

Determination of stability constant of transition metal complexes with Schiff's base ligands derived from aromatic aldehydes and substituted aromatic amines

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Abstract

Ligands were synthesized by the simple condensation reaction of Salicylaldehyde with 7 – Methoxy 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 Bjerrum¹.

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 is in agreement with the natural order proposed by Irving – William².

Key words : Co(II), Ni(II), Cu(II), Zn(II), Schiff's base Ligands, complex compounds, stability constant, Irving – Rossotti titration technique, Salicylaldehyde, 7 – Methoxynaphthyl amine.

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 metals 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^{1,2}.

Schiff's base complexes are biologically³ active and used in many fields. These complexes

are used in catalysis⁴, material science⁵, Electrochemistry⁶ and medicines⁷. It has been observed that metal complexes act as antitumour⁸, antiviral⁹, anti cancer¹⁰ and many other anti bacterial agents¹¹.

A large number of tridentate Schiff's base ligands of Naphthyl amine and salicylaldehyde and their complexes have been synthesized¹². Structure of these complexes were characterised 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'-Methoxynaphthyl - 2 - hydroxyl benzene carbaldimine (MNHBCI)

Experimental

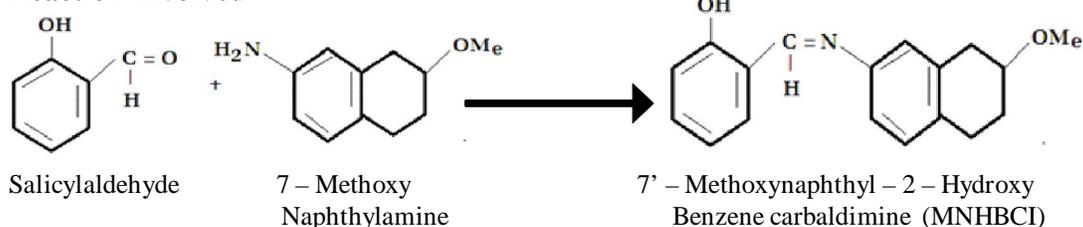
Nitrate salts of all the divalent Co, Ni,

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 methods¹³ Elemental analysis of metals were done by volumetric as well as gravimetric methods¹⁴. Double distilled and deionised CO₂ 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 Salicylaldehyde with 7 - Methoxy naphthalene - 2 - amine 3.5 g of amine were mixed with aqueous solution of 2.6 g aldehyde. The mixture was boiled under reflux in the presence of glacial acetic acid for two hours. The solution was concentrated and cooled to 0°C.

The product obtained was filtered, washed several times and recrystallised from ethanol. The yield of product (mol. mass, 277) was 2.4 g.

Reaction involved



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) KNO₃ solution at temperature 298 K within the limit of ± 1 K.

Titrations were carried out in a cell

and glass electrode in a thermostat with the help of microburette. 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 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 2

Result

A graph between pH – meter reading [B] and volume of alkali added was plotted in each case. Graph No. 1. The three titration curves so obtained are referred as:

- Acid titration curve
- Ligand titration curve and
- Complex titration curves 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 **graph-1** at temperature 298 K.

CALCULATION OF \bar{n}_A , \bar{n} AND P^L

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

$$\bar{n}_A = 1 + [(V_1 - V_2) / (V^0 + V_1)] (N^0 + E^0) / T_L^0$$

$$\bar{n} = [(V_3 - V_2) / (V^0 + V_1)] [(N^0 + E^0) / T_M^0] \times 1 / \bar{n}_A$$

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

Metal ions	V^0 in mL	Y	N^0	E^0	T_L^0	T_M^0
Co (II)	100	1	1.0(M)	1.0×10^{-2} (M)	2.5×10^{-3} (M)	5.0×10^{-4} (M)
Ni (II)	100	1	1.0(M)	1.0×10^{-2} (M)	2.5×10^{-3} (M)	5.0×10^{-4} (M)
Cu (II)	100	1	1.0(M)	1.0×10^{-2} (M)	2.5×10^{-3} (M)	5.0×10^{-4} (M)
Zn (II)	100	1	1.0(M)	1.0×10^{-2} (M)	2.5×10^{-3} (M)	5.0×10^{-4} (M)

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

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 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 0.3210 and 0.7760. 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 .

Table 2.

Ligand – MNHBCI

Temp. 298 ± 1 K $\mu^0 = 0.1(\text{M}) \text{KNO}_3$,

Water – Dioxane medium (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	5.1	5.4	5.4	5.4	5.4	5.41
0.1	5.2	5.5	5.4	5.4	5.4	5.4
0.2	5.3	5.62	5.52	5.48	5.48	5.52
0.3	5.38	5.72	5.7	5.7	5.72	5.68
0.4	5.55	5.88	5.88	5.92	5.96	5.9
0.5	5.86	6.22	6.32	6.2	6.2	6.24
0.6	6.4	6.64	6.66	6.54	6.58	6.58
0.7	7.15	7.25	7.27	7.26	7.26	7.28
0.8	7.86	7.9	7.72	7.78	7.78	7.76
0.9	10.62	10.92	8.45	8.86	8.56	8.51
1.0	11.55	11.88	10.25	9.66	8.84	9.26
1.1	11.78	12.55	11.28	11.56	10.28	10.78
1.2	12.16	12.50	11.86	12.02	10.95	11.12

Graph No. 1

Experimental Curve with ligand MNHBCI

Temp: 298 ± 1 K $\mu^0 = 0.1(\text{M}) \text{KNO}_3$,

Water – Dioxane medium (V/V) = 3:2

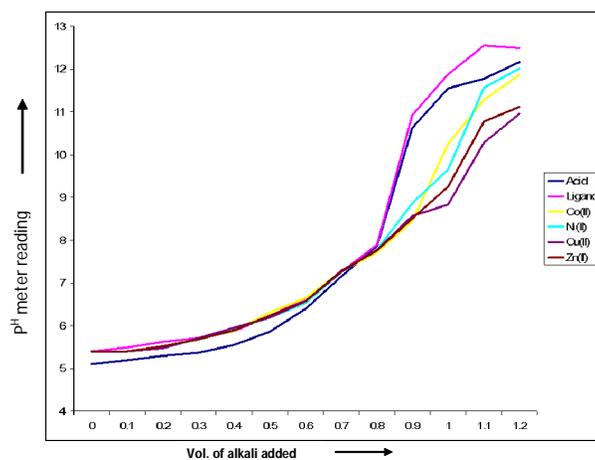


Table 3

Ligand - MNHBCI

Temperature : 298 K

 $\mu^0 = 0.1(\text{M}) \text{KNO}_3$,

Water - Dioxane medium (V/V) = 3:2

[B]	$V_2 - V_1$	\bar{n}_A	$\log \bar{n}_A / (1 - \bar{n}_A)$
5.0	0.030	0.7760	0.8996
5.2	0.032	0.7794	0.8642
5.4	0.034	0.7716	0.8326
5.6	0.036	0.7638	0.8024
5.8	0.038	0.7560	0.7732
6.0	0.040	0.7524	0.7594
6.2	0.042	0.7436	0.7526
6.4	0.044	0.7328	0.6942
6.6	0.046	0.7186	0.6582
6.8	0.046	0.7076	0.6262
7.0	0.050	0.6928	0.5822
7.2	0.054	0.6788	0.5486
7.4	0.056	0.6682	0.5190
7.6	0.060	0.6528	0.4822
7.8	0.064	0.6366	0.4374
8.0	0.068	0.6242	0.4174
8.2	0.072	0.6156	0.4010
8.4	0.076	0.6034	0.3744
8.6	0.078	0.5924	0.3528
8.8	0.080	0.5756	0.3178
9.0	0.084	0.5592	0.2882
9.2	0.808	0.5394	0.2484
9.4	0.090	0.5192	0.2122
9.6	0.102	0.4993	0.1744
9.8	0.104	0.4884	0.1538
10.0	0.106	0.4682	0.1178
10.2	0.110	0.4526	0.0884
10.4	0.116	0.4266	0.0474
10.6	0.122	0.3984	0.0026
10.8	0.132	0.3678	-0.0558
11.0	0.140	0.3210	-0.1422

Graph No. 2
Formation Curve of ligand MNHBCI

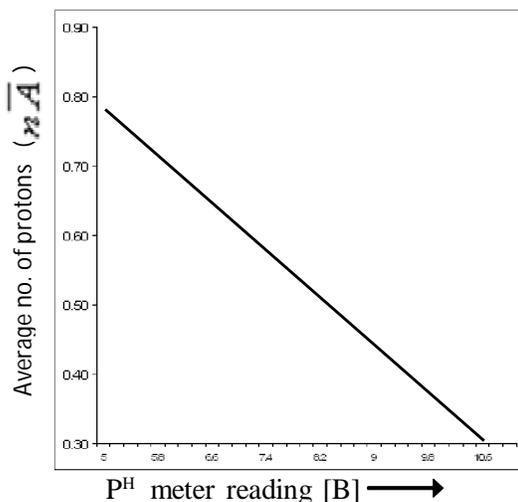
Plot of \bar{n}_A Vs [B]

Temp: 298±1K

$\mu^0 = 0.1(M) KNO_3$,

Water – Dioxane

medium (V/V) = 3:2



Graph No. – 3

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

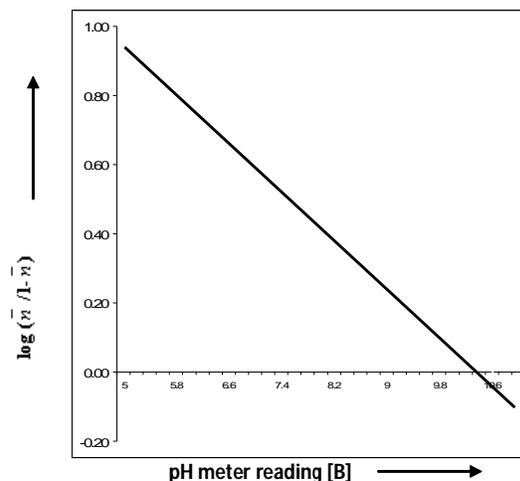
Ligand : MNHBCI

Temp: 298±1K

$\mu^0 = 0.1(M) KNO_3$,

Water – Dioxane

medium (V/V) = 3:2



Co(II) – MNHBCI 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 0.08 and 1.74 (**table no. 4;** **graph no. 4.**) at temperature 298K, indicating the formation of ML and ML₂ types of complexes.

From the formation curves (**graph 4**) the values of $\log K_1$ and $\log K_2$ were calculated by half – integral method at given temperature. The values were further corroborated by mid point slope method and linear plot of $\log \bar{n}/(1 - \bar{n})$ vs P^L (**table 5;** **graph 5**) and plot of $\log(2 - \bar{n})/(\bar{n} - 1)$ vs P^L . (**table 5;** **graph-6**)

at temperature 298 K.

Ni(II) – MNHBCI System :

The complex titration curve 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 0.0452 and 1.9722 (**graph 7;** **table 6,**) at temperature 298 K indicating the formation of ML and ML₂ type of complexes.

From the formation curves, **graph 7**, 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 method and plot of $\log \bar{n}/1-\bar{n}$ vs P^L (**Table 7, Graph 8**) and also by plot of $\log(2-\bar{n}/\bar{n}-1)$ vs P^L (**Table 7, Graph 9**) both at temperature 298 K.

Cu(II) –MNHBCI 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 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 0.0352 to 1.8042 (**graph-10; table 8**) at temperature 298 K indicating the formation of ML and ML_2 type of complexes.

From the formation curves (**graph – 10, and table 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 plot of $\log \bar{n}/1-\bar{n}$ vs P^L (**Table 9, Graph 11**) and also by plot of $\log(2-\bar{n}/\bar{n}-1)$ vs P^L (**Table 9, Graph 12**) both at temperature 298 K.

Zn(II) – MNHBCI (L_2) 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 0.0570 to 1.62 (**table– 10; graph 13**) at temperature 298 K indicating the formation of ML_1 and ML_2 type of complexes.

From the formation curve, (**graph – 13**) 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 14; table 11**) and plot of $\log(2-\bar{n})/(\bar{n}-1)$ vs P^L (**graph– 15; table – 11**) at temperature 298 K.

Table 4

Co (II) MNHBCI Temp: 298±1K
 $\mu^0=0.1(M) KNO_3$ Water – Dioxane
 medium (V/V) = 3:2

[B]	$V_3 - V_2$	\bar{n}	P^L
6.0	0.008	0.0834	8.2142
6.2	0.009	0.2896	8.0224
6.4	0.012	0.3884	7.8316
6.6	0.016	0.3152	7.6394
6.8	0.018	0.4212	7.4542
7.0	0.022	0.5318	7.2644
7.2	0.030	0.6960	7.0822
7.4	0.032	0.8384	6.8962
7.6	0.040	1.2450	6.7190
7.8	0.044	1.2076	6.5372
8.0	0.052	1.4222	6.3634
8.2	0.066	1.7464	6.2082

Table 5

Co (II) MNHBCI Temp: 298±1K
 $\mu^0=0.1(\text{M}) \text{KNO}_3$ Water – Dioxane
 medium (V/V) = 3:2

$\log \bar{n}/(1-\bar{n})$	P^L	$\log (2-\bar{n})/(\bar{n}-1)$	P^L
-0.7494	8.0224	0.8694	6.7190
-0.4910	7.7316	0.2976	6.5474
-0.2486	7.5394	-0.2844	6.3752
0.3350	7.2646	-0.6408	6.2076
0.4912	7.0712		

Table 6

Ni (II) + MNHBCI Temp: 298±1K
 $\mu^0=0.1(\text{M}) \text{KNO}_3$ Water – Dioxane
 medium (V/V) = 3:2

B	$V_3 - V_2$	\bar{n}	P^L
5.2	0.004	0.0452	9.0094
5.4	0.006	0.1374	8.8176
5.6	0.007	0.2316	8.6264
5.8	0.010	0.3510	8.4372
6.0	0.018	0.4936	8.2474
6.2	0.022	0.5930	8.0616
6.4	0.026	0.6982	7.8714
6.6	0.034	0.8550	7.6866
6.8	0.038	1.0414	7.5072
7.0	0.046	1.2392	7.3730
7.2	0.054	1.4636	7.1566
7.4	0.062	1.6946	6.9862
7.6	0.068	1.9722	6.8242

Table 7

Ni (II)+MNHBCI Temp: 298±1K
 $\mu^0=0.1(\text{M}) \text{KNO}_3$ Water – Dioxane
 medium (V/V) = 3:2

$\text{Log } \bar{n}/(1-\bar{n})$	P^L	$\log (2-\bar{n})/(\bar{n}-1)$	P^L
-0.8956	8.8184	0.6024	7.3230
-0.6202	8.6266	0.0636	7.1516
-0.3668	8.4376	-0.4592	6.9862
0.2640	8.0664	-0.5216	6.7326
0.4642	7.8710	-0.5982	6.5429
0.8704	7.6812	-0.6120	5.9832

Table 8

Cu(II)+MNHBCI Temp: 298±1K
 $\mu^0=0.1(\text{M}) \text{KNO}_3$ Water – Dioxane
 medium (V/V) = 3:2 (v/v)

B	$V_3 - V_2$	\bar{n}	P^L
5.0	0.002	0.0352	9.2096
5.2	0.004	0.0813	9.0142
5.4	0.006	0.2604	8.821
5.6	0.010	0.3314	8.5656
5.8	0.012	0.4740	8.3384
6.0	0.018	0.6172	8.1542
6.2	0.026	0.7408	7.965
6.4	0.032	0.8944	7.7822
6.6	0.040	0.8770	7.7014
6.8	0.046	1.2412	7.5176
7.0	0.050	1.4660	7.3436
7.2	0.062	1.7176	7.176
7.4	0.076	1.8042	7.0654

Table 9

Cu(II)+MNHBCI Temp: 298±1K
 $\mu^0=0.1(\text{M}) \text{KNO}_3$, Water – Dioxane
 medium (V/V) = 3:2 (v/v)

$\text{Log } \bar{n}/(1-\bar{n})$	P^{L}	$\log (2-\bar{n})/(\bar{n}-1)$	P^{L}
-0.8172	8.72	0.8872	7.5186
-0.6200	8.5264	0.3394	7.3444
-0.3226	8.3394	-0.3080	7.1760
0.3510	8.1752	-0.2876	6.9234
0.6872	7.9814	-0.2462	6.4356

Table 10

Zn(II)+MNHBCI (L_4) Temp: 298±1K
 $\mu^0=0.1(\text{M}) \text{KNO}_3$, Water – Dioxane
 medium (V/V) = 3:2 (v/v)

[B]	V_3-V_2	\bar{n}	P^{L}
6.0	0.002	0.0570	8.21
6.2	0.004	0.0846	8.0164
6.4	0.006	0.2444	7.8186
6.6	0.012	0.3192	7.6252
6.8	0.014	0.4224	7.4354
7.0	0.016	0.5552	7.2476
7.2	0.018	0.6904	7.0606
7.4	0.030	0.6804	6.8796
7.6	0.032	0.8854	6.7012
7.8	0.032	1.4516	6.5312
8.0	0.054	1.6212	6.3644
8.2	0.064	1.6182	6.2034

Table 11

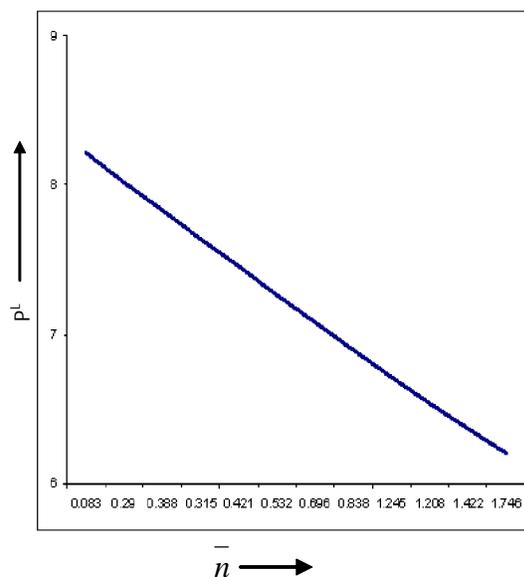
Zn(II)+MNHBCI (L_4) Temp: 298±1K
 $\mu^0=0.1(\text{M}) \text{KNO}_3$, Water – Dioxane
 medium (V/V) = 3:2 (v/v)

$\text{Log } \bar{n}/(1-\bar{n})$	P^{L}	$\log (2-\bar{n})/(\bar{n}-1)$	P^{L}
-0.6502	7.6252	0.5726	6.5312
-0.4228	7.4350	0.0474	6.3640
-0.0882	7.2472	-0.7532	6.2032
0.2586	7.0604		
0.6554	6.8796		

Graph No. 4
 Formation curve of Co(II)

Plot of \bar{n} Vs P^{L}

Metal: Co(II) Ligand : MNHBCI
 Temp: 298±1K $\mu^0=0.1(\text{M}) \text{KNO}_3$,
 Water – Dioxane medium (V/V) = 3:2



Graph No. 5

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

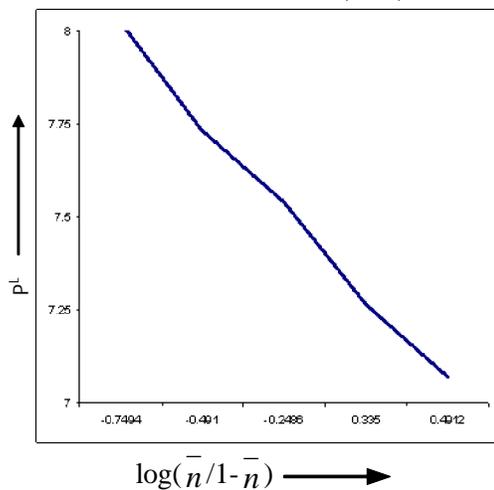
Metal: Co(II)

Ligand : MNHBCI

Temp: 298±1K

 $\mu^0=0.1(M)$ KNO₃,

Water – Dioxane medium (V/V) = 3:2



Graph No. 6

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

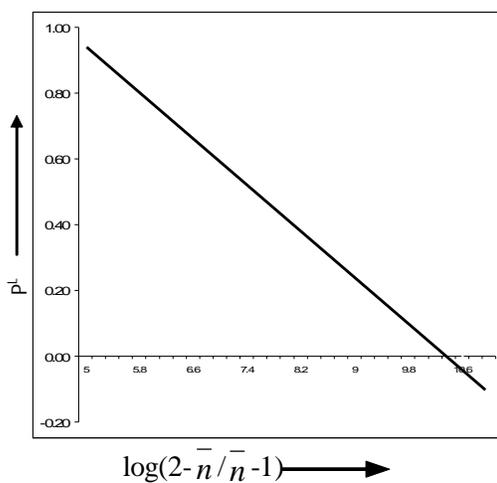
Metal: Co(II)

Ligand : MNHBCI

Temp: 298±1K

 $\mu^0=0.1(M)$ KNO₃,

Water – Dioxane medium (V/V) = 3:2



Graph No. 7

Formation curve of Ni(II)

Plot of \bar{n} Vs P^L

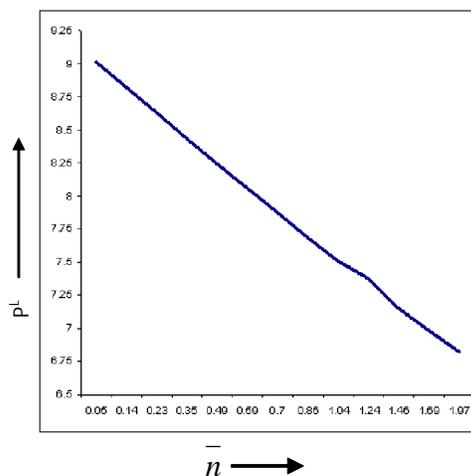
Metal: Ni (II)

Ligand : MNHBCI

Temp: 298±1K

 $\mu^0=0.1(M)$ KNO₃,

Water – Dioxane medium (V/V) = 3:2



Graph No. 8

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

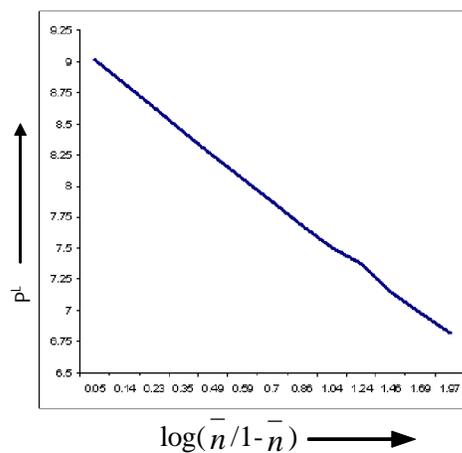
Metal: Ni (II)

Ligand : MNHBCI

Temp: 2981K

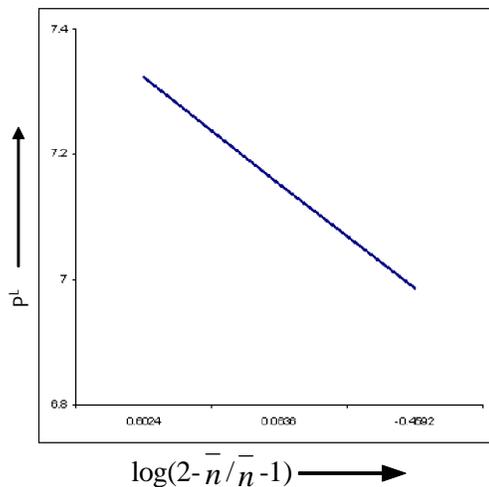
 $\mu^0=0.1(M)$ KNO₃,

Water – Dioxane medium (V/V) = 3:2



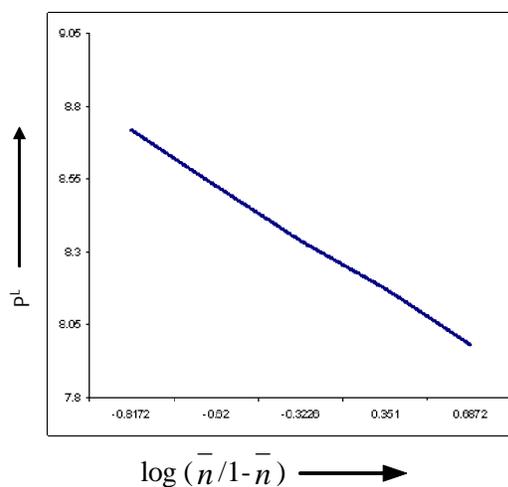
Graph No. 9

Linear plot of $\log(2-\bar{n}/\bar{n}-1)$ Vs P^L
 Metal: Ni (II) Ligand : MNHBCI
 Temp: 298±1K $\mu^0=0.1(M)$ KNO₃,
 Water – Dioxane medium (V/V) = 3:2



Graph No. 11

Linear plot of $\log(\bar{n}/1-\bar{n})$ Vs P^L
 Metal: Cu (II) Ligand : MNHBCI
 Temp: 298±1K $\mu^0=0.1(M)$ KNO₃,
 Water – Dioxane medium (V/V) = 3:2

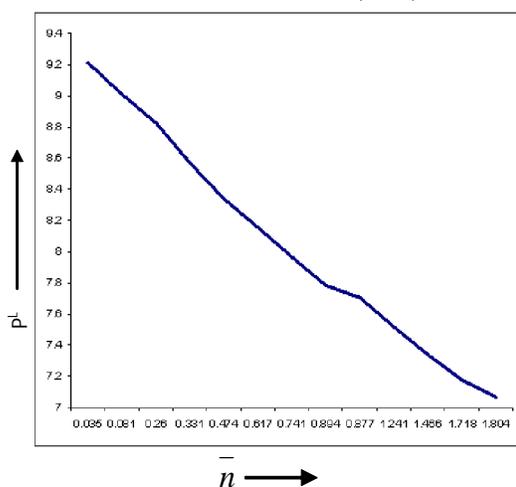


Graph No. 10

Formation curve of Cu (II)

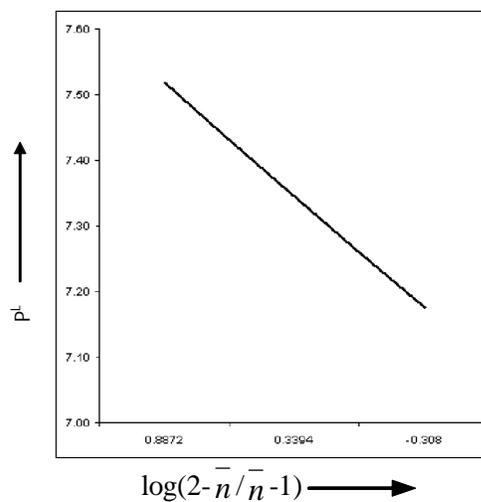
Plot of \bar{n} Vs P^L

Metal: Cu(II) Ligand : MNHBCI
 Temp: 298±1K $\mu^0=0.1(M)$ KNO₃,
 Water – Dioxane medium (V/V) = 3:2



Graph No. 12

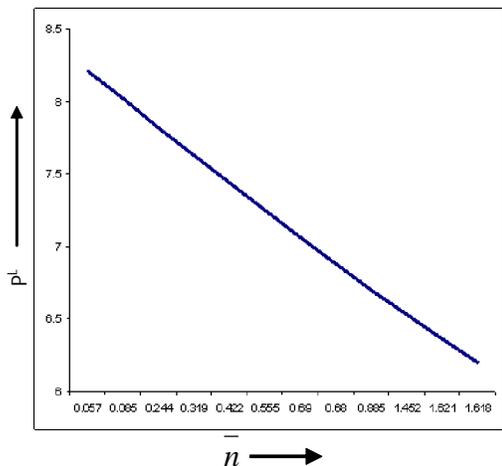
Linear plot of $\log(2-\bar{n}/\bar{n}-1)$ Vs P^L
 Metal: Cu (II) Ligand : MNHBCI
 Temp: 298±1K $\mu^0=0.1(M)$ KNO₃,
 Water – Dioxane medium (V/V) = 3:2



Graph No. 13
Formation curve of Zn (II)

Plot of \bar{n} Vs P^L

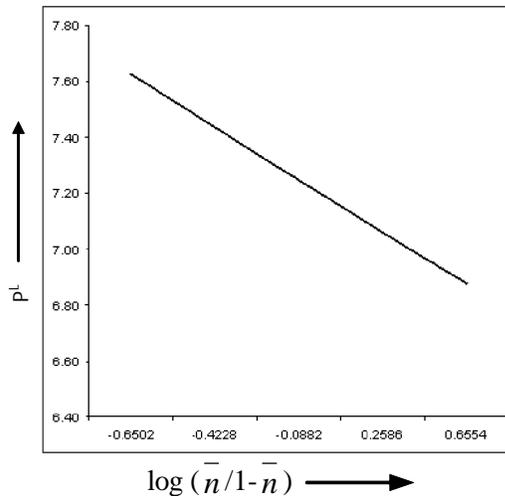
Metal: Zn (II) Ligand : MNHBCI
Temp: 298±1K $\mu^0=0.1(M)$ KNO₃,
Water – Dioxane medium (V/V) = 3:2



Graph No. 14

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

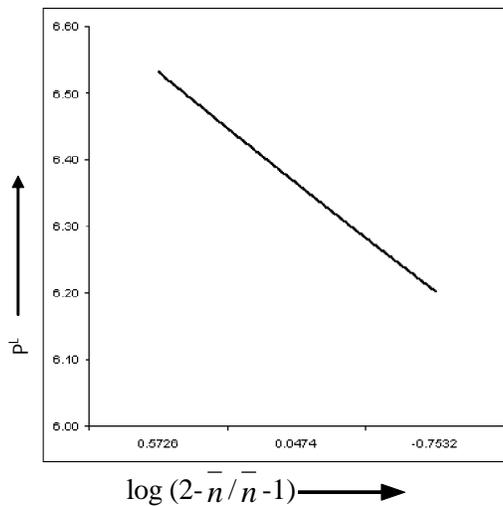
Metal: Zn(II) Ligand : MNHBCI
Temp: 298±1K $\mu^0=0.1(M)$ KNO₃,
Water – Dioxane medium (V/V) = 3:2



Graph No. 15

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

Metal: Zn (II) Ligand : MNHBCI
Temp: 298±1K $\mu^0=0.1(M)$ KNO₃,
Water – Dioxane medium (V/V) = 3:2



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 :-

- Half – integral method
- Mid – point slope calculation method and
- 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 MNHBCI at temperatures 298 K.

Metal ions	Ligand MNHBCI	
	log K ₁	log K ₂
MNHBCI	11.20	-
	-	-
	11.22	-
Co(II)	7.18	6.18
	7.22	6.20
	7.18	6.10
Ni(II)	7.06	5.95
	7.18	6.24
	6.44	5.36
Cu(II)	6.30	5.36
	6.46	5.46
	6.16	5.42
Zn(II)	6.04	5.38
	6.12	5.36
	6.14	5.32

Table 13

Average values of stepwise and over all stability constant of complex compounds of various metals with ligand MNHBCI at temperature 298 K

$\mu^0 = 0.10(\text{M}) \text{KNO}_3$ Water – Dioxane
medium (v/v) = 3:2

Ystem	Ligand MNHBCI		
	log K ₁	log K ₂	log β
MNNCI	10.98	-	10.98
Co (II)	6.86	5.80	12.26
Ni (II)	7.58	6.78	14.30
Cu (II)	7.68	6.76	14.40
Zn (II)	6.70	5.88	12.54

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



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 KNO₃ 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 imino nitrogen ($-\text{C}=\text{N}-$). 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 workers²¹⁻²².

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