alkali added in each case. The three titration curves so obtained for each metal ion are referred as:
Acid titration curve (a)
Ligand titration curve (b)
Complex titration curve (c) respectively
Concentrations used in the experiment are given in table 1. The values of volumes V_1, V_2 & V_3 corresponding to the same pH values were read from acid, ligand and complex titration curves given in fig 1 at temperature 298 K.

Calculation of $\bar{n}_A$, $\bar{n}$ and P^l : The $\bar{n}_A$, $\bar{n}$ & P^L values are calculated using standard expressions

$$\bar{n}_A = 1 + [(V_1-V_2) / (V^O + V_1)\ ] (N^O + E^O) / T_L^O$$

$$\bar{n} = [\ (V_3 - V_2) / (V^O + V_1)][(N^O + E^O) / T_M^O\ ] \text{ x } 1/\ \bar{n}_A$$

$$P^L = \log \left[\sum_{j=0}^{j} \beta_j^0 H\ (1/\text{anti}\log B)(V^O + V_3)/(T_L^O - \bar{n} T_M^O) V^0 \right]$$

Proton Ligand Stability Constant: The ligand titration curve (Fig 2) is above the acid titration curve showing the basic nature of ligand and it is well separated from the acid titration curve at pH=4.80 at temp 298 K. The ligand curves run parallel to the acid titration curve indicating the smooth dissociation of the ligand. The values of $\bar{n}_A$ at various pH readings [B] were calculated from the acid and ligand titration curves at temperature 298 K are recorded in table 3. The formation curve obtained from the plot of $\bar{n}_A$ vs [B] at temp 298K extends from 0.4396 to 0.9878 (Fig 3). As the values of $\bar{n}_A$ does not go beyond 1.0 so this indicates that the ligand is monoprotonic. Dissociation of ligand is given as

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

The value of proton ligand stability constant was calculated by half integral method at 298 K and it was further corroborated by liner plot method. (log $\bar{n}_A$ / (1 - $\bar{n}_A$) vs [B] fig 3.

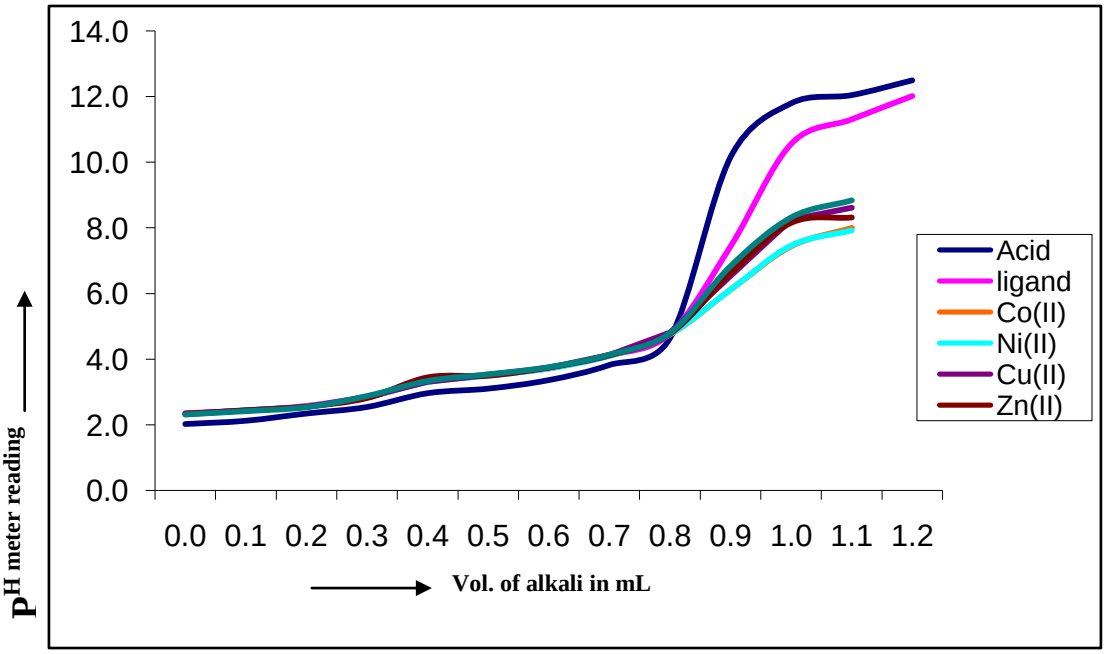


Fig 1. Experimental curve with ligand HNFCI

Temp. 298 ± 1 K, μ^0 = 0.10(M) KNO_3, Water : dioxane = 3:2(v/v)

Table 3. Ligand HNFCI

Temp.: 298 $\pm$1K , μ^0 = 0.10 (M) KNO_3, Water : Dioxane medium (v/v) = 3:2

[B]	$V_2 - V_1$	$\bar{n}_A$	$\log \bar{n}_A / (1 - \bar{n}_A)$
5.2	0.004	0.9878	
5.4	0.005	0.9842	
5.6	0.005	0.9842	
5.8	0.006	0.9810	
6.0	0.006	0.9820	
6.2	0.007	0.9740	
6.4	0.007	0.9726	
6.6	0.008	0.9684	
6.8	0.018	0.9610	
7.0	0.010	0.9440	
7.2	0.012	0.9360	
7.4	0.014	0.9360	1.1642
7.6	0.016	0.9280	1.1094
7.8	0.018	0.9198	1.0602
8.0	0.024	0.9120	1.0152
8.2	0.026	0.8988	0.9536
8.4	0.028	0.8868	0.8946
8.6	0.036	0.8638	0.8024
8.8	0.038	0.8440	0.7323
9.0	0.044	0.8197	0.6582
9.2	0.052	0.7956	0.5907
9.4	0.056	0.7796	0.5493
9.6	0.061	0.7556	0.4908
9.8	0.066	0.7276	0.4272
10.0	0.076	0.6998	0.3676
10.2	0.084	0.6676	0.3032
10.4	0.092	0.6320	0.2342
10.6	0.102	0.5880	0.1536
10.8	0.116	0.5398	0.0692
11.0	0.126	0.4874	0.0214
11.2	0.142	0.4396	-0.1052

Co (II) – HNFCI System: The complex titration curve of the system crossed the ligand mixture curve at pH = 5.18 indicating the start of complex formation. As the metal titration curves did not join up and run parallel to the ligand titration curve indicating liberation of extra proton due to the hydrolysis of metal ions. Precipitation was observed at pH = 7.8. Hence, in order to preclude error due to the hydrolysis in the calculation of $\bar{n}$, only the lower pH regions of titration curves were used. The values of $\bar{n}$ extend between 0.1224 to1.9684 (Fig 4a, and Table 4) at temperature 298 K indicating the formation of ML and ML_2 type of complexes. From the formation curve of $\bar{n}$ vs P^L (graph 4a , at temperature 298 K the values of log K_1 and log K_2 were calculated by half integral method. It was further verified by the mid-

point calculation method and the linear plot of log $\bar{n}$ / (1- $\bar{n}$) vs p^L graph no. 5a table 5 and plot of log (2- $\bar{n}$) / ($\bar{n}$ -1) vs p^L (Fig 6a, Table 5) at temperature 298 K.

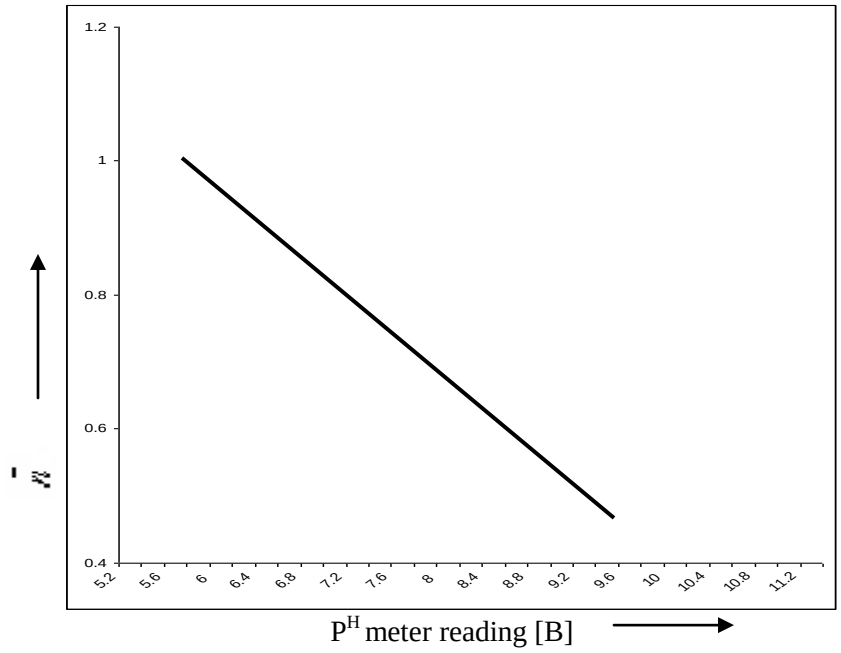


Fig 2. Formation curve of ligand HNFCI, Plot of $\bar{n}$ Vs [B]

Temp. 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

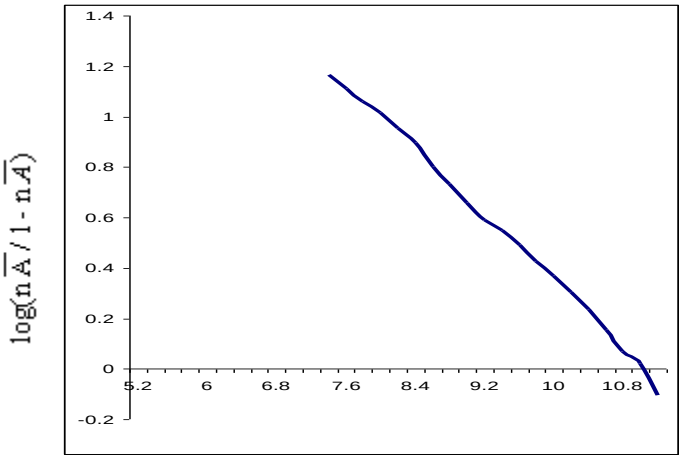


Fig 3. Linear plot of log(n Ā / 1- n Ā) Vs [B]

Ligand: HNFCI; Temp. 298 ± 1K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

Table 4. Co (II) + HNFCI

Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

[B]	$V_3 - V_2$	$\bar{n}$	P^L
5.0	0.006	0.1224	8.1656
5.2	0.012	0.2242	7.9764
5.4	0.016	0.3270	7.7868

5.6	0.024	0.4916	7.6020
5.8	0.036	0.6770	7.4130
6.0	0.048	0.8872	7.2418
6.2	0.054	1.0968	7.0640
6.4	0.066	1.2944	6.8860
6.6	0.074	1.4842	6.7094
6.8	0.080	1.6970	6.5370
7.0	0.092	1.9684	6.3744

Table 5. Co (II) + HNFCI

Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

log $\bar{n}$ /(1- $\bar{n}$)	**P^L**	**Log (2 - $\bar{n}$ /($\bar{n}$ -1)**	**P^L**
-0.8570	7.9756	0.0264	6.7098
-0.3138	7.7852	-0.3624	6.5366
0.3216	7.4134	-0.4239	6.3821
0.8908	7.2408	-0.4862	5.9826

Ni (II) – HNFCI System : The complex titration curve on the system crossed the ligand mixture curve at pH = 5.2 indicating the start of complexation. The curve increased regularly upto pH = 7.38 indicating constant rate of release of proton and then complex titration curve diverges indicating quick but incomplete dissociation of ligand. No turbidity appear, hence hydrolysis does not take place. Value of $\bar{n}$ falls in the range of 0.0406 to 1.8684 at temperature 298 K (Table 6, Fig 4b). The values of log K_1 and log K_2 were calculated by half integral method and verified by midpoint slope method and linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs P^L fig 5b, table 7 and plot of log (2-$\bar{n}$)/($\bar{n}$ -1) vs P^L(Table 7, Fig 6b) at temperature 298 K.

Table 6. Ni (II) + HNFCI

Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

[B]	**$V_3 - V_2$**	**$\bar{n}$**	**P^L**
5.0	0.004	0.0406	8.1590
5.2	0.006	0.1016	7.9644
5.4	0.010	0.2454	7.7768
5.6	0.018	0.4086	7.5930
5.8	0.026	0.6154	7.4128
6.0	0.038	0.8036	7.2322
6.2	0.046	0.9932	7.0520
6.4	0.052	1.2306	6.8786
6.6	0.066	1.4638	6.7064
6.8	0.082	1.6972	6.5366
7.0	0.094	1.8684	6.3738

Table 7. Ni (II) + HNFCI

Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2- $\bar{n}$) / ($\bar{n}$ - 1)	P^L
-0.9454	7.9644	0.5226	6.8786
-0.4882	7.7774	0.0626	6.7068
-0.1606	7.5928	-0.3622	6.5362
0.2044	7.4128		
0.6118	7.2322		

Cu (II) - HNFCI System: Complex titration curve crossed the acid titration curve and well separated from ligand titration curve at pH = 5.76. The curve increased regularly and run parallel to the ligand titration curve upto pH = 8.0. During the titration equilibrium is attained very quickly, no turbidity appear, hence hydrolysis does not take place. The values of $\bar{n}$ extended from 0.0820 to 1.8242 at temperature 298 K indicating the formation of ML and ML_2 type of complexes, (Table 8; Fig 4c) at 298 K. Formation curves (Fig4c) is very symmetrical, it gave the values of log K_1 and log K_2 by half integral method at given temperature. These values were further verified from mid-point slope method and the linear plot of log ($\bar{n}$ /1-$\bar{n}$) vs P^L fig 5c, table 9 and plot of log (2 -$\bar{n}$)/($\bar{n}$ -1) vs P^L. (Table 9,fig 5c) , at temperature 298K.

Table 8. Cu (II) + HNFCI

Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

[B]	$V_3 - V_2$	$\bar{n}$	P^L
6.2	0.008	0.0820	7.5630
6.4	0.012	0.1642	7.3704
6.6	0.014	0.2678	7.1799
6.8	0.018	0.3724	6.9898
7.0	0.026	0.4798	6.8000
7.2	0.030	0.6152	6.6130
7.4	0.036	0.7638	6.4278
7.6	0.048	0.9414	6.2470
7.8	0.054	1.1440	6.0690
8.0	0.066	1.3278	5.8915
8.2	0.070	1.5370	5.7158
8.4	0.082	1.8242	5.5531

Table 9. Cu (II) + HNFCI

Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2-$\bar{n}$) / ($\bar{n}$ - 1)	P^L
-0.7058	7.3702	0.7752	6.0688
-0.4362	7.1798	0.3118	5.8902
-0.2261	6.9894	-0.0646	5.7156
-0.0352	6.7996	-0.6714	5.534
0.2040	6.6132		
0.5092	6.4286		

Zn (II) – HNFCI System: Metal ligand titration curve is well separated from ligand titration cure at pH = 5.92 and complex titration curve diverges at higher pH, indicates the incomplete dissociation of ligand. For the calculation of value of $\bar{n}$ only the symmetrical region of the curve were considered. The values of $\bar{n}$ extended from 0.1428 to 1.7217 at temperature 298 K, indicating the formation of ML and ML_2 type complexes only.(Table 10, Fig 4d) at temperature 298 K. The value of log K_1 and log K_2 were calculated from the formation curves (Fig 4d), by using half – integral method at temperature 298 K. These values of log K_1 and log K_2 were further verified by the mid-point slope calculation method and straight – line plot of log $\bar{n}$ /(1- $\bar{n}$) vs P^L table 11, fig 5d and plot of log (2-$\bar{n}$) / ($\bar{n}$ - 1) (Table 11,Fig 6d) at Temperature 298 K.

Table 10. Metal: Zn(II), Ligand : HNFCI

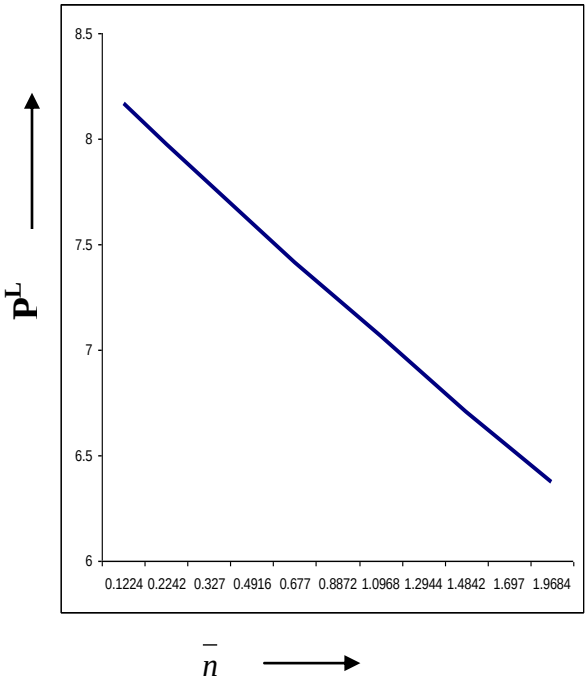
Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

B	$V_3 - V_2$	$\bar{n}$	P^L
6.0	0.008	0.1428	7.3652
6.2	0.010	0.1854	7.1732
6.4	0.014	0.2916	6.9830
6.6	0.018	0.3752	6.7888
6.8	0.024	0.5094	6.6034
7.0	0.030	0.6368	6.4164
7.2	0.040	0.8346	6.2356
7.4	0.048	1.0354	6.0570
7.6	0.054	1.2614	5.8834
7.8	0.078	1.6668	5.7298
8.0	0.082	1.7217	5.8266

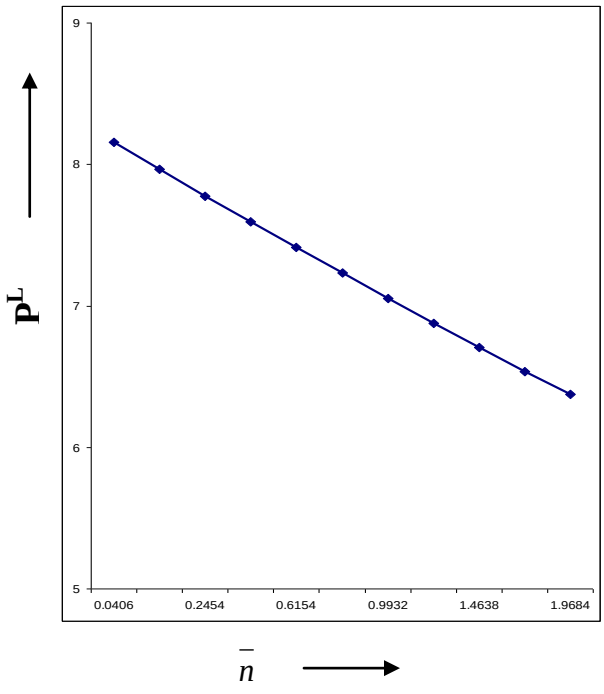
Table 11. Metal: Zn(II), Ligand **:** HNFCI

Temp: 298 ± 1 K, μ^0 = 0.10 (M) KNO_3, Water: Dioxane = 3:2(v/v)

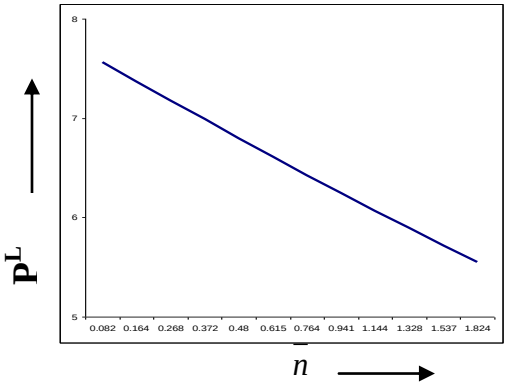
$\log \bar{n}/(1-\bar{n})$	P^L	$\log (2-\bar{n})/(\bar{n}-1)$	P^L
-0.6428	7.1722	0.4524	5.8824
-0.3864	6.982	-0.2628	5.7298
-0.2216	6.7898		
0.2434	6.5152		
0.7024	6.2354		



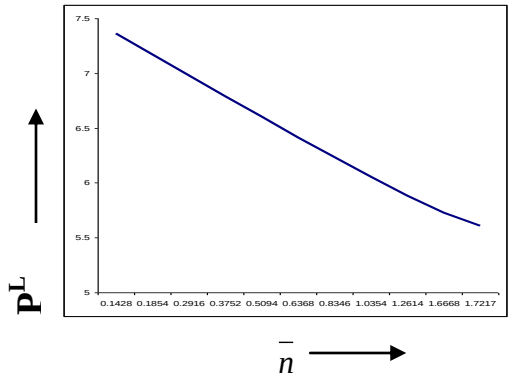
Metal : Co(II) 4a



Metal: Ni (II) 4b

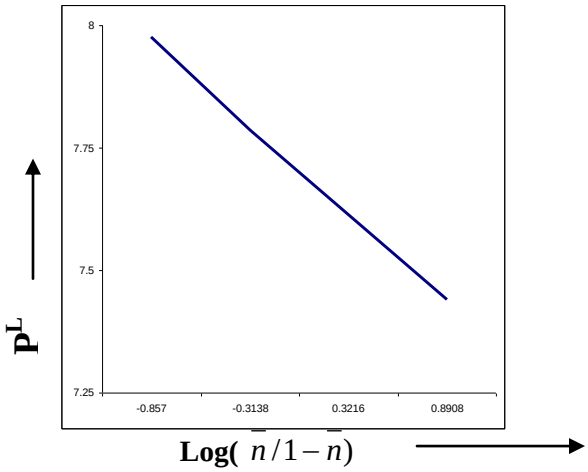


Metal : Cu(II) 4c

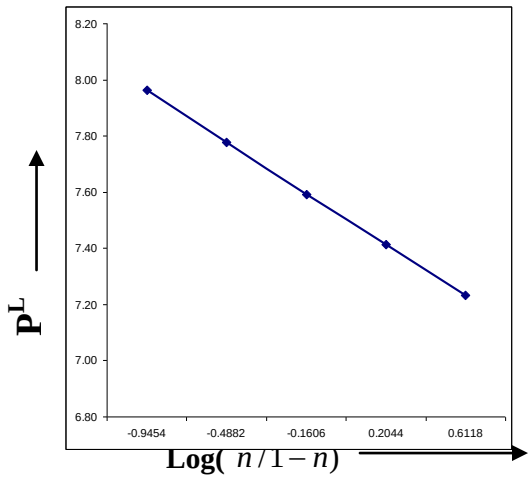


Metal: Zn (II) 4d

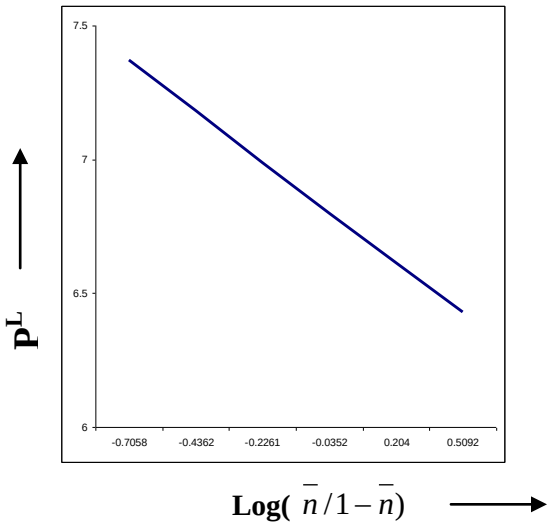
Fig 4 Formation curve Plot of $\bar{n}$ Vs P^L Ligand HNFCI



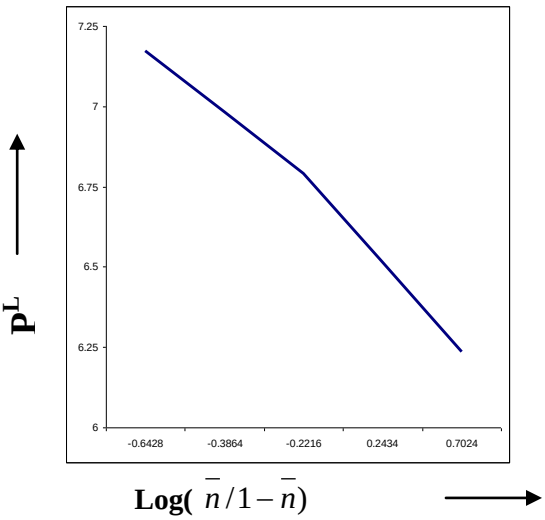
Metal: Co (II) 5a



Metal: Ni (II) 5b

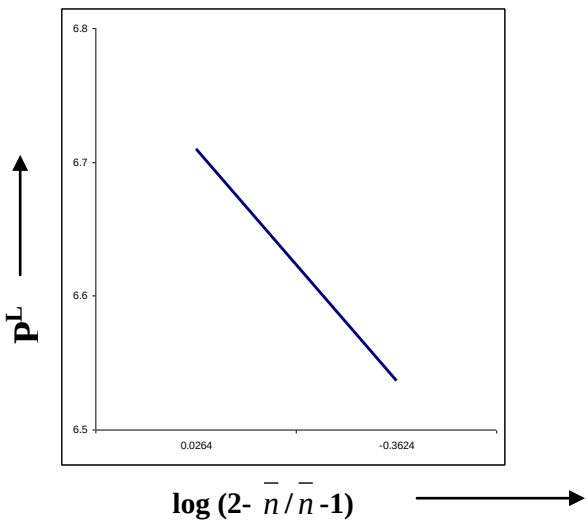


Metal: Cu (II) 5c

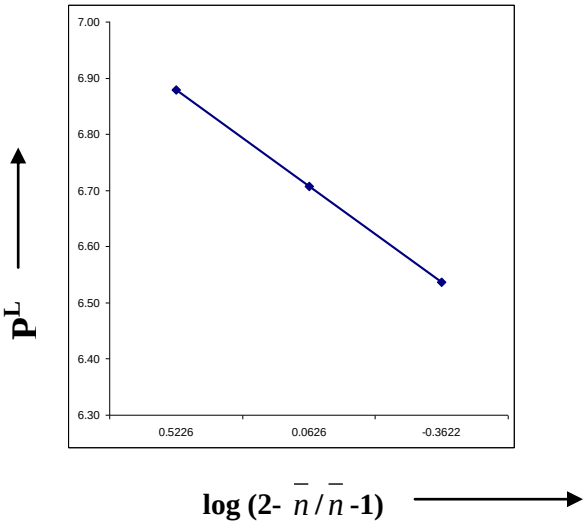


Metal: Zn (II) 5d

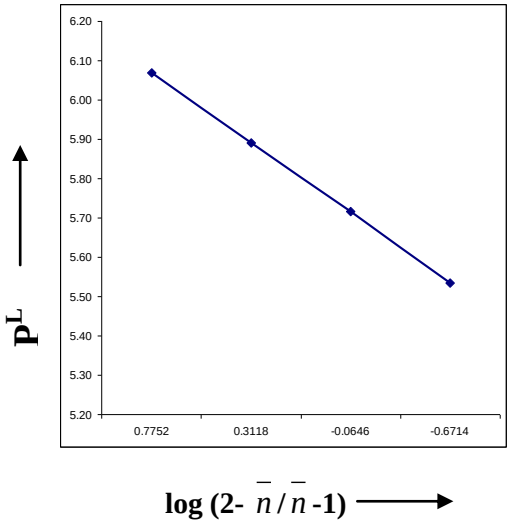
Fig 5. Linear plot of log ($\bar{n}$/1-$\bar{n}$) Vs P^L, Metal ion : HNFCI



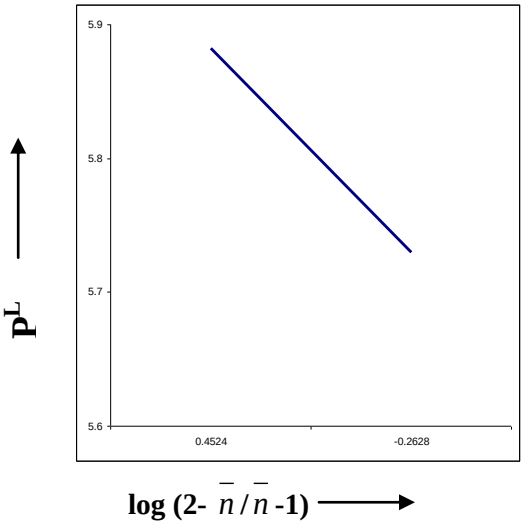
Metal: Co (II) 6a



Metal: Ni (II) 6b



Metal: Cu (II) 6c



Metal: Zn (II) 6d

Fig 6. Linear plot of log (2- $\bar{n}/\bar{n}$ -1) Vs P^L, Metal ion : HNFCI

The value of protonation constant and stepwise stability constant obtained from different computational methods at temperatures 298 K are summarized in table 12. The different computational methods are-

a) Half – integral method
b) Mid – point slope calculation method and
c) Straight – line plot method.

Table 12. Values of protonation constant of ligand and stepwise stability constant of complexes of Co(II), Ni(II), Cu(II) & Zn(II) with ligand HNFCI at temperatures 298 K.

Metal ions	HNFCI		
		log K_1	log K_2
HNFCI	A	11.16	-
	b.	-	-
	c.	11.08	-
Co(II)	A	7.20	6.25
	b.	7.38	6.38
	c.	7.30	6.20
Ni(II)	A	7.24	6.06
	b.	7.26	6.23
	c.	6.38	5.44
Cu(II)	A	6.24	5.32
	b.	6.34	5.44
	c.	6.38	5.40
Zn(II)	A	6.26	5.38
	b.	6.40	5.48
	c.	6.38	5.40

The most representative values of log K_1, log K_2 and log β are given in table 13.

Table 13. Average values of log of stepwise and overall stability constants of complex compounds of various metals with ligand HNFCI at 298 K

System	Ligand HNFCI		
	log K_1	log K_2	log β
HNFCI	11.10	-	11.10
Cu (II)	7.31	6.43	13.74
Ni (II)	7.22	6.24	13.40
Co (II)	6.49	5.59	12.08
Zn(II)	6.24	5.54	11.78

HNFCI - Cu(II) > Ni(II) > Co(II) > Zn(II)

The values of stepwise stability constants and over all stability constants are given in table 13. For the given ligand the stability constants of complexes for different metals show the sequence

Cu(II) > Ni(II) > Co(II) > Zn(II)

This is natural order given by Irving – William. A theoretical justification of the order of stability constants follows from the consideration of the reciprocal of the ionic radii and 2nd ionization enthalpy of metal. Calvin – Bjerrum titration technique modified by Irving and Rossotti was used to determine the practical proton ligand and metal ligand stability constants at constant ionic strength maintained by using dilute KNO_3 solution. Irving and Rossotti pointed out that the formation constant of metal chelates can be obtained without converting the pH – meter reading [B] to stoichiometric hydrogen ion concentration and without knowing the stoichiometric concentration of neutral salts added to maintain ionic strength. This method is valid for both aqueous and non-aqueous medium. The nitrate (NO_3^-) ion has very slight complexing tendency. Therefore, competition between nitrate ion and the ligand under study is of no importance. The stability of the chelates is greatly affected by the electron density around the imine nitrogen (- C = N -). Higher the electron density around the nitrogen atom, stronger is the metal ligand bond.

The difference between the successive stepwise stability constant is large, which suggest that the formation of ML and ML_2 chelates take place. The results obtained are in conformity of our previous studies [16-20, 23] and other workers [21-22].

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AUTHOR ADDRESS

1. **Dr. Prem Mohan Mishra**
Dept. of Chemistry, MLSM College,
Darbhanga, India
Email: mishrapm6@gmail.com