

DETERMINATION OF STABILITY CONSTANT AND RELATED THERMODYNAMICS OF BIVALENT TRANSITION METAL COMPLEXES WITH DERIVATIVE OF SCHIFFS BASE AS LIGANDS
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ABSTRACT

Schiff's base ligands were synthesized by the condensation reaction of salicylaldehyde with 7-hydroxy naphthalene – 2 – amine. Nitrate salts of divalent cobalt, nickel, copper and zinc were estimated by standard volumetric and gravimetric methods. Ligand was analysed for elements by literature methods. pH metric titrations were carried out in an inert atmosphere of nitrogen gas at constant ionic strength of 0.1M KNO₃ with the help of digital pH meter and stability constant of complexes of these metals with the ligands synthesized were computed by Irving- Rossotti technique¹ modified by Calvin Bjerrum² at temperature 298K.

The stability constant values of metals for the given ligand at the given temperature were found to be in the order Cu(II) > Ni(II), Co(II) > Zn (II).

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

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INTRODUCTION

In continuation of our previous work here also, we have been interested in studying the stability of complexes of transition metals with biologically active ligands.

Here we are presenting determination of stability constant and related thermodynamic parameters of complex compounds using ligands synthesised from salicylaldehyde with 7-Hydroxy naphthalene 2 – amine with bivalent transition metals i.e. Co(II), Ni(II), Cu(II) and Zn(II).

Schiff's base offers a versatile and flexible series of ligands capable to bind with variety of metal ions to give complexes with varying properties. These complexes are biologically active³, have wide potential applications in many fields such as catalysis⁴, electrochemistry⁵ and medicines like anti tumour, anti viral⁶, anti cancer⁷ and other many anti bacterial agents⁸.

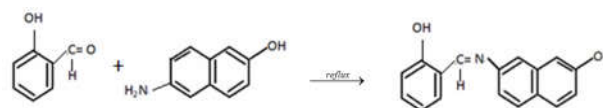
Metal ions play vital role in a vast number of widely different biological processes. The interaction of these ions with biologically active ligands is a subject of considerable interest. Some of the biologically active compounds act via Chelation⁸. A large number of such chelates have been synthesized, their structure and activity have been studied, but little is known about its stability in solution which will be its functioning condition.

Experimental

Nitrate salts of divalent Co, Ni, Cu and Zn 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 methods¹¹. Double distilled and deionised water was used throughout the experiment. All titrations were done in aqueous-dioxane medium in the ratio 3:2 (v/v). Dioxane was purified by standard method.

Schiff's base ligands were synthesised by reported method¹² 2.6 g salicylaldehyde in solution were mixed with 3.0 g 7 – Hydroxy naphthalene – 2 – amine. The mixture was refluxed in the presence of glacial acetic acid for 2 – 2.5 hours. The solution was concentrated and cooled to 0^o C. The product obtained was filtered, washed several times and recrystallised from ethanol. The yield of product was nearly 2.10 g



7' – Hydroxynaphthyl – 2 – hydroxy benzene Carbaldimine (HNBCI)

Solution of metal salts, ligands, electrolytes etc were prepared in doubly distilled CO₂ free water – strength of various solutions used were tabulated in table – 1.

pH metric titration of acid, acid + ligand and acid + ligand + metal ion solutions were done at constant ionic strength of 0.1 M KNO₃ at temperature 298k in an inert atmosphere of nitrogen.

The same process of titration were 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 no. 2.

RESULTS

A graph was plotted between pH meter reading [B] and volume of alkali added in each case, graph-1. The three titration curves obtained for each metal ions are acid titration curve (a), ligand titration curve (b) and complex titration curve (c) respectively.

Table No 1 Concentrations Used In the Experiment

Metal / Ions	V ^o (mL)	Y	N ^o	E ^o	T _L ^o	T _M ^o
Co (II)	100	1	1.0 (M)	1.0 x 10 ⁻² (M)	2.4 x 10 ⁻³ (M)	5.0 x 10 ⁻⁴ (M)
Ni(II)	100	1	1.0 (M)	1.0 x 10 ⁻² (M)	2.4 x 10 ⁻³ (M)	5.0 x 10 ⁻⁴ (M)
Cu(II)	100	1	1.0 (M)	1.0 x 10 ⁻² (M)	2.4 x 10 ⁻³ (M)	5.0 x 10 ⁻⁴ (M)
Zn(II)	100	1	1.0 (M)	1.0 x 10 ⁻² (M)	2.4 x 10 ⁻³ (M)	5.0 x 10 ⁻⁴ (M)

The values of volumes (V₁, V₂, & V₃) corresponding to the same pH values were read from acid, ligand and complex titration curves (a), (b) and (c) respectively from the experimental curves at temperature 298 K given in **graph 1**.

Table No. – 2

Volume of alkali consumed in different titrations of acid, acid + ligand and acid + ligand + metal ion solution.

Ligand: HNHBCI

Temperature 298 ± 1K

μ^o=0.1(M) KNO₃, water–dioxane (v/v) = 3:2

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	5.4	5.4	5.5	5.52	5.6	5.6
0.1	5.4	5.8	5.66	5.6	5.56	5.8
0.2	5.6	5.76	5.85	5.86	5.62	5.8
0.3	5.8	5.86	5.92	5.98	5.76	5.92
0.4	5.9	6.34	6.45	6.56	6.38	6.3
0.5	6.2	6.42	6.57	6.74	6.4	6.48
0.6	6.4	6.76	6.85	6.86	6.66	6.78
0.7	6.6	7.34	7.41	7.36	7.28	7.3
0.8	7.7	7.92	7.93	7.86	7.76	7.34
0.9	11.4	8.64	8.63	8.8	8.06	8.82
1.0	12.16	12.28	10.35	10.3	9.74	10.46
1.1	12.48	12.64	11.44	11.56	10.52	11.76
1.2	12.76	12.86	11.8	11.65	10.75	11.96

Calculation Of \bar{n}_A , \bar{n} AND P^L

The \bar{n}_A , \bar{n} & P^L were calculated using standard expressions

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

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

\bar{n}_A

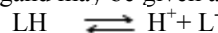
$$P^L = \log \left[\sum_{j=0}^j \beta_j^O H (1 / \text{antilog} B) (V^O + V_3) / (T_L^O - \bar{n} T_M^O) V^O \right]$$

Proton – Ligand Stability Constant.

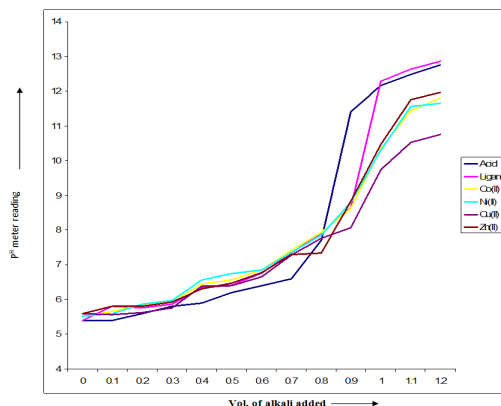
The ligand titration curve separates from acid titration curve at pH 5.16 at temperature 298 K. The ligand titration curves run parallel to the acid titration curves indicating the smooth

dissociation of ligand. The value of \bar{n}_A at various pH reading [B] were calculated from the acid and ligand titration curves (**table no. 3**) at temperature 298 K. The formation curves obtained from the plot of \bar{n}_A vs [B] (**graph 2**) at temperature 298 K, show that values of \bar{n}_A lies between 0.3324 and 0.7920. This indicates that ligand is monoprotic.

Dissociation of ligand may be given as,



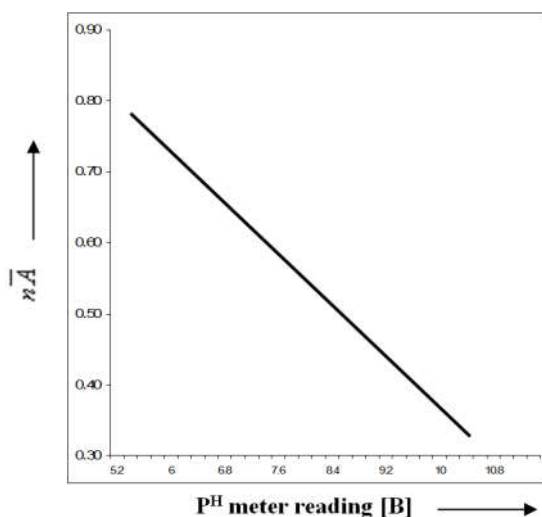
The value of proton ligand stability constant was calculated by half – integral method and it was further corroborated by linear plot method (log $\bar{n}_A / (1 - \bar{n}_A)$ vs [B]) (**graph 3**) at temperature 298 K .



Graph No. 1 Experimental Curve with ligand – HNHBCI
μ^o=0.1 M KNO₃ Temp: 298 ± 1K Water: Dioxane 3:2 (v/v)

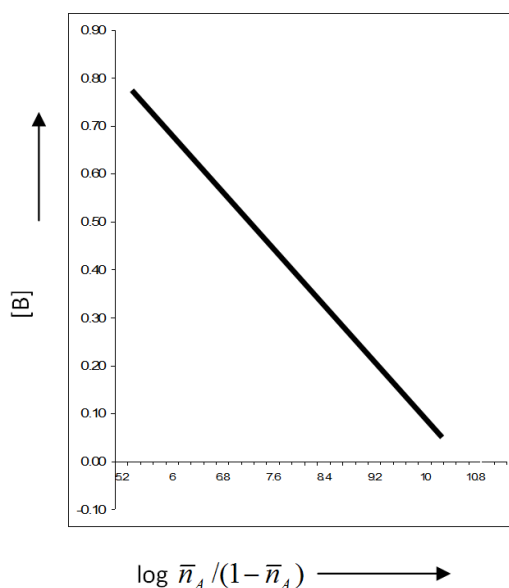
Table No 3 Ligand: HNHBCI Temperature 298 ± 1K
μ^o=0.1(M) KNO₃, Water–Dioxane medium (V/V) = 3:2

B	V ₂ – V ₁	\bar{n}_A	log $\bar{n}_A / (1 - \bar{n}_A)$
5.2	0.032	0.7920	0.8157
5.4	0.028	0.7870	0.7986
5.6	0.032	0.7792	0.7645
5.8	0.034	0.7720	0.7332
6.0	0.036	0.7632	0.7224
6.2	0.034	0.7560	0.6725
6.4	0.042	0.7434	0.6730
6.6	0.040	0.7352	0.6056
6.8	0.046	0.7240	0.5680
7.0	0.046	0.7120	0.5340
7.2	0.052	0.6990	0.5026
7.4	0.056	0.6880	0.4690
7.6	0.058	0.6760	0.4342
7.8	0.056	0.6642	0.4090
8.0	0.060	0.6474	0.3722
8.2	0.064	0.6362	0.3442
8.4	0.702	0.6192	0.3092
8.6	0.076	0.6026	0.2736
8.8	0.082	0.5914	0.2506
9.0	0.080	0.579	0.2264
9.2	0.086	0.5674	0.2030
9.4	0.082	0.5642	0.1950
9.6	0.084	0.5554	0.1790
9.8	0.084	0.5562	0.1790
10.0	0.086	0.5394	0.1492
10.2	0.096	0.519	0.1130
10.4	0.012	0.4962	0.0682
10.6	0.106	0.467	0.0178
10.8	0.114	0.4298	0.0380
11.0	0.126	0.3728	-0.0540
11.2	0.132	0.3442	-0.0736
11.4	0.136	0.3324	-0.0838



Graph No. 2 Formation Curve of ligand HNHBCI

Plot of \bar{n}_A Vs [B] Temp: 298 ± 1 K $\mu^0 = 0.1$ M KNO_3 Water: Dioxane 3:2 (v/v)



Graph No. 3 Formation Curve of ligand HNHBCI

Plot of $\log \bar{n}_A / (1 - \bar{n}_A)$ Vs [B] Temp: 298 ± 1 K $\mu^0 = 0.1$ M KNO_3 Water: Dioxane 3:2 (v/v)

Co(II) –HNHBCI System

Complex titration curves separated from ligand mixture curve at pH = 6.23 the curves diverge at pH above 9.58.

The value of \bar{n} lies between 0.2172 and 1.6806 (table no. 4 graph no.4a) at temperature 298 K. indicating the formation of ML and ML_2 types of complexes.

From the formation curves (graph 4a) the values of $\log K_1$ and $\log K_2$ were calculated by half – integral method¹³ at given temperature. The values were further corroborated by mid point slope method¹⁴ and linear plot of $\log \bar{n}/(1 - \bar{n})$ vs P^L (table no. 5 graph no. 5a) and plot of $\log (2 - \bar{n})/(\bar{n} - 2)$ vs P^L .(table no. 5, graph 6a) at temperature 298K.

Ni (II) – HNHBCI System

The complex titration curves crossed the ligand titration curve at pH = 5.38 indicating the start of complexation. The curve increases regularly upto pH = 7.62 indicating quick but incomplete dissociation of ligand.

No turbidity appears; hence hydrolysis does not take place. values of \bar{n} falls between 0.07 and 1.89 (graph 4b ; table no. 6) at temperature 298 K indicating the formation of ML and ML_2 type of complexes.

From the formation curves, graph 4b, the values of $\log K_1$ and $\log K_2$ were calculated by half integral method at given temperature and verified by mid – point slope method¹³ and linear plot of $\log (\bar{n}/1 - \bar{n})$ vs P^L (Table no. 7, graph no. 5b) and plot of $\log ((2 - \bar{n})/(\bar{n} - 1))$ vs P^L (Table 7, graph no. 6b).

Cu(II) –HNHBCI System

The complex, titration curve separated from ligand mixture curve at pH 6.30 indicating the start of complex formation.

As the metal titration curves did not join up and run parallel to the ligand titration curves indicating liberation of extra proton due to hydrolysis which was observed at pH = 8.46. Hence, in order to preclude error due to hydrolysis in the calculation of \bar{n} , only the lower pH region of titration curves were used.

The values of \bar{n} lies between 0.04 to 1.90 (graph – 4c, table no. 8) at temperature 298 K indicating the formation of ML and ML_2 type of complexes.

From the formation curves (graph – 4c, table no. 8) of \bar{n} vs P^L , the value of $\log K_1$ and $\log K_2$ at the given temperature were calculated by half – integral method. It was verified by the mid point slope method and straight line plot method and linear plot of $\log (\bar{n}/1 - \bar{n})$ vs P^L (Table no. 9; graph no. – 5c) and also plot of $\log ((2 - \bar{n})/(\bar{n} - 1))$ vs P^L (table no. 9, graph no. 6c).

Zn(II) – HNHBCI SYSTEM

The complex curves separated from ligand titration curves at pH = 5.74 and diverges at pH above 7.58

During the titration no turbidity appears, hence hydrolysis does not take place.

The values of \bar{n} lies between 0.056 to 1.68 (table – 10, graph 4d) at temperature 298 K indicating the formation of ML and ML_2 type of complexes.

From the formation curve (graph –4d) at 298 K values of $\log K_1$ and $\log K_2$ were calculated by half – integral method. It was further verified by mid-point slope method and linear plot of $\log \bar{n}/(1 - \bar{n})$ vs P^L (graph no. 5d, table no. 11) and plot of $\log (2 - \bar{n})/(\bar{n} - 1)$ vs P^L (graph – 6d, table – 11) at temperature 298 K.

Table No. 4 Co(II) HNHBCI Temp: 298 ± 1 K μ⁰=0.1 M KNO₃
Water:Dioxane 3:2 (v/v)

B	V ₃ - V ₂	\bar{n}	P ^L
6.0	0.006	0.2172	8.3160
6.2	0.008	0.2896	8.1222
6.4	0.010	0.3644	7.9264
6.6	0.014	0.4644	7.7694
6.8	0.014	0.5938	7.5516
7.0	0.020	0.6256	7.3640
7.2	0.024	0.6622	7.1774
7.4	0.030	0.8284	6.9950
7.6	0.036	1.2042	6.8144
7.8	0.048	1.2126	6.6386
8.0	0.050	1.4282	6.4642
8.2	0.066	1.6806	6.2730

Table No. 5 Co (II) HNHBCI Temp: 298 ± 1 K μ⁰=0.1 M KNO₃
Water: Dioxane 3:2 (v/v)

$\log \bar{n}/(1-\bar{n})$	P ^L	$\log (2-\bar{n})/(\bar{n}-1)$	P ^L
-0.9764	8.3160	0.8350	6.8140
-0.7300	8.1226	0.4430	6.6386
-0.5402	7.9290	-0.0584	6.4646
-0.3410	7.7384	-0.6506	6.2730
0.3230	7.3640		
0.5714	7.1764		

Table No. -6 Ni (II) + HNHBCI Temp : 298 ± 1 K μ⁰=0.1 M KNO₃
Water:Dioxane 3:2 (v/v)

[B]	V ₃ - V ₂	\bar{n}	P ^L
5.2	0.006	0.0774	9.1114
5.4	0.008	0.2364	8.9180
5.6	0.016	0.3396	8.7262
5.8	0.016	0.4240	8.5350
6.0	0.018	0.5456	8.3460
6.2	0.020	0.6690	8.1580
6.4	0.024	0.7962	7.9712
6.6	0.030	0.9504	7.7870
6.8	0.036	1.0212	7.6042
7.0	0.042	1.2012	7.4254
7.2	0.050	1.3972	7.2486
7.4	0.062	1.6254	7.0770
7.6	0.064	1.8920	6.9132

Table No. 7 Ni (II) + HNHBCI Temp: 298 ± 1 K μ⁰=0.1 M KNO₃
Water: Dioxane 3:2 (v/v)

$\log \bar{n}/(1-\bar{n})$	P ^L	$\log (2-\bar{n})/(\bar{n}-1)$	P ^L
-0.7004	8.9174	0.5974	6.4256
-0.6258	8.7264	0.1796	6.2486
-0.4182	8.5350	-0.2234	6.0772
-0.0846	8.3466		
0.2214	8.1586		
0.4606	7.9710		
0.8550	7.7872		

Table No. - 8 Cu(II) + HNHBCI Temp: 298 ± 1 K μ⁰=0.1 M KNO₃
Water:Dioxane 3:2(v/v)

[B]	V ₃ - V ₂	\bar{n}	P ^L
5.2	0.004	0.0450	9.3096
5.4	0.006	0.1132	9.1154
5.6	0.010	0.1820	8.9220
5.8	0.014	0.2752	8.7304
6.0	0.018	0.3940	8.5416
6.2	0.020	0.5162	8.3530
6.4	0.022	0.6644	8.1680
6.6	0.032	0.8160	7.9832
6.8	0.040	0.9966	7.8026
7.0	0.042	1.1834	7.6234
7.2	0.052	1.4022	7.4776
7.4	0.066	1.6260	7.2772
7.6	0.074	1.9092	7.1158

Table No. - 9 Cu(II) + HNHBCI Temp: 298 ± 1 K
μ⁰=0.1 M KNO₃ Water:Dioxane 3:2(v/v)

$\log \bar{n}/(1-\bar{n})$	P ^L	$\log (2-\bar{n})/(\bar{n}-1)$	P ^L
-0.9940	9.1152	0.7472	7.6230
-0.7526	8.9222	0.2726	7.4490
-0.2860	8.5410	-0.3240	7.2772
0.3966	8.1682		
0.5486	7.9830		

Table No. 10 Zn(II) + HNHBCI Temp: 298 ± 1 K
μ⁰=0.1 M KNO₃ Water: Dioxane 3:2(v/v)

[B]	V ₃ - V ₂	\bar{n}	P ^L
6.0	0.004	0.0564	8.3102
6.2	0.006	0.0852	8.1140
6.4	0.008	0.2682	7.9204
6.6	0.012	0.3424	7.7274
6.8	0.014	0.4204	7.5346
7.0	0.016	0.3256	7.3448
7.2	0.020	0.5094	7.1624
7.4	0.032	0.8992	6.9822
7.6	0.036	1.0352	6.8054
7.8	0.040	1.3516	6.6292
8.0	0.052	1.5730	6.4582
8.2	0.064	1.6802	6.2980

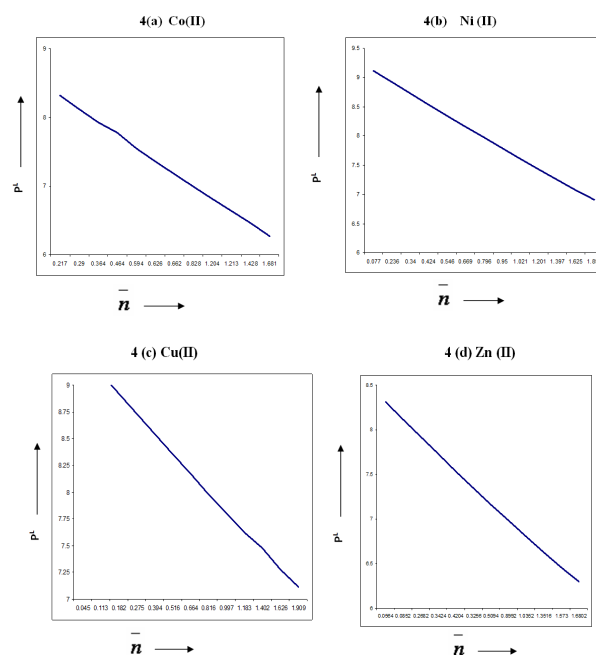
Table No. - 11 Zn(II) + HNHBCI Temp: 298 ± 1 K
μ⁰=0.1 M KNO₃ Water:Dioxane 3:2(v/v)

$\log \bar{n}/(1-\bar{n})$	P ^L	$\log (2-\bar{n})/(\bar{n}-1)$	P ^L
-0.7946	7.9206	0.6214	6.6292
-0.5932	7.7278	0.0356	6.4582
-0.4262	7.5346	-0.4498	6.2984
-0.2300	7.3442		
0.2942	7.1628		
0.5010	6.9822		

Graph No. 4
Formation Curve
Plot of \bar{n} Vs [P^L]

Ligand : HNHBCI
μ⁰=0.1 M KNO₃

Temp: 298 ± 1K
Water:Dioxane 3:2 (v/v)

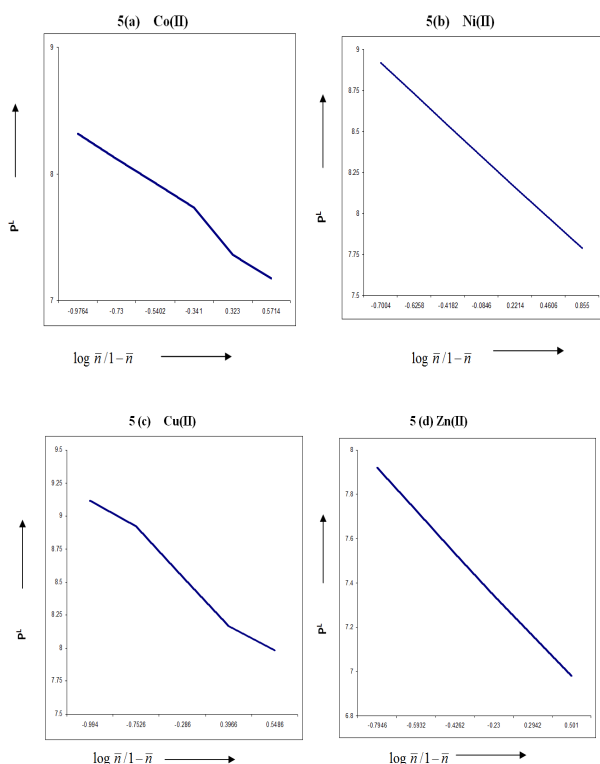


Graph No. 5

Linear Plot of $\log(\bar{n}/1-\bar{n})$ Vs P^L

Ligand : HNHBCI
 $\mu^0=0.1$ M KNO_3

Temp: 298 ± 1 K
Water:Dioxane 3:2 (v/v)

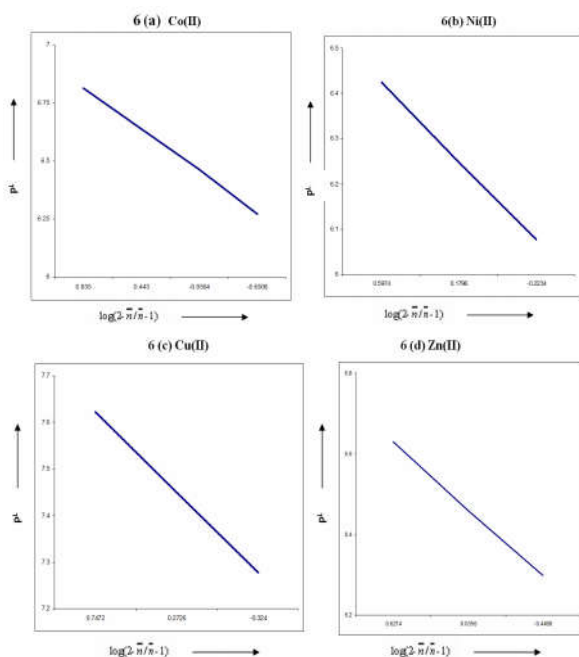


Graph No. 6

Linear Plot of $\log(2-\bar{n}/\bar{n}-1)$ Vs P^L

Ligand : HNHBCI
 $\mu^0=0.1$ M KNO_3

Temp: 298 ± 1 K
Water:Dioxane 3:2 (v/v)



The most representative values of $\log K_1$ and $\log K_2$ obtained are given in table – 12.

Table No. – 12 log of stepwise and overall stability constants of complex compounds of various metals with ligand HNHBCI at 298.

$\mu^0 = 0.10$ (M) KNO_3 Water – dioxane medium (V/V) = 3:2

System	Ligand (HNHBCI)		
	$\log K_1$	$\log K_2$	$\log \beta$
Co (II)	11.10	-	11.10
Ni (II)	7.31	6.31	13.62
Cu (II)	7.22	6.14	13.36
Zn(II)	6.49	5.42	11.91
Zn(II)	6.24	5.42	11.66

DISCUSSION

The values of stepwise stability constants and over all stability constants are given in table no. 12. 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 – William¹⁵. 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 importance¹⁶.

The stability of the chelates is greatly affected by the electron density around the imino nitrogen ($-C=N-$)¹⁷. 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 studies¹⁸⁻²⁶ and other workers²¹⁻²²

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