Vol 5 | Issue 3 | 2015 | 137-142.

e-ISSN 2248 – 9142
print-ISSN 2248 – 9134

International Journal of
Current Pharmaceutical & Clinical Research

www.ijcpcr.com

PH- METRIC INVESTIGATION ON MIXED LIGAND COMPLEXES OF Cr(III), Th(III) & Nd(III) WITH SUBSTITUTED ISOXAZOLINES IN 70% DIOXANE – WATER MIXTURE

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ABSTRACT

The complex formation between Cr(III),Th(III),&Nd(III) metal ions and 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(4-methoxyphenyl)isoxazoline [HNMP4MI] L_1, 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(phenyl)isoxazoline [HNMP5PI] L_2 have been studied at 0.1M Ionic Strength (26±0.1)^oC in 70% Dioxane water mixture by Bjerrum method as adopted by Calvin & Wilson.It is observed that Cr(III)&Th(III)&Nd(III)metal ions form 1:1 & 1:2 complexes with ligand L_1&L_2.The data obtained were used to estimate & compare the values of proton ligand stability constant (p^K) & metal ligand stability constant (log K).From estimated data (p^K & log K),the effect of substituents were studied.

Key words: Substituted 3,5-diarylisoxazoline, Dioxane-water mixture, Stability constant.

INTRODUCTION

The studies in metal ligand complexes in solution of a number of metal ion with carboxylic acids, oximes, phenol etc. Would be interesting which throw light on the mode of storage and transport of metal ions in biological Kingdom. Sonkamble et al [1-2] have studied metal-ligand stability constant of some substituted ketone and Lorazepam. Routh et al [3] have studied speciation of binary complexes of Co(II),Ni(II)&Cu(II) with bidentate ligand in low dielectric medium.

Recently many co-worker have studied proton and metal-ligand stability constant of mixed ligand complexes [4-7]. Ramteke et al [8] have studied effect of ionic strength on stability constant of complexes of substituted pyrazole with Cu(II),Tb(III)&Nd(III) metal ions. Heterocyclic compounds provide a great synthetic and structural versatility due to their having a number of potential substitution positions. Furthermore heteroatoms offer the possibility of several modes of coordination [9]. The pyrazole moiety is present in a large number of biologically active compounds which find wide applications in pharmaceuticals [10] and agro- chemical industries [11]. Sasmita Rani Devi [12] has studied Stability and Configurational Changes of Nickel and Copper Ethambutol Dihydrochloride and Metformin Hydrochloride in both Cationic and Anionic Surfactants. Agrawal D et al [13] have studied the pH Metric Study On Thermodynamic And Ionization Constant Of 2,5-Diaminopentanoic Acid. Talele R.D.et al [14] have studied the stabilities of Schiff base of (5-hydroxy-3-methyl-1-(2,4-dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 4-amino antipyrine complexes with metal ions in mixed solvent at 0.1M ionic strength and 303K by pH metric method. In present work an attempt has been made to study the interactions between Cr(III),Th(III)&Nd(III) Cations At 0.1 M Ionic Strength with Ligand at 0.1 ionic strength, pH metrically in 70% Dioxane-water mixture.

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MATERIALS AND METHODS

The ligands L_1,&L_2 was synthesized in the laboratory by known literature method. The purity of these compounds exceeds 99.5% and structures were confirmed by NMR, IR and melting points.

The stock solution of the ligand was prepared by dissolving required amount of ligand in a minimum volume of dioxane subsequently diluted to final volume. Metal ion solution was prepared by dissolving metal nitrate (Sigma - Aldrich) and standardized by EDTA titration method as discussed in literature . Carbonate free sodium hydroxide solution was prepared by dissolving the Analar pellets in deionised water and solution was standardized 22. The stock solution of percholric acid was prepared and used after standardization 23.

Measurements

All measurements were carried out at (26±0.1) ^{0}C. Systronic microprocessor based pH meter with magnetic stirrer and combined glass and calomel electrode assembly used for pH measurements. The sensitivity of pH meter is 0.01 units. The instrument could read pH in the range 0.00 to 14.00 in the steps of 0.005. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. It was calibrated before each titration with an aqueous standard buffer solution of pH 7.00 and 9.20 at (26±0.1)^{0}C prepared from a 'Qualigens' buffer tablets. The hydrogen ion concentration was measured with combined glass electrode.

Procedure

The experimental procedure involved the titrations of

i. Free acid $HClO_4$ (0.01 mol.dm^{-3})

ii. Free acid $HClO_4$ (0.01 mol.dm^{-3}) and ligand (20 x 10^{-4} mol.dm^{-3})

iii. Free acid $HClO_4$ (0.01 mole dm^{-3}) and ligand (20 x 10^{-4} mol.dm^{-3}) and metal ion (4 x 10^{-4}mol.dm^{-3}) against standard carbonate free sodium hydroxide(0.15 mol.dm$^{-3)}$ solution using Calvin-Bjerrum and Calvin-Wilson pH titration techniques. The ionic strength of all the solutions were maintained constant by adding appropriate amount of $NaClO_4$ solution. All titrations were carried out in 70 percentages of Dioxane-water mixtures and reading were recorded for each 0.1 ml addition. The curves of pH against volume of NaOH solution were plotted (fig 1,2). The Proton-Ligand constants were calculated from pH values obtained from the titration curves using the Irvin-Rossotti method and MATLAB computer program (Table 1) .

RESULTS AND DISCUSSION

The extent of deviation may be the dissociation of -OH group. 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(4-methoxyphenyl)isoxazoline[HNMP4MI] L_1, 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(phenyl)isoxazoline[HNMP5PI] L_2 may be considered as a monobasic acid having one replaceable H^+ ion from phenolic -OH group and can be represented as,

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

The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A+L) and acid + ligand + metal ion curve (A+L+M)] between volume of NaOH against pH.The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Table1)

$$\bar{n}_A = \gamma - \frac{(V_2 - V_1)\ (N + E^o)}{(V^o + V_1)\ (T_L^o)} \quad .....01$$

Where γ denotess the number of dissociable protons, N is the concentration of sodium hydroxide(0.15 mol.dm-3), (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, where V_2 and V_1 are the volume of alkali added to reach the same pH reading to get accurate values of (V_2-V_1): the titration curves were drawn on an enlarged scale: E^0 and $T_L{}^0$are the resultant concentration of perchloric acid and concentration of Ligand, respectively. V_0 is the initial volume of reaction mixture (50 cm^3). Proton-Ligand stability constant p^k values of Ligand were calculated by algebraic method point wise calculation and also, estimated from formation curves n_A Vs p^H (Half integral method) by noting p^H at which n_A = 0.5[Bjerrum 1957] (Table 2).

Metal-Ligand stability constants (log k) were determined by the half integral method by plotting ṅ Vs pL. The experimental ṅ values determined using expression

$$\bar{n} = \frac{(V_3 - V_2)\ (N + E^o)}{(V^o + V_2)\ \bar{n}_A\ T_M^o} \quad .....01$$

Where N, E^0, V_o and V_2have same significance as in equation (1), V_3 is the volume of NaOH added in the metal ion titration to attain the given p^H reading and $T_M{}^0$ (4 x 10^{-4} mol dm-3) is the concentration of metal ion in reaction mixture. The stability constants for various binary complexes have been calculated (Table 3).

Metal Ligand Stability Constant (Log K)

It is observed that (Table3a-b) sufficiently large difference between log K_1 & logK_2Values of Cr(III) & Th(III)for ligand L_1 ;Nd(III) & Cr(III) for ligand L_2 indicates the stepwise formation of complex between metal ion and ligand except Nd(III) for ligand –L_1&Th(III),for ligand L_2. It showed that less difference between log K_1 & log K_2 values indicates complexes are occurring simultaneously. The higher value of ratio(Log K1/ Log K2) for Cr(III) & Th(III)- Ligand- L_1 ;Cr(III) & Nd(III)-Ligand L_2 complex indicates the more stable stepwise complex formation as compare to Nd(III) –Ligand-L_1 & Th(III)-Ligand L_2 complexes.

Table 1. Proton Ligand Formation number ($\dot{n}_A$) at $(26\pm0.1)^0$C and at ionic strength μ=0.1 moldm^{-3} $NaClO_4$ in 70%Dioxane-Water mixture

a)System : HNMP4MI(L_1)

P^H	V_1	V_2	$V_2 - V_1$	$\dot{n}_A$
3.35	3.2021	3.3958	0.1937	0.7087
3.70	3.2042	3.5031	0.2989	0.5506
3.84	3.2074	3.5351	0.3277	0.5073
4.00	3.2083	3.5445	0.3362	0.4945
4.35	3.2475	3.6225	0.3750	0.4365
4.42	3.2518	3.6638	0.4120	0.3810
4.49	3.2519	3.6639	0.4120	0.3810
5.07	3.2743	3.7029	0.4286	0.3564
5.14	3.2743	3.7033	0.4290	0.3557
5.21	3.2743	3.7033	0.4290	0.3553
5.42	3.3000	3.7313	0.4313	0.3548
5.63	3.3330	3.7643	0.4313	0.3523
6.00	3.3330	3.7792	0.4562	0.3157
6.14	3.3330	3.7892	0.4562	0.3157
6.21	3.3413	3.7977	0.4564	0.3154
6.42	3.3660	3.8330	0.4670	0.3147
6.84	3.4496	3.9166	0.4670	0.3009
7.35	3.4662	3.9349	0.4687	0.2984
7.42	3.4662	3.9349	0.4687	0.2984
7.56	3.4867	3.9565	0.4698	0.2976
7.70	3.4867	3.9567	0.4700	0.2969
8.35	3.5000	3.8720	0.4720	0.2942
8.70	3.5660	4.0401	0.4741	0.2815
9.35	3.6660	4.1410	0.4750	0.2813
9.70	3.7660	4.2440	0.4780	0.2811
10.00	3.8000	4.2784	0.4784	0.2578
10.07	3.8330	4.3116	0.4786	0.2576
10.21	3.8660	4.3517	0.4857	0.2564
10.28	3.9000	4.3950	0.4950	0.2489
10.35	3.9000	4.4000	0.5000	0.2472

System: HNMP5PI(L_2)

P^H	V_1	V_2	$V_2 - V_1$	$\dot{n}_A$
3.00	3.1551	3.2131	0.0580	0.9126
3.28	3.1555	3.2217	0.0662	0.9003
3.35	3.2021	3.2719	0.0698	0.8950
3.37	3.2024	3.2878	0.0854	0.8716
3.56	3.2038	3.3368	0.1330	0.8000
3.70	3.2042	3.3527	0.1485	0.7767
4.00	3.2083	3.4083	0.2000	0.6992
4.35	3.2475	3.4642	0.2167	0.6745
4.37	3.2482	3.4649	0.21672	0.6745
4.42	3.2518	3.4818	0.2300	0.6545
4.49	3.2519	3.4849	0.2330	0.6499
5.07	3.2743	3.5570	0.2827	0.5754
5.14	3.2743	3.5570	0.2827	0.5754
5.21	3.2743	3.5570	0.2827	0.5754
5.42	3.3000	3.5848	0.2848	0.5725
5.63	3.3330	3.6247	0.2917	0.5622
6.00	3.3330	3.6247	0.2917	0.5622
6.14	3.3330	3.6247	0.2917	0.5622
6.21	3.3413	3.6272	0.2959	0.5562

6.28	3.3413	3.6372	0.2959	0.5562
6.35	3.3572	3.6572	0.3000	0.5501
6.37	3.3589	3.6589	0.3000	0.5502
6.42	3.3660	3.6779	0.3119	0.5323
6.49	3.3661	3.6780	0.3119	0.5324
6.63	3.3662	3.6918	0.3256	0.5119
6.84	3.4496	3.7938	0.3442	0.4839
7.00	3.4582	3.8026	0.3444	0.4832
7.35	3.4662	3.8108	0.3446	0.4829
7.42	3.4662	3.8108	0.3446	0.4829
7.56	3.4867	3.8354	0.3487	0.4784
7.70	3.4867	3.8437	0.3570	0.4660
8.00	3.5000	3.8582	0.3582	0.4643
8.35	3.5000	3.8617	0.3617	0.4591
8.42	3.5330	3.8972	0.3642	0.4559
8.70	3.5332	3.9024	0.3692	0.4485
9.00	3.6660	3.9408	0.3748	0.4413
9.35	3.6330	4.0660	0.4330	0.3545
9.70	3.7661	4.2016	0.4356	0.3506

Table 2. Proton Ligand Stability Constant p^K

System	p^K	
	Half integral method	Pointwise calculation method
HNMP4MI(L_1)	3.8527	3.9675
HNMP5PI (L_2)	6.6507	6.5728

Table 3. Metal Ligand Stability Constant(Log K)

a) HNMP4MI(L_1)

System	Log K_1	Log K_2	Log K1-LogK_2	LogK_1/LogK_2
Cr(III)	4.3859	1.7565	2.6294	2.4969
Th(III)	4.5403	2.5599	1.9804	1.7736
Nd(III)	5.0728	3.4340	1.6388	1.4772

b) HNMP5PI (L_2)

System	Log K_1	Log K_2	Log K1-LogK_2	LogK_1/LogK_2
Cr(III)	6.8175	3.0774	3.7401	2.2153
Th(III)	7.2605	5.7256	1.5349	1.2681
Nd(III)	7.1899	3.2116	3.9783	2.2387

Figure 1. System: L1

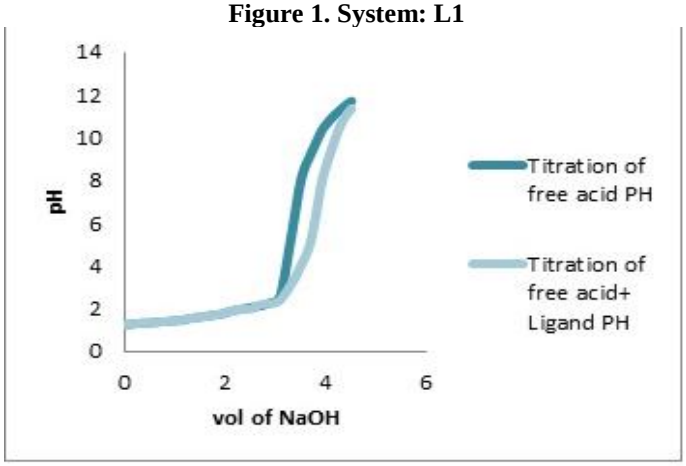


Figure 2. System: L2

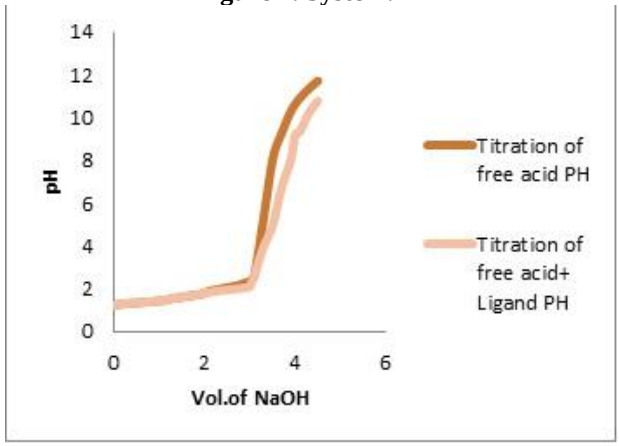
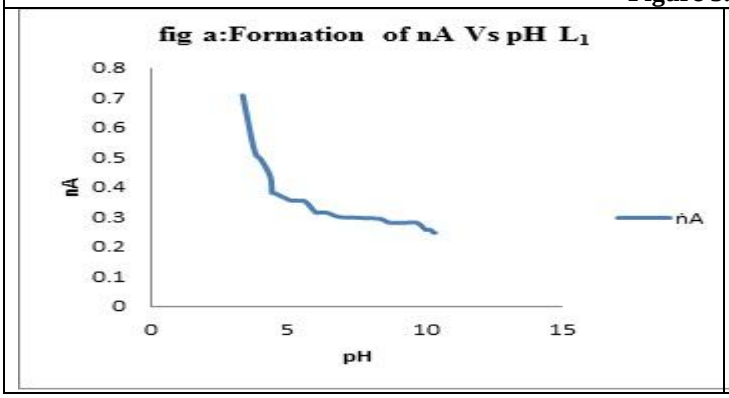


Figure 3. a,b



Proton-Ligand stability constant (pK)

It is observed from titration curve in (fig.1,2,)shows that the ligand curves starts deviating from free acid (HClO4) curves at pH > 2.25,2.14 respectively. The extent of deviation s may be the dissociation of –OH group completely.

CONCLUSION

From the titration curve, it is observed that the departure between (Acid + Ligand) curve & (Acid+Ligand +Metal) Curve for all system of L_1,& L_2 started from pH=2.14 to 3.47, this indicate the commencement of complex formation. Also change in color from yellow to brown in pH range from 3.35 to 9.87 during the titration showed the complex formation between Metal & Ligand.

ACKNOWLEDGEMENT

Author is thankful to Principal Dr. R.D. Deshmukh and Dr. S.D.Thakur dept. of Chemistry, Bar.R.D.I.K. & N.K.D. College Badnera for encouragement and providing facilities.

REFERENCES

1. Sonkamble SG. PH metric Studies of Synthesized Ligands 1-(2'-hydroxyphenyl)-3-Phenylpropane-1, 3-dione with Fe(II), Cd(II), Co(II), Ni(II), Zn(II) cations at 0.1M ionic strength. *Int J Chem and Pharma Sci*, 5(3), 2014, 55-59.
2. Sonkamble Shivanand. Metal-ligand stability constants of Fe (III), Cd(II), Co(II), Ni(II), Zn(II) metal ion complexes with Lorazepam in aquo-organic media at 0.1 M ionic strength pH metrically. *Adv In Appl Sci Res*, 5(4), 2014, 171-175.
3. Routh SR and Gollapalli NR. Speciation of Binary Complexes of Co(II), Ni(II) and Cu(II) With Bidentate Ligand in Low Dielectric Medium. *Int J Res Method In Phys and Chem*, 1(1), 2014, 20-30.
4. Khambre AD. Narwade ML. Studies of proton and metal-ligand stability constants of Pr(III), Nd(III)and Gd(III) complexes of substituted Schiff's Bases & Dibromo Chalcones. *Int J Adv Res In Sci and Enginee*, 3(12), 2014, 253-257.
5. Meshram UP. Khobragade BG. Narwade ML. Chandak HS. Studies on Formation constant of Co(II), Ni(II), Cr(III)&Fe(III)ion Complexes with Some Hetrocycles By pH metrically, Spectrophotometrically & Refractometrically. *Int J Pharma Chem and Bio Sci*, 4(3)2014, 706-710.
6. Wadekar MP. Shrirao AS. Tayade RR. pH metric Study of Substituted Thiopyrimidine Complexes in mixed Solvent Media. *J Chem and Pharma Res*, 6(11), 2014, 420-426.
7. Santhee Devi KV. Rama Raju B. Nageshwara Rao G. pH-Metric Investigation on mixed ligand complexes of Ca(II), Mg(II) & Zn(II) with L-Dopa & 1, 10-phenanthroline in Propylene glycol-water mixtures. *Res and Reviews J Chem*, 1(1), 2012, 13-22.
8. Ramteke AA. Chavan SP. Patil SD. Narwade ML. Effect of ionic Strength on the stability constants of complexes of 3-(4-Chlorophenyl)-4-(3-pyridine)-5-(2-hydroxyphenyl)-pyrazole with Cu(II), Tb(III) &Nd(III) metal ions. *Int J Chem Studies*, 2(4), 2014, 01-05.
9. Naik AB. Spectrophotometric studies of Dy(III), Nd(III), Sm(III) and Tb(III) complexes with substituted pyrazole, *World J of Chem*, 6, no.2, 2011, 118-121.
10. Sharma K, Jain R. Synthesis, reaction and anthelmintic activity of 1-[benzimidazol-2-yl-]-4-formyl-3-[2'(-substitut- ed phenyl) indole-3-yl] pyrazole. *Ind J Chem*, 51B, 2012, 1462 -1469.
11. Rahimizadeh M. Pordel M. Bakavoli M. Rezgeian S. Sadghian A. Synthesis and antibacterial activity of some new derivatives of pyrazole. *World J Microbiol Biotechnol*, 26, 2010, 317-321.
12. Sasmita Rani Devi, Studies on Stability and Configurational Changes of Nickel and Copper Ethambutol Dihydrochloride and Metformin Hydrochloride in both Cationic and Anionic Surfactants. *Int J Enginee Sci Inven*, 2(4), 2013, 39-50.

13. Agrawal D. Gupta K.D. pH Metric Study On Thermodynamic And Ionization Constant Of 2, 5-Diaminopentanoic Acid (DL-ornithine), *Int J Res Adv Tech*, 2(10), 2014, 51-55.
14. Talele R.D. and Sonar A.N.Studies of stabilities of Schiff base of (5-hydroxy-3-methyl-1-(2, 4-dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 4-amino antipyrine complexes with metal ions in mixed solvent at 0.1M ionic strength and 303K by pH metric method. *Int J Basic & App Chem Sci*, 4(3), 2014, 13-15.