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Research Article

DETERMINATION OF STABILITY CONSTANT AND EVALUATION OF RELATED THERMODYNAMIC PARAMETERS OF COORDINATION COMPOUNDS OF TRANSITION METALS WITH SCHIFF'S BASE LIGANDS

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A B S T R A C T

In continuation of our previous projects here also we are going to report study of the thermodynamic stability constant of transition metal complex with biologically active Schiff's base ligands. Here we are going to present results of determination of stability constant of complex compounds using ligands derived from 3- Hydroxy phenyl- 8-methyl coumarin imide (HPMCI) with bivalent transition metals of first transition series. Schiff's base ligands were synthesized by the condensation of 8-methyl coumarin with 3 - amino phenol.

Nitrate salts of bivalent cobalt, nickel, copper, zinc and manganese were estimated by standard methods ligand was analysed for elements by reported methods. pH metric titrations were carried out in an inert atmosphere of nitrogen gas at constant ionic strength of 0.1 M KNO_3 with the help of digital pH meter . Stability constant of complexes of these metals with the ligands were computed at two temperature i.e. 298 K and 308 K by Irving-Rossotti titration technique[1] modified by Calvin-Bjerrum[2].

The stability constant values of metals for the given ligand at both the temperatures were found to be Cu (II) > Ni (II) > Co(II) > Zn (II) > Mn(II) stability of complex of given metal and given ligand is higher at 298 K than at 308 K.

INTRODUCTION

Transition metals play a vital role in various biological processes. Interaction of most of the metal ions with biologically active molecules undergo chelation. These chelates are very important for large number of life processes. Out of various ligands Schiff's base are one of the important ligands. These are versatile and most privileged ligands.

Schiff's bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in large variety of useful applications like biolgocial, medicinal, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis. Transition metal complexes with Schiff's base ligands have played a very important role in the development of modern co-ordination chemistry. A large number of coordination compounds of transition metals with Schiff's base ligand have been synthesized and their structure determined with help of chemical and spectroscopic methods[3-14].

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These are also screened for their biological and chemical sensitivity but little is done for the determination of their thermodynamic stability. Therefore we have under taken the title project for our investigation.

Experimental

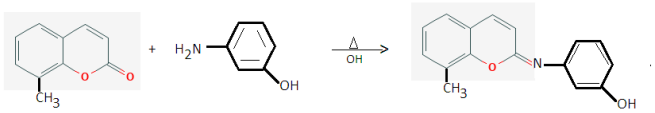
The solvent (1,4-dioxane) was purified by standard method ($\mu = 1.436$). Anala R grade E Merck German sample of sodium hydroxide, KNO_3 and BDH of HNO_3 was used, Double distilled CO_2 free water was used throughout the experiment.Anala R grade metal nitrates were used to prepare metal ion solution and these were standardized using EDTA titrations and gravimetrically.

Different reagents used for the estimation of metal ions

Metals	Volu. Metric	Gravi metric
Co	EDTA with Xylenol orange	α - nitroso - β - naphthol
Ni	"	Dimethyl glyoxime
Cu	"	Iodometrically
Zn	"	Pyrophosphate
Mn	"	8-Hydroxy quinoline

3- Hydroxy Phenyl 8-Methyl coumarin Imide (HPMCI) was prepared by the condensation of 8-methyl coumarin with 3 - amino phenol in alkaline medium.

pH metric titrations were done in 1, 4-dioxane water (1:1) medium at constant ionic strength of standard KNO_3 at two different temperature i.e. 298 and 308 K. A set of 3 titrations (acid, acid + ligand, acid + ligand + metal ion) were carried out for each metals, at each temperature at a given ionic strength. In every case the reproducibility. The results obtained are tabulated.



8-Methyl Coumarin 3-amino phenol 3- Hydroxy Phenyl 8-Methyl Coumarin Imide (HPMCI)

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)	1.0×10^{-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)
Mn(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 given in graph - 1 at temperature 298 K and graph- 2 at temperature 308 K separately for each metal ions.

Table No 2 Volume of alkali consumed in different titrations

Ligand **HPMCI** Temp. 298 ± K

μ^0 = 0.10 (M) KNO_3 Water-dioxane medium (v/v) = 1:1

	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)	H^+ + L+ Mn(II)
0.0	4.04	4.34	4.3	4.32	4.32	4.32	4.30
0.1	4.12	4.42	4.42	4.45	4.44	4.46	4.40
0.2	4.32	4.56	4.54	4.56	4.52	4.54	4.52
0.3	4.52	4.86	4.82	4.85	4.84	4.80	4.86
0.4	4.94	5.30	5.30	5.30	5.30	5.44	5.32
0.5	5.12	5.52	5.52	5.50	5.54	5.52	5.52
0.6	5.34	5.72	5.70	5.72	5.72	5.76	5.74
0.7	5.8	6.14	6.12	6.10	6.12	6.10	6.12
0.8	6.62	6.76	6.74	6.76	6.80	6.76	6.82
0.9	11.14	11.26	8.10	8.12	8.52	8.60	8.82
1.0	12.8	13.10	9.42	9.46	9.24	9.14	9.30
1.1	13.06	13.42	9.86	9.92	9.60	10.3	9.82
1.2	13.08	13.50					

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

The $\bar{n}_A$, $\bar{n}$ & P^L are calculated using standard expressions[3,4]

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

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

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

Proton ligand stability constant:

The ligand titration curve is above the acid titration curve showing the basic nature of ligand and it is well separated from the acid titration curve at pH=6.2 at temp 298 K. The ligand curves run parallel to the acid titration curve indicating the smooth dissociation of the ligand.

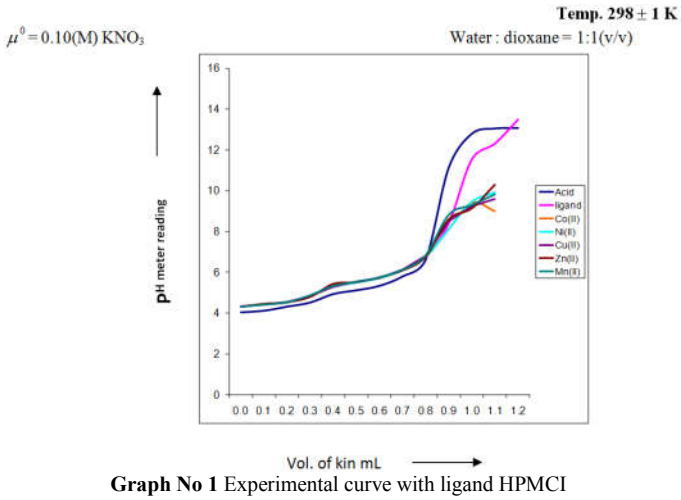
The values of $\bar{n}_A$ at various pH reading [B] was calculated from the acid and ligand titration curves and recorded in table no. 3 at temperature 298 K and in table no. 15, at temperature 308 K.

The formation curve obtained from the plot of $\bar{n}_A$ vs [B] extends from 0.46 to 0.96 (graph no. 3) at temp 298 K and from 0.36 to 0.98 (graph no.–4) at temperature 308 K. As the values of $\bar{n}_A$ does not go beyond 1.0 so this indicates that the ligand is monoprotonic.

Dissociation of ligand may be given as

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

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 no.-5 at 298 K and graph no.-6 at 308 K.

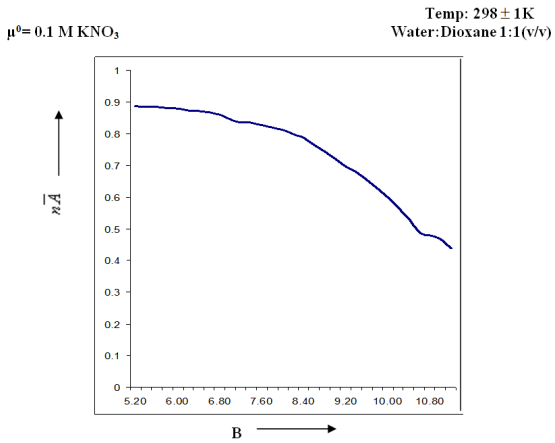


Graph No 1 Experimental curve with ligand HPMCI

Table No 3

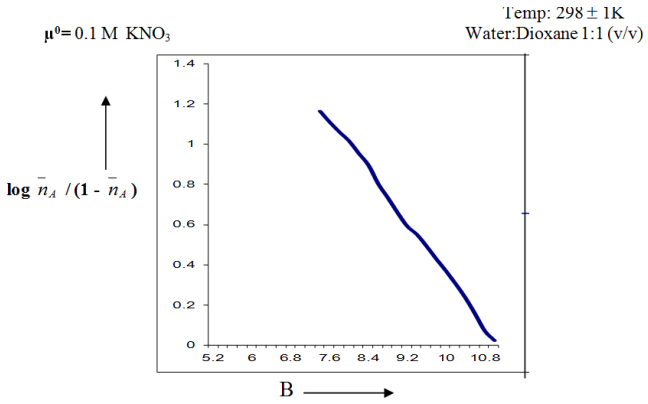
Ligand-**HPMCI** Temp.: 298 ±1K

[B]	V_2-V_1	$\bar{n}_A$	log $\bar{n}_A$ / (1 - $\bar{n}_A$)
5.2	0.005	0.8878	
5.4	0.006	0.8842	
5.6	0.006	0.8842	
5.8	0.007	0.881	
6.0	0.007	0.88	
6.2	0.008	0.874	
6.4	0.008	0.8726	
6.6	0.009	0.8684	
6.8	0.016	0.861	
7.0	0.012	0.844	
7.2	0.014	0.836	
7.4	0.016	0.836	1.2640
7.6	0.018	0.828	1.2092
7.8	0.016	0.8198	1.0400
8.0	0.020	0.812	1.0250
8.2	0.024	0.7988	0.8534
8.4	0.026	0.7868	0.7944
8.6	0.034	0.7638	0.7022
8.8	0.036	0.744	0.6322
9.0	0.042	0.7197	0.4580
9.2	0.050	0.6956	0.3906
9.4	0.054	0.6796	0.3492
9.6	0.062	0.6556	0.2906
9.8	0.064	0.6276	0.2270
10.0	0.072	0.5998	0.4674
10.2	0.082	0.5676	0.4030
10.4	0.090	0.532	0.3340
10.6	0.104	0.488	0.2534
10.8	0.112	0.478	0.0490
11.0	0.124	0.4674	0.0312
11.2	0.140	0.4396	-0.2050



Graph No 3 Formation Curve of ligand HPMCI

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



Graph No 5 Formation Curve of ligand HPMCI Plot of log $\bar{n}_A$ / (1 - $\bar{n}_A$) Vs [B]

Co(II) - HPMCI System

The complex titration curve of the system crossed the ligand mixture curve at pH = 5.26 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 = 9.0. 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 0.22 to 1.86 (graph no.– 7(a), table no.-4) at temperature 298 K and 0.20 to 1.82 (graph no.-7(d), table no. 16) at temperature 308 K indicating the formation of ML_1 and ML_2 type of complexes. From the formation curve of $\bar{n}$ vs P^L (graph no. 7(a), at temperature 298 K and (graph no. 7(d)), at temperature 308 K, the values of log K_1 and log K_2 at the given two temperatures 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. 7(b), table no. 5) at 298K and (graph no. 7(e), table no. 17) at temperature 308 K, and log (2- $\bar{n}$) / ($\bar{n}$ -1) vs p^L (graph no. 7(c), Table no. 5,) at temperature 298 K and (graph no. 7(f), Table no. 17) at temperatures 308 K respectively.

NI(II) - HPMCI System

The complex titration curve on the system crossed the ligand mixture curve at pH = 4.90 indicating the start of complexation. The curve increased regularly upto pH = 7.48 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 0.04 to 1.96 at temperature 298 K (table no.– 6, graph no.-8(a)) and 0.10 to 1.95 at temperature 308 K (table no. 18, graph no. 8(d)). 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 no. - 8(b), Table no. - 7) at temperature 298 K and (graph no. 8(e), table no. 19) at temperature 308 K. log (2-$\bar{n}$)/($\bar{n}$-1) vs P^L. (Table no.-7 , graph no. 8(c)) at temperature 298 K and (table no. -19, graph no.- 8(f)) at temperature 308 K. respectively.

Cu (II)-HPMCI System

Complex titration curve crossed the acid titration curve and well separated from ligand titration curve at pH = 5.92. 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 hydrolysis does not take place. The values of $\bar{n}$ extended from 0.08 to 1.82 at temperature 298 K and 0.16 to 1.86 at temperature 308 K indicating the formation of ML and ML_2 type of complexes, at both temperatures (table no.– 8, graph no. 9(a)) at 298 K and (table no.– 20; graph no. 9(d)) at temperature 308K.

Formation curves (graph no.- 9(a), and graph no.– 9(d)) are also very symmetrical, it gave the values of log K_1 and log K_2 by half integral method at given two temperatures. 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. 9(b), table no. 9) at temperature 298 K and (graph no. 9(e), table no. 21) at temperature 308 K. and log (2 - $\bar{n}$)/($\bar{n}$ -1) vs P^L. (table no.-9, graph no.-9(c)) at temperature 298 K & (table no. - 21, graph no. - 9(f)) at temperature 308 K respectively.

Zn (II)-HPMCI System

Metal ligand titration curve is well separated from ligand titration curve 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 0.12 to 1.72 at temperature 298 K and from 0.40 to 1.86 at temperature 308 K, indicating the formation of ML and ML_2 type complexes only. (table no. - 10, graph no. - 10(a)): at temperature 298 K and (table no.- 22, graph no. 10(d)) at temperature 308K.Curves (graph no.-10(a)) at temperature 298 K and (graph no. 10(d)) at 308 K by using half-integral method at two given temperatures. 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 no. - 11, graph no. 10(b)) at temperature 298 K and (table no. 23, graph no. 10(e)) at temp. 308 K. and plot of log (2- $\bar{n}$) / ($\bar{n}$ - 1). (table no. - 11, Graph no. - 10(c)) at 298 K and (table no. - 23, graph no. - 10 (f)) at temperature 308 K.

Mn - (II) HPMCI System

Complex titration curve are well separated from ligand titration curve at pH = 6.46 Complex titration curves diverge at higher pH indicating incomplete dissociation of ligand and lower rate of dissociation at higher pH.No turbidity is observed and hydrolysis does not take place. The values of $\bar{n}$ extended from 0.06 to 1.71 at temperature 298 K and from 0.04 to 1.72 at temperature 308 K.indicating the formation of ML and ML_2 type complexes at both the temperature (table no. - 12, graph no.–11(a)); at temperature 298 K and (table no. 24, graph no.– 11(d)) at temperature 308 K.

Formation curves were nearly symmetrical (graph no.-11(a)) at temperature 298 K and (graph no.-11(d)) at temperature 308 K; The values of log K_1 and log K_2 were calculated from the formation curve by half-integral method. It was further corroborated from mid-point slope method and linear plot of log $\bar{n}$ /(1- $\bar{n}$) (table no. 13, graph no. 11(b)) at temperature 298 K and (table no. 25, graph no. 11(e)) at temperature 308 K and plot of log (2- $\bar{n}$) / ($\bar{n}$ - 1) vs P^L. (table no. 13 graph no.-11(c)) at temp. 298 K and table no. 25, graph no. 11(f), at 308 K.

Table No 4

Co (II) + HPMCI Temp: 298 ± 1 K

[B]	V_3-V_2	$\bar{n}$	P^L
5.0	0.006	0.2220	8.1652
5.2	0.008	0.3242	7.9760
5.4	0.016	0.4266	7.7864
5.6	0.020	0.5912	7.6016
5.8	0.036	0.5766	7.4126
6.0	0.044	0.7872	7.2414
6.2	0.050	1.8660	7.0636
6.4	0.062	1.2840	6.8856
6.6	0.070	1.58406	6.7090
6.8	0.076	1.7966	6.5366
7.0	0.092	1.8680	6.3740

Table No 5

Co (II) + HPMCI Temp: 298 K

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2 - $\bar{n}$ /($\bar{n}$ -1)	P^L
-0.9568	8.9756	0.0260	7.7094
-0.4136	8.7852	-0.3620	7.5362
0.4214	8.4130		
0.7906	8.2404		

Table No 6

Ni (II) + HPMCI Temp : 298 ± 1K

[B]	V_3-V_2	$\bar{n}$	P^L
5.0	0.006	0.0408	8.1592
5.2	0.008	0.1014	7.9642
5.4	0.010	0.2456	7.7766
5.6	0.016	0.4084	7.5932
5.8	0.024	0.6152	7.4126
6.0	0.036	0.8038	7.2320
6.2	0.044	0.9930	7.0522
6.4	0.050	1.2308	6.8784
6.6	0.064	1.4636	6.7066
6.8	0.084	1.6970	6.5364
7.0	0.092	1.9686	6.3736

Table No 7

Ni (II) + HPMCI Temp : 298 ± 1K

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2- $\bar{n}$) / ($\bar{n}$ - 1)	P^L
-0.9456	8.9642	0.6224	7.8784
-0.4880	8.7772	0.0624	7.7066
-0.1608	8.5926	-0.4620	7.5360
0.2042	8.4126		
0.6116	8.2320		

Table No 8

Cu (II) + HPMCI Temperature 298 ± 1K

[B]	V_3-V_2	$\bar{n}$	P^L
6.2	0.008	0.0816	8.5626
6.4	0.012	0.1642	8.3700
6.6	0.014	0.2674	8.1796
6.8	0.016	0.3720	7.9894
7.0	0.022	0.4794	7.7996
7.2	0.026	0.6152	7.6126
7.4	0.032	0.7634	7.4274
7.6	0.044	0.9410	7.2466
7.8	0.050	1.1436	7.0686
8.0	0.062	1.3274	6.8914
8.2	0.066	1.5366	6.7154
8.4	0.082	1.8242	6.5528

Table No 9

Cu (II) + HPMCI Temperature 298 ± 1K

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2- $\bar{n}$) / ($\bar{n}$ - 1)	P^L
-0.7058	8.3702	0.7750	7.0686
-0.4362	8.1798	0.3116	6.8900
-0.2261	7.9894	-0.0644	6.7154
-0.0352	7.7996	-0.6712	6.536
0.2040	7.6132		
0.5092	7.4286		

Table No 10

Zn (II) + HPMCI Temp: 298 ± 1K

B	V_3-V_2	$\bar{n}$	P^L
6.0	0.008	0.1228	7.3648
6.2	0.010	0.1854	7.1728
6.4	0.012	0.2916	6.9826
6.6	0.014	0.3752	6.7884

6.8	0.024	0.5094	6.6030
7.0	0.026	0.6368	6.4160
7.2	0.032	0.8346	6.2352
7.4	0.048	1.0354	6.0566
7.6	0.054	1.2614	5.8830
7.8	0.074	1.6668	5.7294
8.0	0.082	1.7217	5.8262

Table No 11

Zn (II) + **HPMCI** Temp: 298 ± 1K

$\log \bar{n}/(1-\bar{n})$	P^L	$\log (2-\bar{n})/(\bar{n}-1)$	P^L
-0.6426	8.1720	0.4524	6.8820
-0.3862	7.9818	-0.2628	6.7294
-0.2214	7.7896		
0.2432	7.4150		
0.7022	7.2352		

Table No 12

Mn (II) + **HPMCI** Temp: 298 ± 1 K

B	V_3-V_2	$\bar{n}$	P^L
6.0	0.028	0.0618	8.1614
6.2	0.008	0.1442	8.9685
6.4	0.014	0.2298	7.7765
6.6	0.020	0.3608	7.5887
6.8	0.026	0.5518	7.4068
7.0	0.038	0.7488	7.2268
7.2	0.046	0.9710	7.0497
7.4	0.058	1.2186	6.8777
7.6	0.066	1.4492	6.7046
7.8	0.080	1.7134	6.5388

Table No 13

Mn (II) + **HPMCI** Temp: 298 ± 1 K

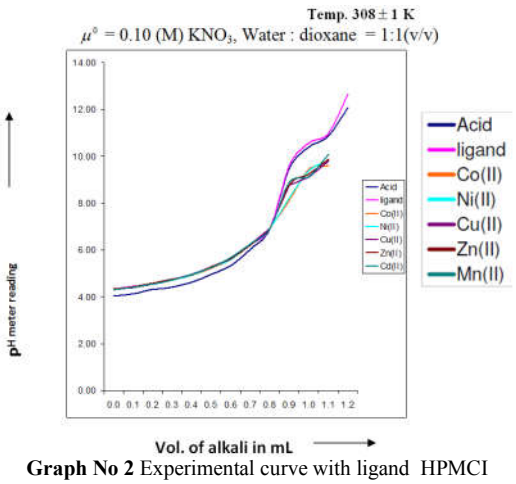
$\log \bar{n}/(1-\bar{n})$	P^L	$\log (2-\bar{n})/(\bar{n}-1)$	P^L
-0.7716	7.9686	0.5528	6.8778
-0.5263	7.7768	0.0886	6.7047
-0.2484	7.5887	-0.3956	6.5388
0.0894	7.4068		
0.4740	7.2267		

Table No 14 Volume of alkali consumed in different titrations

Ligand **HPMCI** Temperature: 308 ± 1K

μ^0 = 0.10 (M) KNO_3 Water-dioxane medium (v/v) = 1: 1

	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)**	**H^+ + L +Mn(II)**
0.0	4.04	4.32	4.30	4.32	4.32	4.34	4.30
0.1	4.14	4.46	4.44	4.42	4.40	4.44	4.42
0.2	4.32	4.54	4.54	4.56	4.54	4.58	4.54
0.3	4.42	4.74	4.76	4.74	4.72	4.76	4.72
0.4	4.62	4.96	4.92	4.92	4.96	4.94	4.96
0.5	4.96	5.28	5.23	5.26	5.24	5.28	5.24
0.6	5.34	5.62	5.62	5.60	5.62	5.64	5.68
0.7	6.04	6.24	6.22	6.26	6.25	6.22	6.26
0.8	6.90	6.92	6.96	6.94	6.92	6.94	6.92
0.9	9.50	9.62	8.14	8.22	8.78	8.80	8.90
1.0	10.40	10.56	9.46	9.40	9.12	9.24	9.14
1.1	10.86	10.98	9.60	9.78	9.80	9.86	10.08
1.2	12.08	12.65					



Graph No 2 Experimental curve with ligand HPMCI

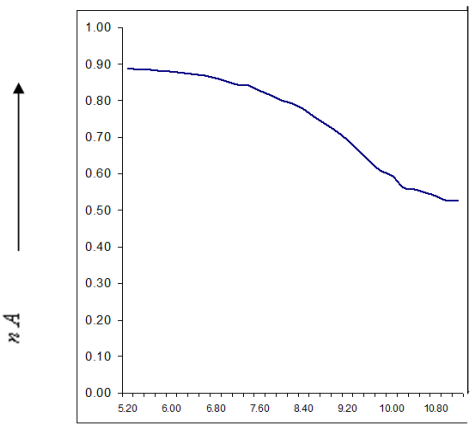
Table No 15

Ligand : **HPMCI** Temp: 308 ± 1K

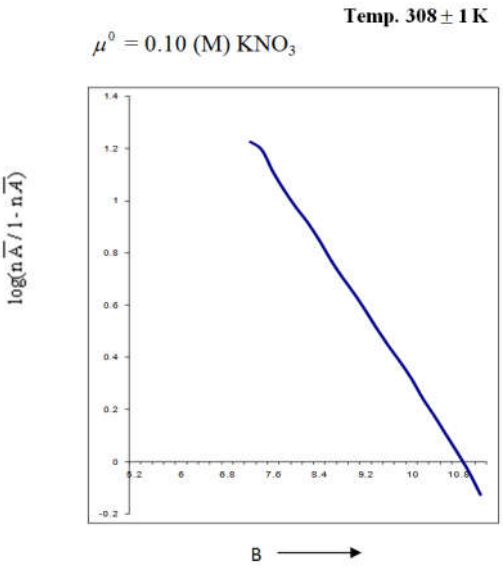
[B]	V_2-V_1	$\bar{n}_A$	$\log \bar{n}_A/(1-\bar{n}_A)$
5.2	0.005	0.888	
5.4	0.005	0.884	
5.6	0.006	0.8842	
5.8	0.006	0.8812	
6.0	0.007	0.8802	
6.2	0.007	0.876	
6.4	0.008	0.8732	
6.6	0.008	0.868	
6.8	0.020	0.8612	
7.0	0.012	0.8522	
7.2	0.014	0.8442	1.3260
7.4	0.014	0.8412	1.2950
7.6	0.016	0.8282	1.2092
7.8	0.020	0.8156	1.0470
8.0	0.022	0.8012	0.8730
8.2	0.026	0.7922	0.8162
8.4	0.030	0.7762	0.7486
8.6	0.032	0.7554	0.6730
8.8	0.040	0.7354	0.6066
9.0	0.042	0.7152	0.5462
9.2	0.052	0.6922	0.4802
9.4	0.056	0.6642	0.4096
9.6	0.062	0.6356	0.3442
9.8	0.070	0.6074	0.2840
10.0	0.080	0.5952	0.2184
10.2	0.096	0.5632	0.1412
10.4	0.106	0.5584	0.2752
10.6	0.110	0.5492	0.2040
10.8	0.116	0.5396	0.0442
11.0	0.126	0.5274	-0.0494
11.2	0.140	0.527	-0.2262

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

Temp. 308 ± 1 K, μ^0 = 0.10 (M) KNO_3



Graph No. 4 Formation curve of ligand HPMCI



Graph No 6 Linear plot of log ($\bar{n}_A / 1 - \bar{n}_A$) Vs [B]

Table No 16

Co (II) + HPMCI Temperature: 308 ± 1K

B	$V_3 - V_2$	$\bar{n}$	P^L
5.2	0.008	0.2018	9.0646
5.4	0.010	0.3036	8.8736
5.6	0.014	0.3274	8.6854
5.8	0.022	0.4014	8.5026
6.0	0.028	0.6056	8.3220
6.2	0.040	0.7448	8.1366
6.4	0.052	1.10346	7.9568
6.6	0.064	1.3408	7.7800
6.8	0.076	1.5726	7.6076
7.0	0.082	1.6758	7.4334
7.2	0.090	1.8170	7.2666

Table No 17

Co (II) + HPMCI Temperature 308 ± 1 K

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2- $\bar{n}$) / ($\bar{n}$ - 1)	P^L
-0.9454	9.0646	0.5994	7.7800
-0.5922	8.8734	0.0578	7.6076
-0.3134	8.6850	-0.4190	7.4332
0.3792	8.3224		
0.7356	8.1362		

Table No 18

Ni (II) + HPMCI Temp : 308 ± 1K

B	V_3-V_2	$\bar{n}$	P^L
5.0	0.006	0.1016	7.8648
5.2	0.012	0.2656	7.6796
5.4	0.020	0.4294	7.4946
5.6	0.032	0.6156	7.3132
5.8	0.038	0.8034	7.1322
6.0	0.046	0.9932	6.9520
6.2	0.054	1.2096	6.7766
6.4	0.066	1.4306	6.6024
6.6	0.082	1.6972	6.4364
6.8	0.090	1.9598	6.2722

Table No 19

Ni (II) + HPMCI Temp: 308 ± 1K

μ^0 = 0.10(M) KNO_3 Water: Dioxane = 1:1(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 No 20

Cu(II) + HPMCI Temp : 308 ± 1K

[B]	V_3-V_2	$\bar{n}$	P^L
6.2	0.012	0.1640	7.2700
6.4	0.016	0.2472	7.0782
6.6	0.014	0.3722	6.8892
6.8	0.020	0.5006	6.7018
7.0	0.026	0.6314	6.5146
7.2	0.036	0.7846	6.3302
7.4	0.040	0.9372	6.1460
7.6	0.052	1.1220	5.9662
7.8	0.060	1.3116	5.7880
8.0	0.070	1.5724	5.6206
8.2	0.082	1.8632	5.4584

Table No 21

Cu (II) + HPMCI Temp: 308 ± 1K

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2- $\bar{n}$) / ($\bar{n}$ - 1)	P^L
-0.7072	8.2704	0.8566	6.9666
-0.3496	8.0786	0.3444	6.7888
-0.2270	7.8896	-0.1274	6.6206
-0.2332	7.5144	-0.7996	6.4590
0.5626	7.3306		

Table No 22

Zn (II) + HPMCI Temp: 308 ± 1K

B	V_3-V_2	$\bar{n}$	P^L
6.0	0.006	0.406	7.4590
6.2	0.008	0.1020	7.2698
6.4	0.010	0.1854	7.0782
6.6	0.014	0.3718	6.8896
6.8	0.020	0.5006	6.7014
7.0	0.026	0.6310	6.5146
7.2	0.034	0.7846	6.3302
7.4	0.040	0.9372	6.1460
7.6	0.052	1.1220	5.9666
7.8	0.064	1.3116	5.7880
8.0	0.076	1.5724	5.6206
8.2	0.088	1.8636	5.4584

Table No 23

Zn (II) + HPMCI Temp: 308 ± 1 K

log $\bar{n}$ /(1- $\bar{n}$)	P^L	log (2- $\bar{n}$) / ($\bar{n}$ - 1)	P^L
-0.7070	8.2700	0.8566	6.9666
-0.3494	8.0786	0.3440	6.7888
-0.2268	7.8896	-0.1274	6.6206
-0.2330	7.5146	-0.7996	6.4586
0.5624	7.3302		

Table No 24

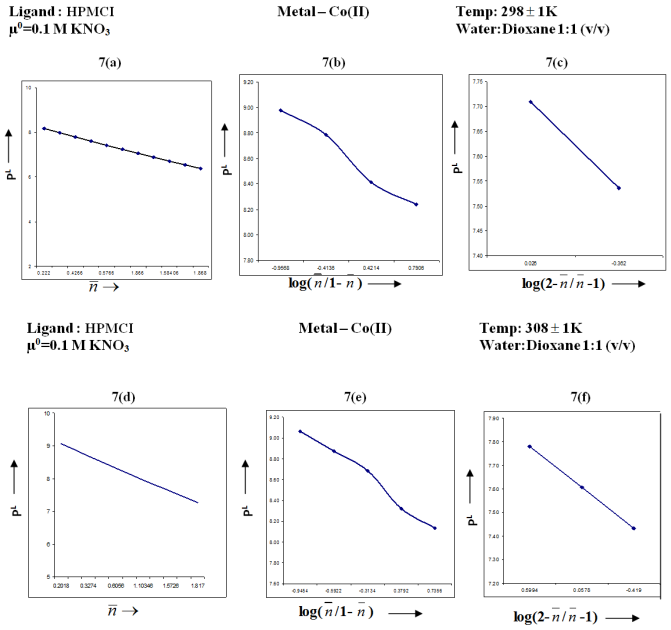
Mn(II) + HPMCI Temp : 308 ± 1K

B	V_3-V_2	$\bar{n}$	P^L
6.0	0.006	0.0414	8.0590
6.2	0.008	0.1240	7.8664
6.4	0.010	0.2296	7.6764
6.6	0.014	0.3784	7.4902
6.8	0.026	0.5726	7.3086
7.0	0.036	0.7668	7.1280
7.2	0.044	0.9710	6.9496
7.4	0.058	1.2024	6.7756
7.6	0.066	1.4354	6.6036
7.8	0.076	1.7280	6.4407

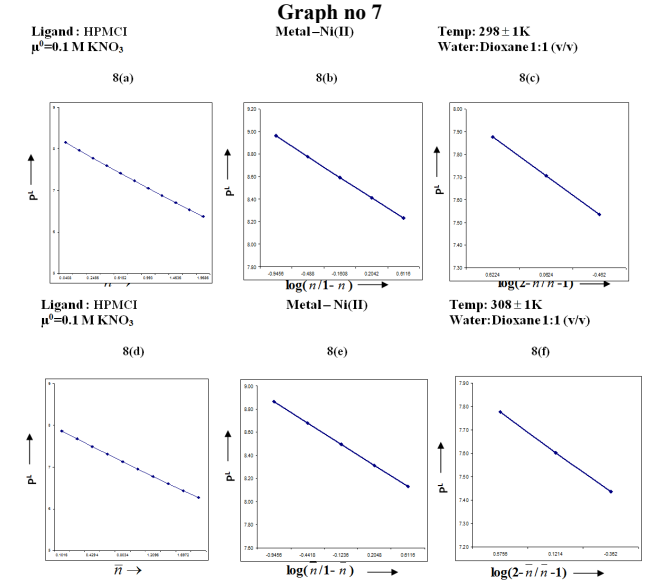
Table No 25

Mn (II) + **HPMCI** Temp 308 ± 1K

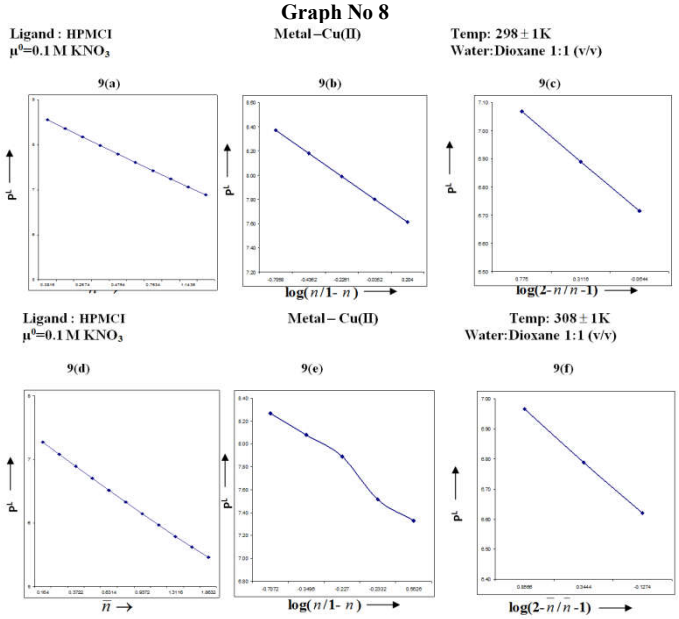
$\log \bar{n}/(1-\bar{n})$	P^L	$\log (2-\bar{n})/(\bar{n}-1)$	P^L
-0.8476	7.8668	0.5956	6.7757
-0.5262	7.6766	0.1120	6.6032
-0.2152	7.4902	-0.4286	6.4406
0.1276	7.3086		
0.5778	7.2180		



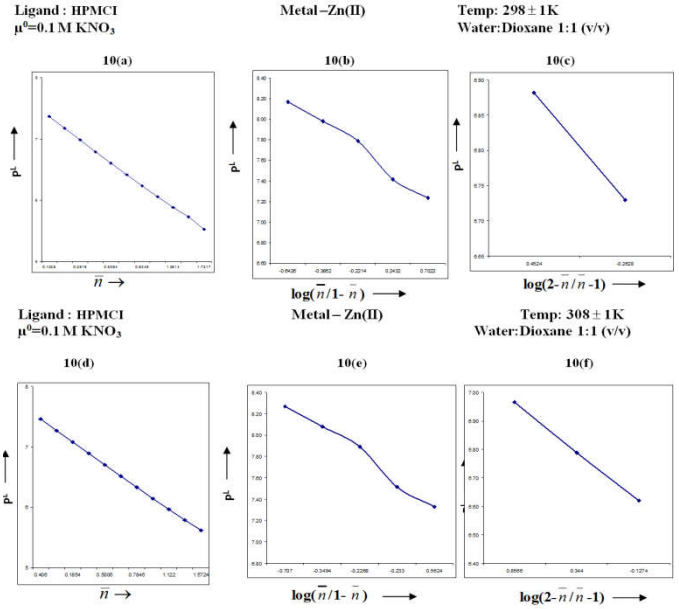
Graph no 7



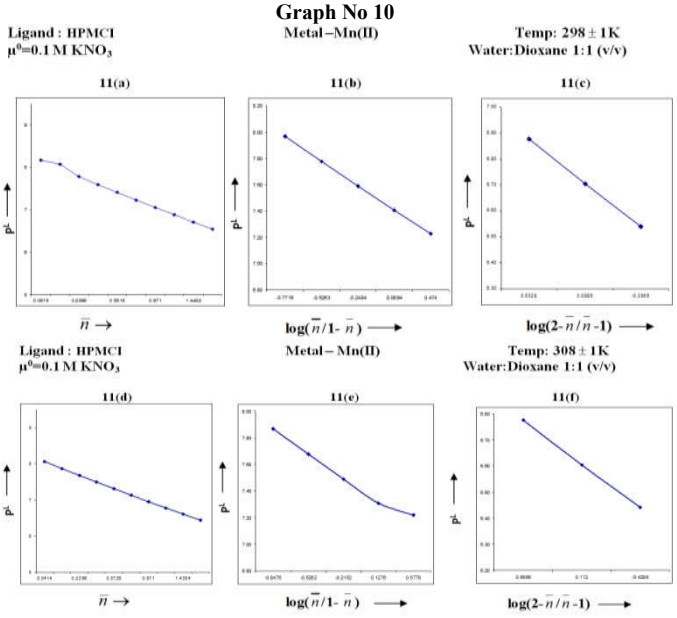
Graph No 8



Graph No 9



Graph No 10



Graph No 11

The values of protonation constant and stepwise stability constant obtained by different computational methods at temperatures 298 K and 308 K are summarized in table 26
The different methods are:-

1. half-integral method
2. Mid-point calculation method
3. Straight line plot method.

Table No 26 Values of protonation constant of ligand and stepwise stability constant of complexes of Co(II), Ni(II), Cu(II), Zn(II) and Mn(II) with ligand HPMCI at temperature 298 K and 308 K

System		Temp 298 K		Temp. 308 K	
		log K_1	log K_2	log K_1	log K_2
HPMCI	A	10.94			10.84
	b	-			-
	c	10.94			10.84
Co (II)	A	7.58	6.66	7.48	6.56
	b	7.56	6.64	7.46	6.50
	C	7.60	6.66	7.50	6.54
Ni (II)	A	7.50	6.68	7.40	6.50
	b	7.46	6.60	7.36	6.56
	c	7.44	6.66	7.38	6.58
Cu (II)	A	6.74	5.78	6.70	5.66
	b	6.66	5.02	6.60	5.60
	C	6.82	5.76	6.76	5.62
Zn (II)	A	6.60	5.78	6.50	5.66
	b	6.56	5.70	6.56	5.72
	C	6.68	5.86	6.46	5.70
Mn (II)	A	6.40	5.66	6.32	5.56
	b	6.42	5.62	6.36	5.30
	C	6.46	5.64	6.36	5.58

Table 27 Stepwise and over all stability constant at temperature 298 and 308 K respectively of complex compounds of various metals.

Ligand-HPMCI water-dioxane medium (V/V) = 1:1

μ^0 = 0.10(M) KNO_3

System	Temp. 298 K			Temp. 308 K		
	log K_1	log K_2	log β	log K_1	log K_2	log β
H-HPMCI	10.98	-	10.98	10.86	-	10.84
Co (II)-HPMCI	7.58	6.66	14.20	7.44	6.56	14.10
Ni (II)-HPMCI	7.48	6.68	14.10	7.38	6.56	13.90
Cu (II)-HPMCI	6.76	5.70	12.46	6.68	5.68	12.36
Zn (II)-HPMCI	6.60	5.78	12.34	6.50	5.70	12.24
Mn (II)-HPMCI	6.46	5.60	12.08	6.36	5.56	11.84

Thermodynamic Parameters

The values of the change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) have been calculated at two temperatures at ionic strength 0.10 (M) KNO_3 with the help of standard expressions[5-7].

Table No 28 Values of stepwise free energy changes. Enthalpy changes and entropy changes in the formation of complexes of different metals with the ligand HPMCI

Ligand-HPMCI

Water-dioxane medium (V/V) = 1:1

μ^0 = 0.10(M) KNO_3

	Temp 298 ± 1 K		Temp 308 ± 1K				
System	ΔG_1 in k.cal	ΔG_2 in k.cal	ΔG_1 in	ΔG_2 in	ΔH_1 in	ΔH_2 in	ΔS_1
	k. cal	k. cal	k. cal	k. cal			ΔS_2 in e.u. at 298 K
Co (II)	-9.06	-7.66	-9.26	-7.80	-3.6	-3.6	+20.6 +15.0
Ni (II)	-10.00	-8.90	-10.20	9.06	-4.4	-4.0	+21.6 +16.6
Cu (II)	-10.16	-8.92	-10.36	-9.08	-4.4	-4.0	+22.2 +16.6
Zn (II)	-8.86	-7.76	-9.06	-7.86	-4.4	-3.6	+17.6 +15.2
Mn(II)	-8.62	-7.56	-8.76	-7.70	-3.6	-3.4	+17.0 +14.6

DISCUSSION

The values of stepwise stability constants and over all stability constants are given in table no. 26. For the given ligand the stability constants of complexes for different metals show the sequence

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

This is natural order given by Irving-William[15]. 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[16]. 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 studies[18-26] and that of other workers[27-28].

References

1. Irving H.M., Rossotti H.S., *J. Chem Soc*., 2904, 1954.
2. Bjerrum, J.: Metal amine formation in aqueous solution. P. Hasse and Sons. Copenhagen 1941.
3. Liu C. M.; Xiong R.G.; You X. Z.; Liu Y.J.; Cheung K.K., *Polyhedron*,15 1996, 45651.
4. Djebbar S.S.; Benali B.O.; Deloume J.P., Transit Metal Chem., 23, 1998,443.
5. Hamada Y.J., IEEE Trans. *Electron Devices*, 44, 1997, 1208.
6. Srivastava R.S., *Ind. J. Chem*., 29, 1990, 1024-1026.
7. Waish C., *Nature*, 409, 2001, 226.
8. He L.; Gou S. H. ; Shi Q.F., *J. Chem. Crystallogr*., 29, 1999, 207.
9. Wu J.C.; Tang N.: Liu W.S.; Tan M.Y.; Chan A.S., *Chin Chem. Lett*., 12, 2001, 757.
10. Pandey V. K.; Sarah, T and Zehra T: *Indian J. Chem*. 43 B, 2004, 180
11. Joshi, L.D.; Kumar, R. and Parmar, S.S., *Curr.Sci*. 42,1973,847
12. Otto, H. and Houlohan, W.W.; Swiss Pat 1971, 499, 540, Chem Abstr. 75, 1771,20435

13. Djebbar S. S.; Benali B.O.; Deloume J.*P. Polyhedron*, 16, 1997, 2175.
14. Irving, H. and Rossotti, H. J. *J. Chem. Soc*. 3397 (1953)
15. Bhattacharrya P.; Parr J.; Ross A. T., *Chem. Soc. Dalton*, 1998, 3149.
16. Brown D. H., Smith W.E., Teape J.W. *et al*., *J. Med. Chem*., 23(7), 1980,729.
17. Mukherjee, S. K. and Rawat N.S., J. Ind. Chem. Soc. 58,614,1981
18. P. M. Mishra *et al*: *Asian Journal of Chemistry* vol. 21(7) p-5055-5060 (2009).
19. P. M. Mishra *et al*: *Asian Journal of Chemistry* vol. 21(9) p –7195-7199(2009).
20. P. M. Mishra *et al*: *Journal of Ultra Chemistry* vol. 5(2) p-131-136 (2009).
21. P. M. Mishra *et al*: *Journal of Ultra Chemistry* vol. 9(1) p-149 - 155 (2013).
22. P. M. Mishra *et al*: *Rasayan Journal of Chemistry* vol. 4(2) p-303-319 (2011).
23. T. Suresh *et. al*: *J. Ind. Council of Chem*. Vol. 24(1) pp-123 (2007)
24. T. Suresh *et. al*: *J. Ind. Council of Chem*. Vol. 25(2) pp-68-70 (2008)
25. P. M. Mishra, Bimlesh Kumar Yadav: Ultra Scientist Vol. 27(3) B, p-139-154 (2015)
26. P. M. Mishra: *Journal of Applicable Chemistry* vol. 5 No.-5, p. 1163-74 (2016)
27. P. M. Mishra: *Oriental Journal of Chemistry* vol. 32 No.-5, (2016)
28. P. M. Mishra: *Journal of Ultra Chemistry* vol. 12 No.-2, p. 38-51 (2016)

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