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Physico – Chemical study of Transition Metal Complexes with Schiff's base derived from Naphthaldehyde and substituted aromatic amines

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Abstract

Schiff's base ligands were synthesized by the condensation reaction of $\beta -$ Naphthaldehyde with 7- Methoxy naphthalene – 2 – amine. Nitrate salts of divalent cobalt, nickel, copper and zinc were estimated by usual methods. Ligand was analysed for elements by standard method. pH metric titrations were carried out with the help of digital pH meter and stability constant of complexes of these metals with the ligands synthesized were computed by Irving- Rossoti technique modified by Calvin Bjerrum.

The stability constant values of metals for the given metal 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.

Key words : Co(II), Ni(II), Cu(II), Zn(II), Schiff's base, complex compounds, stability constant, Irving – Rossotti titration technique, Naphthaldehyde, substituted naphthyl amine, Thermodynamic parameters.

Introduction

These days considerable attention is being paid to the chemistry of complex compounds of Schiff's base containing nitrogen and other donor atoms.[1-4] Schiff's base offer a versatile and flexible series of ligands capable to bind with variety of metal ions to

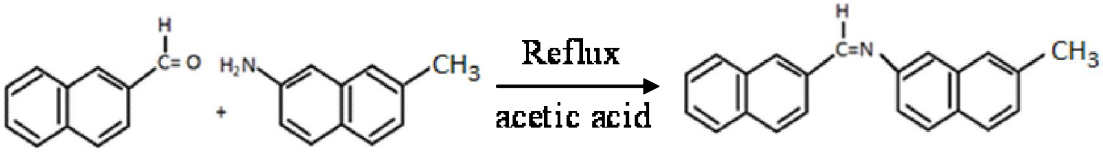
give complexes with varying properties. These complexes are biologically active[5] have wide potential applications in many fields such as catalysis[6], electrochemistry[7] and medicines studies[8] have shown that metal complexes act as antitumur, antiviral, anti cancer[10] and other many anti bacterial agents.

A large number of poly-dentate Schiff's base compounds have been synthesized and their complexes have been structurally characterized and extensively investigated. But little is known for their stability in aqueous solution in which it is used. Hence, the title project have been under taken. Here in, the stability constant of complexes of divalent transition metals *i.e.* Co(II), Ni(II), Cu(II) and Zn(II) with Schiff's base ligands have been determined.

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 methods. 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 synthesized by the condensation of β – Naphthaldehyde with 7 – Methoxy naphthalene – 2 – amine. 3.5g of aldehyde in solution was mixed with nearly 3.5 g naphthyl amine. The mixture was boiled under reflux in the presence of glacial acetic acid for about 2 hours. The solution was concentrated and cooled to 0°C. The product obtained was filtered, washed several times and re-crystallized from ethanol. The yield of product was nearly 2.8 g.



pH metric titration of acid, acid + ligand and acid + ligand + metal ion solutions were done at constant ionic strength of 0.1 M KNO_3 at temperature 298 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.

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 1. Concentrations used in the Experiment

Metal / Ions	V^o (mL)	Y	N^O	E^O	T^O_L	T^O_M
Co (II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)
Ni(II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)
Cu(II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)
Zn(II)	100	1	1.0 (M)	1.0×10^{-2} (M)	2.4×10^{-3} (M)	5.0×10^{-4} (M)

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 (a), (b) and (c) respectively from the experimental curves at temperature 298 K given in graph 1.

Calculation of $\bar{n}_A$, $\bar{n}$ and P^L

$\bar{n}_A$, $\bar{n}$ and P^L were calculated using standard expressions.

Proton – Ligand Stability Constant :

The ligand titration curve separates from acid titration curve at pH 5.24 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 298K.

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 0.5272 and 0.886. This indicates that ligand is monoprotic.

Dissociation of ligand may be given as,

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

The value of proton ligand stability constant was calculated by half – integral method and it was further corroborated by linear plot method[3-4] (log $\bar{n}_A/(1-\bar{n}_A)$ vs [B] (graph -3) at temperature 298 K .

Graph No. 1

Experimental curve with ligand MNNCI
Temp. 298±1 K

μ^0 = 0.10 (M) KNO_3

Water : dioxane = 3:2(v/v)

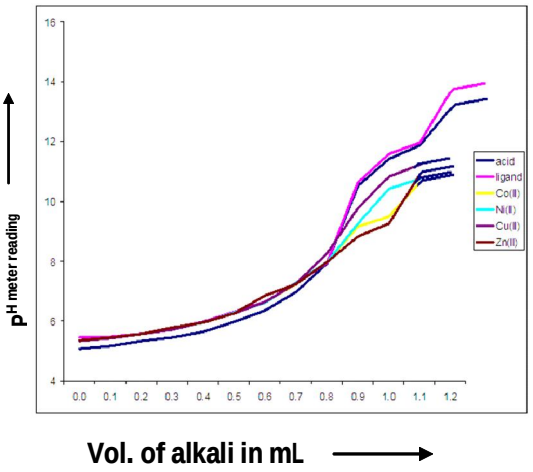


Table 2. Volume of alkali consumed in different titrations

Ligand: MNNCI Temperature: 298 1 K

μ^0 = 0.10 (M) KNO_3 Water – dioxane medium (v/v) = 3:2

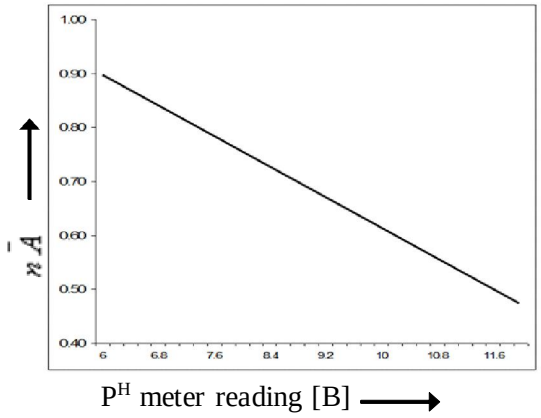
Vol. of alkali added in mL	H^+	H^++ L	pH – meter reading [B]			
			H^+ + L +Co(II)	H^+ + L + Ni(II)	H^+ + L + Cu(II)	H^+ + L +Zn(II)
0.0	5.06	5.44	5.32	5.34	5.34	5.36
0.1	5.16	5.48	5.46	5.44	5.42	5.46
0.2	5.34	5.56	5.56	5.58	5.56	5.56
0.3	5.44	5.76	5.78	5.76	5.7	5.78
0.4	5.64	5.98	5.94	5.94	5.98	5.96
0.5	5.98	6.3	6.25	6.28	6.26	6.26
0.6	6.36	6.64	6.64	6.62	6.64	6.86
0.7	6.96	7.26	7.24	7.28	7.26	7.24
0.8	7.92	7.94	7.98	7.96	8.26	7.96
0.9	10.52	10.64	9.16	9.24	9.78	8.82
1.0	11.42	11.58	9.48	10.42	10.82	9.26
1.1	11.86	11.96	10.62	10.76	11.22	10.88
1.2	13.1	13.68				

Graph No. 2. Formation curve of ligand MNNCI

Plot of $n\bar{A}$ Vs [B]

Temp. 298±1 K

μ^0 = 0.10 (M) KNO_3 Water : Dioxane 3:2(v/v)



Graph No. 3.

Linear plot of log(n $\bar{A}$ / 1- n $\bar{A}$) Vs [B]

Ligand – MNNCI Temp. 298 ± 1 K

μ^0 = 0.10 (M) KNO_3 Water : Dioxane 3:2(v/v)

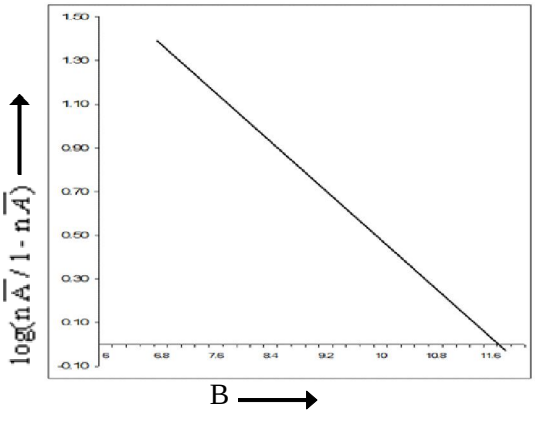


Table 3.

Ligand : MNNCI Temp: 298 ± 1K

$\mu = 0.1M\ KNO_3$ Water:Dioxane(3:2)v/v

[B]	$V_2 - V_1$	$\bar{n}_A$	$\log \bar{n}_A / (1 - \bar{n}_A)$
6.0	0.006	0.886	
6.2	0.006	0.886	
6.4	0.007	0.8844	
6.6	0.007	0.8814	
6.8	0.008	0.8804	
7.0	0.008	0.8766	
7.2	0.009	0.8734	
7.4	0.009	0.8682	
7.6	0.022	0.8614	
7.8	0.014	0.8524	
8.0	0.016	0.8444	1.3262
8.2	0.016	0.8414	1.2952
8.4	0.018	0.8284	1.2094
8.6	0.022	0.8158	1.0472
8.8	0.024	0.8014	0.8732
9.0	0.028	0.7924	0.8164
9.2	0.032	0.7764	0.7488
9.4	0.034	0.7556	0.6732
9.6	0.042	0.7356	0.6068
9.8	0.044	0.7154	0.5464
10.0	0.054	0.6924	0.4804
10.2	0.058	0.6644	0.4098
10.4	0.064	0.6358	0.3444
10.6	0.072	0.6076	0.2842
10.8	0.082	0.5954	0.2754
11.0	0.098	0.5634	0.2042
11.2	0.108	0.5586	0.1414
11.4	0.112	0.5494	0.1042
11.6	0.118	0.5398	0.0444
11.8	0.128	0.5276	-0.05
12.0	0.142	0.5272	-0.226

Co (II) – MNNCI System :

The complex titration curve of the system crossed the ligand mixture curve at pH = 5.30 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 $P^H = 8.78$. Hence, in order to preclude error due to hydrolysis in the calculation of $\bar{n}$, only the lower P^H regions of titration curves were used.

The values of $\bar{n}$ extend between 0.20 to 1.81 (graph – 4a, & 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 (graph 6a, Table 5) at temperature 298 K.

Ni(Ii) – MNNCI System :

The complex titration curve of the system crossed the ligand mixture curve at pH = 4.73 indicating the start of complexation. The curve increased regularly upto pH = 7.42 indicating constant rate of release of proton and then complex titration curve diverges indicating quick but incomplete dissociation of ligand.

No turbidity appears; hence hydrolysis does not take place.

Values of $\bar{n}$ falls in the range of 0.1014 to 1.9596 at temperature 298 K (table – 6, graph – 4(b)).

The values of log K_1 and log K_2 were calculated by half integral method and verified by mid point slope method and linear plot of log $\bar{n}$ /(1- $\bar{n}$) vs P^L (graph 5(b), Table 7) and plot of log (2- $\bar{n}$)/($\bar{n}$ -1) vs P^L. (Table 7, graph 6(b),) at temperature 298 K.

Cu(II) – MNNCI System :

Complex titration curve crossed the acid titration curve and well separated from ligand titration curve at pH = 5.68. The curve increased regularly and run parallel to the ligand titration curve upto pH = 9.2.

During the titration equilibrium is attained very quickly, no turbidity appears, hence it may be expected that hydrolysis does not take place.

The values of $\bar{n}$ extended from 0.1642 to 1.86 at temperature 298 K indicating the formation of ML and ML_2 type of complexes, (table – 8, graph 4(c)) at 298 K.

Formation curve (4(c)) are also 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 (graph no. 5(c); table no. 9) and plot of log (2 - $\bar{n}$)/($\bar{n}$-1) vs P^L. (table 9, graph – 6(c)) at temperature 298 K.

Zn (II) – MNNCI System :

Metal ligand titration curve is well separated from ligand titration curve at pH = 5.85 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 0.40 to 1.86 at temperature 298 K, indicating the formation of ML and ML_2 type complexes only. (table 10, graph 4(d)) at temperature 298 K.

Formation curve (Graph – 4(d)) are also very symmetrical. It gave the value of log K_1 and log K_2 by half integral method at given temperature of 298 K. These values were further verified from mid point slop method and the linear plot of log ($\bar{n}$/1-$\bar{n}$) vs P^L (Graph 5(d)) Table 11, at and also from plot of log (2-$\bar{n}$)($\bar{n}$-1) vs P^L (Graph 6(d). table 11) both at temperature 298K.

Table 4

Co (II) + MNNCI — Temperature: 298 ± 1K

μ = 0.1 M KNO_3 — Water:Dioxane 3:2 (v/v)

B	V_3 - V2	$\bar{n}$	P^L
5.2	0.006	0.2016	9.0644
5.4	0.008	0.3034	8.8734
5.6	0.012	0.3272	8.6856
5.8	0.024	0.4012	8.5028
6.0	0.026	0.6054	8.3222
6.2	0.042	0.7446	8.1364
6.4	0.050	1.10344	7.9566
6.6	0.066	1.3406	7.7802
6.8	0.078	1.5728	7.6074
7.0	0.080	1.6752	7.4332
7.2	0.092	1.8172	7.2664

Table 5

Co (II) + MNNCI Temperature: 298 ± 1K

$\mu = 0.1$ 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	9.0644	0.5992	7.7802
-0.5922	8.8732	0.0576	7.6074
-0.3134	8.6852	-0.4192	7.4332
0.3792	8.3226	-0.3816	7.2496
0.7356	8.1360	-0.2615	7.0528

Table 6

Metal: Ni (II)

Ligand : MNNCI Temp. 298 ±1 K

$\mu = 0.1$ M KNO_3 Water:Dioxane 3:2 (v/v)

B	$V_3 - V_2$	$\bar{n}$	P^L
5.0	0.004	0.1014	7.8646
5.2	0.010	0.2654	7.6798
5.4	0.022	0.4296	7.4948
5.6	0.030	0.6158	7.3134
5.8	0.036	0.8032	7.1324
6.0	0.044	0.9934	6.9522
6.2	0.052	1.2094	6.7764
6.4	0.064	1.4304	6.6026
6.6	0.084	1.6974	6.4366
6.8	0.092	1.9596	6.2724

Table 7

Ni (II) + MNNCI Temp: 298 ± 1K

$\mu^0 = 0.10$(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
-0.9456	8.8646	0.5756	7.7766
-0.4418	8.6798	0.1214	7.6025
-0.1236	8.4948	-0.3620	7.4363
0.2048	8.3134		
0.6116	8.1326		

Table 8

Cu(II) + MNNCI Temp : 298 ± 1K

μ^0 = 0.10(M) KNO_3 Water : Dioxane = 3:2(v/v)

[B]	$V_3 - V_2$	$\bar{n}$	P^L
6.2	0.014	0.1642	7.2702
6.4	0.014	0.2470	7.0780
6.6	0.016	0.3724	6.8890
6.8	0.022	0.5004	6.7016
7.0	0.024	0.6316	6.5144
7.2	0.034	0.7848	6.3300
7.4	0.042	0.9370	6.1462
7.6	0.050	1.1222	5.9660
7.8	0.062	1.3114	5.7882
8.0	0.072	1.5726	5.6204
8.2	0.080	1.8630	5.4586

Table 9

Cu(II) + MNNCI Temp : 298 ± 1K

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
-0.7072	8.2702	0.8568	6.9668
-0.3496	8.0788	0.3446	6.7886
-0.2270	7.8894	-0.1272	6.6204
-0.2332	7.5146	-0.7998	6.4592
0.5626	7.3308	-0.6834	6.2691

Table 10

Zn (II) + MNNCI Temp: 298 ± 1K

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	0.404	7.4592
6.2	0.010	0.1022	7.2696
6.4	0.012	0.1856	7.0784
6.6	0.016	0.3716	6.8894
6.8	0.022	0.5004	6.7016
7.0	0.024	0.6312	6.5144
7.2	0.036	0.7844	6.3300
7.4	0.042	0.9370	6.1462
7.6	0.050	1.1222	5.9664
7.8	0.066	1.3114	5.7882
8.0	0.074	1.5726	5.6204
8.2	0.086	1.8638	5.4580

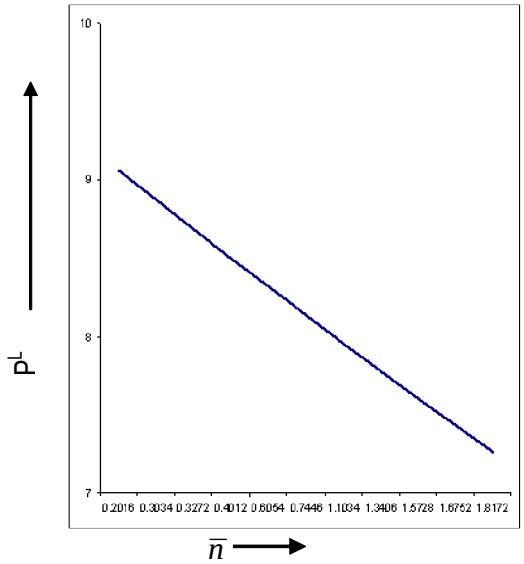
Table 11

Zn (II) + MNNCI Temp: 298 ± 1K

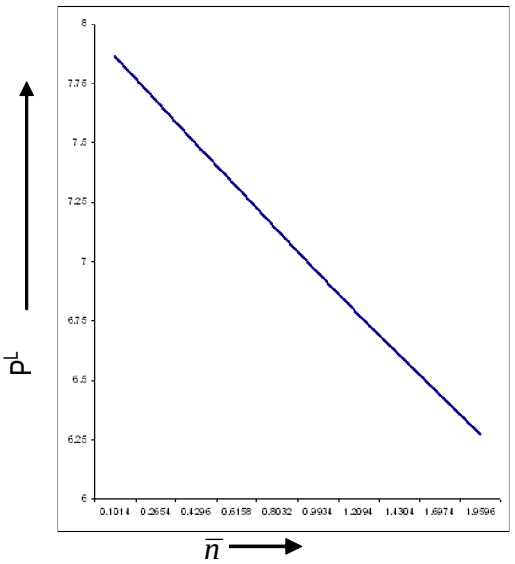
μ^0 = 0.10(M) KNO_3 Water : Dioxane = 3:2(v/v)

$\log \bar{n}/(1-\bar{n})$	P^L	$\log (2-\bar{n})/(\bar{n}-1)$	P^L
-0.7070	8.2702	0.8564	6.9664
-0.3494	8.0784	0.3442	6.7886
-0.2268	7.8894	-0.1276	6.6204
-0.2330	7.5144	-0.7994	6.4584
0.5624	7.3300	-0.8312	6.3214

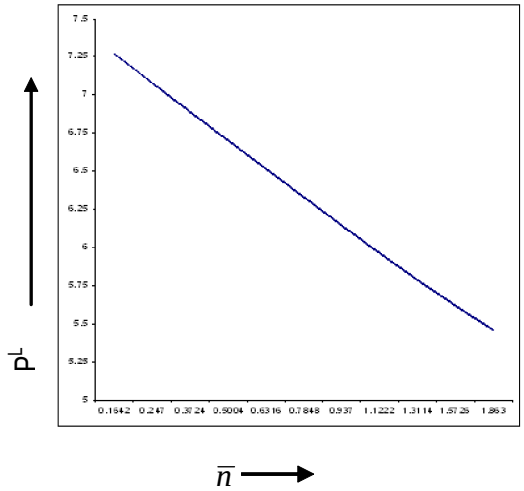
Graph 4(a)
Formation curve of Co (II)
Plot of $\overline{n}$ Vs P^L
Ligand : MNNCI Temp. 298 ±1 K
$\mu = 0.1$ M KNO_3 Water:Dioxane 3:2 (v/v)



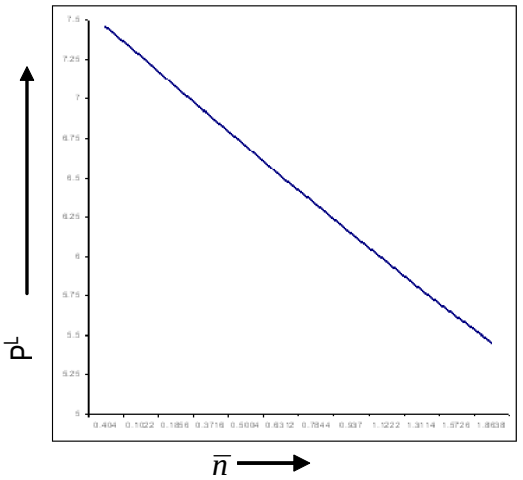
Graph 4(b)
Formation curve of Ni (II)
Plot of $\overline{n}$ Vs P^L
Ligand : MNNCI Temp. 298 ±1 K
$\mu = 0.1$ M KNO_3 Water:Dioxane 3:2 (v/v)



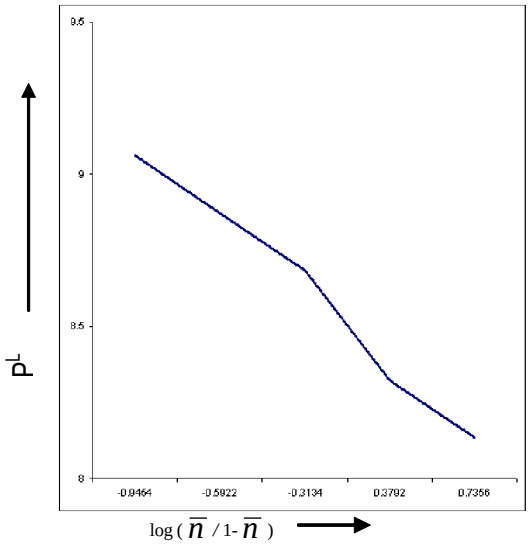
Graph 4(c)
Formation curve of Cu (II)
Plot of $\overline{n}$ Vs P^L
Ligand : MNNCI Temp. 298 ±1 K
$\mu = 0.1$ M KNO_3 Water:Dioxane 3:2 (v/v)



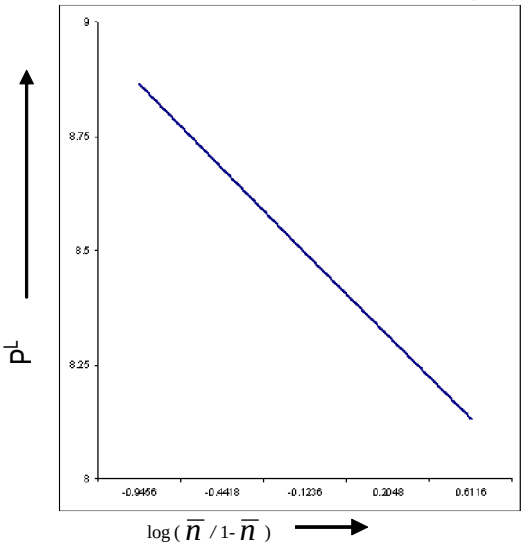
Graph 4(d)
Formation curve of Zn(II)
Plot of $\overline{n}$ Vs P^L
Ligand : MNNCI Temp. 298 ±1 K
$\mu = 0.1$ M KNO_3 Water:Dioxane 3:2 (v/v)



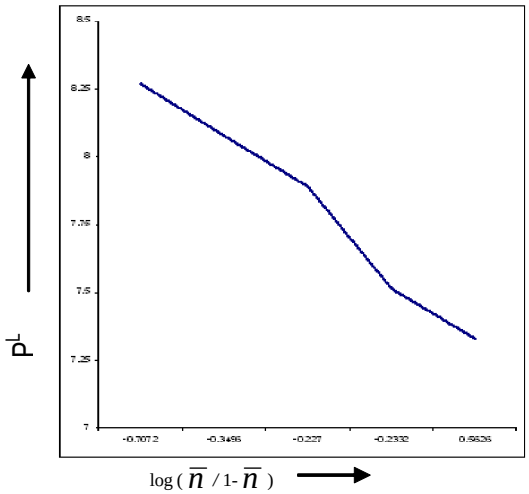
Graph 5(a)
Formation curve of Co (II)
Linear Plot of log ($\bar{n}$/1- $\bar{n}$) Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



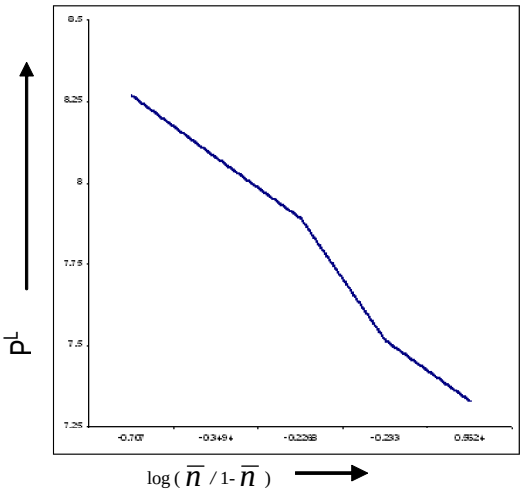
Graph 5(b)
Formation curve of Ni (II)
Linear Plot of log ($\bar{n}$/1- $\bar{n}$) Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



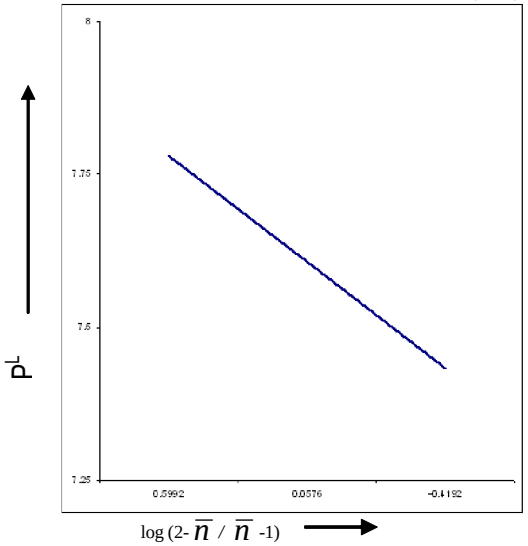
Graph 5(c)
Formation curve of Cu (II)
Linear Plot of log ($\bar{n}$/1- $\bar{n}$) Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



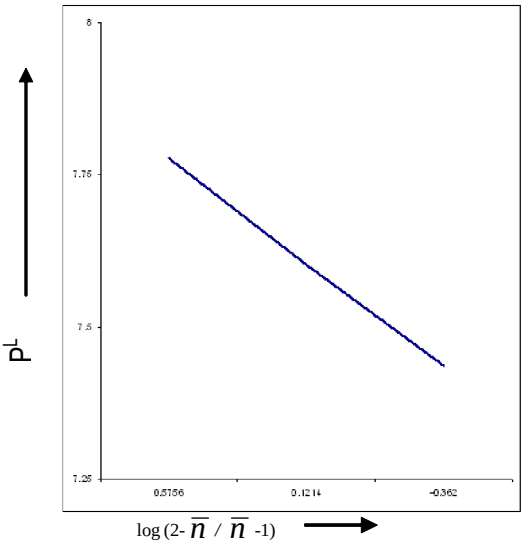
Graph 5(d)
Formation curve of Zn(II)
Linear Plot of log ($\bar{n}$/1- $\bar{n}$) Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



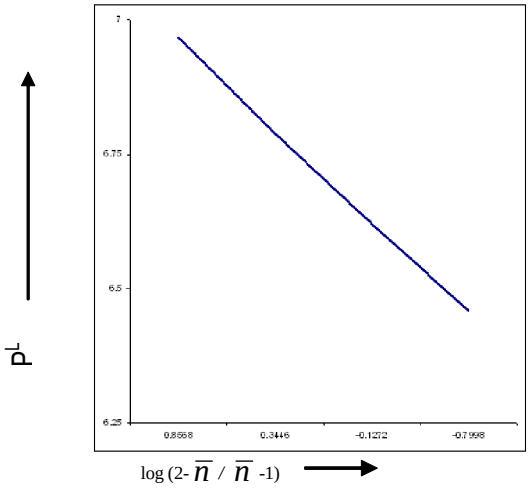
Graph 6(a)
Formation curve of Co (II)
Linear Plot of log $(2-\bar{n}/\bar{n}-1)$ Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



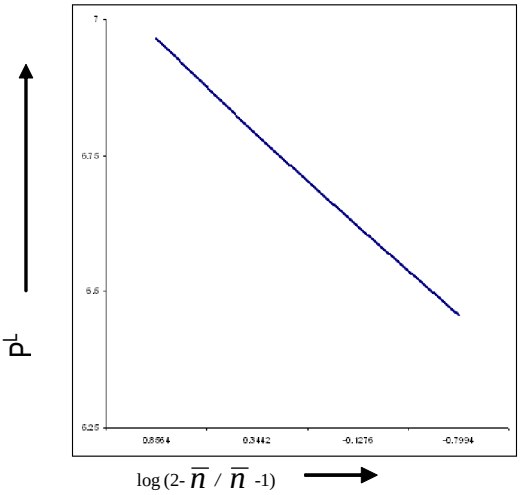
Graph No. 6(b)
Formation curve of Ni (II)
Linear Plot of log $(2-\bar{n}/\bar{n}-1)$ Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



Graph 6(c)
Formation curve of Cu (II)
Linear Plot of log $(2-\bar{n}/\bar{n}-1)$ Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



Graph 6(d)
Formation curve of Zn (II)
Linear Plot of log $(2-\bar{n}/\bar{n}-1)$ Vs P^L
Ligand : MNNCI Temp. 298±1 K
μ = 0.1 M KNO_3 Water:Dioxane 3:2 (v/v)



The values of protonation constant and stepwise stability constant obtained by different computational methods at temperatures 298 K are summarized in Table 12
The different methods are :-

a) Half – integral method
b) Mid – point calculation method
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) and Zn(II) with ligand MNNCI at temperature 298.

System Metal ions		Ligand MNNCI	
		log K_1	log K_2
MNNCI	a		10.84
	b		-
	c		10.84
Co (II)	a	7.46	6.56
	b	7.48	6.50
	c	7.52	6.54
Ni (II)	a	7.42	6.50
	b	7.32	6.56
	c	7.36	6.58
Cu (II)	a	6.72	5.66
	b	6.62	5.60
	c	6.74	5.62
Zn (II)	a	6.52	5.66
	b	6.54	5.72
	c	6.48	5.70

Stepwise and over all stability constant complex compounds of various metals with ligand MNNCI at temperature 298

Water – Dioxane medium (v/v) = 3:2 μ^0 = 0.10(M) KNO_3

Table 13

System	Ligand MNNCI		
	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 No. 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 stiochiometric 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 (- 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[11-15] and other workers[16-17].

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