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STUDIES OF PROTON AND METAL-LIGAND STABILITY CONSTANTS OF Cr(III),Th(III),& Nd(III) COMPLEXES OF SUBSTITUTED ISOXAZOLINES

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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-(2-phenylethenyl)isoxazoline [HNMP2EI] L₁, 3-(2-hydroxy-3-bromo-4-nitro-5-methyl)-5-(3-nitrophenyl)isoxazoline [HBN M3NI] L₂ have been studied at 0.1M Ionic Strength (26±0.1)°C 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 L₁&L₂.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.

INTRODUCTION

Isoxazolines possess medicinal activities such as anti-inflammatory^[1], antibacterial, anticonvulsant^[2], antibiotic^[3], antitubercular^[4], antifungal^[5] and anxiolytic activity^[6]. The studies in metal ligand complexes in solution of a number of metal ions 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. Routh et al^[7] have studied speciation of binary complexes of Co(II), Ni(II) & Cu(II) with bidentate ligand in low dielectric medium. Wadekar MP et al^[8] have studied pH metric study of substituted Thiopyrimidine complexes in mixed solvent media. Recently many co-workers have studied proton and metal-ligand stability constant of mixed ligand complexes^[9]. Ramteke et al^[10] have studied effect of ionic strength on stability constant of complexes of substituted pyrazole with Cu(II), Tb(III) & Nd(III) metal ions. Sonkamble et al^[11] have studied metal-ligand stability constant of some substituted diketone. Khambre AD et al^[12] have studied studies of proton and metal-ligand stability constants of Pr(III), Nd(III) and Gd(III) complexes of substituted Schiff's bases & dibromo Chalcones. Meshram UP et al^[13] have studied studies on formation constant of Co(II), Ni(II), Cr(III) & Fe(III) ion complexes with some heterocycles by pH metrically, spectrophotometrically & refractometrically. Sonkamble et al^[14] have studied metal-ligand stability constant of some substituted Lorazepam. 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^[15]. The pyrazole moiety is present in a large number of biologically active compounds which find wide applications in pharmaceuticals^[16] and agro-chemical industries^[17]. Sasmita Rani Devi^[18] have studied studies on stability and configurational changes of nickel and copper ethambutol dihydrochloride and metformin hydrochloride in both cationic and anionic surfactants. Agrawal D et al^[19] have studied pH metric study on thermodynamic and ionization constant of 2,5-Diaminopentanoic Acid (DL-ornithine). Talele R.D. et al^[20] have studied 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. 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.

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 solutions 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 perchloric acid was prepared and used after standardization 23.

Measurements:-

All measurements were carried out at $(26 \pm 0.1) ^\circ\text{C}$. 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 $(26 \pm 0.1) ^\circ\text{C}$ prepared from a 'Qualigens' buffer tablets. The hydrogen ion concentration was measured with combined glass electrode.

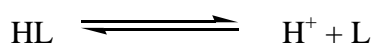
Procedure

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 ($20 \times 10^{-4} \text{ mol.dm}^{-3}$)
- iii. Free acid HClO_4 ($0.01 \text{ mole dm}^{-3}$) and ligand ($20 \times 10^{-4} \text{ mol.dm}^{-3}$) and metal ion ($4 \times 10^{-4} \text{ mol.dm}^{-3}$) 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-(2-phenylethenyl)isoxazoline [HNMP2EI] L₁, 3-(2-hydroxy-3-bromo-4-nitro-5-methyl)-5-(3-nitrophenyl)isoxazoline [HBNM3NI] L₂ may be considered as a monobasic acid having one replaceable H⁺ ion from phenolic -OH group and can be represented as



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 (Table 1)

$$\bar{n}_A = \gamma - \frac{(V_2 - V_1) (N + E^0)}{(V^0 + V_1) (T_L^0)} \quad \dots\dots 01$$

Where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.15 mol.dm⁻³), (V₂-V₁) is the measure of displacement of the ligand curve relative to acid curve, where V₂ and V₁ are the volume of alkali added to reach the same pH reading to get accurate values of (V₂-V₁): the titration curves were drawn on an enlarged scale: E⁰ and T_L⁰ are the resultant concentration of perchloric acid and concentration of Ligand, respectively. V₀ is

the initial volume of reaction mixture (50 cm³). 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 \bar{n} Vs pL. The experimental \bar{n} values determined using expression

$$\bar{n} = \frac{(V_3 - V_2) (N + E^0)}{(V^0 + V_2) \bar{n}_A T_M^0} \quad \dots\dots 01$$

Where N, E⁰, V₀ and V₂ have same significance as in equation (1), V₃ is the volume of NaOH added in the metal ion titration to attain the given p^H reading and T_M⁰ (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 $\log K_1$ & $\log K_2$ Values of Nd(III)&Th(III)for ligand L_1 & L_2 indicates the stepwise formation of complex between metal ion and ligand except Cr(III) for ligand $-L_1$ & 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($\log K_1 / \log K_2$) for Cr(III)&Nd(III)- Ligand- L_1 ;Th(III)&Nd(III)-Ligand L_2 complex indicates the more stable stepwise complex formation as compare to Th(III) – Ligand- L_1 & Cr(III)-Ligand L_2 complexes.

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 ($HClO_4$) curves at $pH > 2.12, 2.00$ respectively. The extent of deviation s may be the dissociation of $-OH$ group completely.

Table no.1 :Proton Ligand Formation number (\dot{n}_A) at $(26 \pm 0.1)^\circ C$ and at ionic strength $\mu=0.1 \text{ mol dm}^{-3}$ $NaClO_4$ in 70% Dioxane- Water mixture. System : HNMP2EI(L_1)

P^H	V_1	V_2	$V_2 - V_1$	\dot{n}_A
2.70	3.1351	3.1665	0.0314	0.9527
2.77	3.1353	3.1985	0.0632	0.9048
3.00	3.1551	3.2194	0.0643	0.9032
3.35	3.2021	3.2681	0.0660	0.9008
3.37	3.2024	3.2706	0.0682	0.8974
3.56	3.2038	3.2879	0.0841	0.8735
3.70	3.2042	3.3031	0.0989	0.8513
4.00	3.2083	3.3370	0.1287	0.8064
4.35	3.2475	3.3972	0.1497	0.7751
4.37	3.2482	3.3979	0.1497	0.7751
4.42	3.2518	3.4117	0.1599	0.7597
4.70	3.2519	3.4501	0.1982	0.7023
5.07	3.2743	3.5030	0.2287	0.6566
5.14	3.2743	3.5039	0.2296	0.6552
5.21	3.2743	3.5060	0.2317	0.6520
5.42	3.3000	3.5327	0.2327	0.6507
5.63	3.3330	3.5659	0.2329	0.6504
6.00	3.3330	3.5660	0.2330	0.6503

6.14	3.3330	3.5660	0.2330	0.6503
6.21	3.3413	3.6083	0.2670	0.5996
6.28	3.3413	3.6293	0.2880	0.5681
6.35	3.3572	3.6568	0.2996	0.5506
6.37	3.3589	3.6589	0.3000	0.5502
6.42	3.3660	3.6807	0.3147	0.5282
6.49	3.3661	3.6889	0.3228	0.5608
6.70	3.3662	3.6977	0.3315	0.5030
6.84	3.4496	3.7824	0.3328	0.5018
7.00	3.4582	3.7912	0.3330	0.5016
7.35	3.4662	3.8159	0.3497	0.4767
7.42	3.4662	3.8159	0.3497	0.4767
7.56	3.4867	3.8464	0.3597	0.4619
7.70	3.4867	3.8509	0.3642	0.4552
8.00	3.5000	3.8670	0.3670	0.4512
8.35	3.5000	3.8670	0.3670	0.4512
8.42	3.5330	3.9112	0.3782	0.4349
8.56	3.5332	3.9119	0.3787	0.4342
8.70	3.5660	3.9502	0.3842	0.4260
9.00	3.6330	4.0330	0.4000	0.4037
9.35	3.6660	4.1227	0.4567	0.3192
9.70	3.7661	4.2487	0.4826	0.2805

b)System : HBNM3NI(L2)

PH	V1	V2	V2 – V1	ñ A
3.35	3.2021	3.2608	0.0587	0.9117
3.37	3.2024	3.2638	0.0614	0.9078
3.56	3.2038	3.2708	0.0670	0.8994
3.70	3.2042	3.3042	0.1000	0.8499
4.00	3.2083	3.3250	0.1167	0.8248
4.35	3.2475	3.3755	0.1280	0.8061
4.37	3.2482	3.3780	0.1298	0.8048
4.42	3.2518	3.3818	0.1300	0.8047

4.49	3.2519	3.3819	0.1300	0.8047
5.07	3.2743	3.4321	0.1578	0.7630
5.14	3.2743	3.4332	0.1589	0.7614
5.21	3.2743	3.4333	0.1590	0.7612
5.42	3.3000	3.4641	0.1641	0.7537
5.63	3.3330	3.4982	0.1652	0.7522
6.00	3.3330	3.4982	0.1652	0.7522
6.14	3.3330	3.4991	0.1661	0.7520
6.21	3.3413	3.5077	0.1664	0.7517
6.28	3.3413	3.5082	0.1669	0.7507
6.35	3.3572	3.5242	0.1670	0.7496
6.37	3.3589	3.5259	0.1670	0.7496
6.42	3.3660	3.5330	0.1670	0.7496
6.49	3.3661	3.5332	0.1671	0.7493
6.70	3.3662	3.5333	0.1671	0.7493
6.84	3.4496	3.6333	0.1837	0.7243
7.00	3.4582	3.6569	0.1987	0.7010
7.35	3.4662	3.6665	0.2003	0.7003
7.42	3.4662	3.6828	0.2166	0.6755
7.56	3.4867	3.7033	0.2166	0.6757
7.70	3.4867	3.7034	0.2167	0.6759
8.00	3.5000	3.7503	0.2503	0.6256
8.35	3.5000	3.7506	0.2506	0.6253
8.42	3.5330	3.7922	0.2592	0.6126
8.56	3.5332	3.7930	0.2598	0.6117
8.70	3.5660	3.8328	0.2668	0.6039
9.00	3.6330	3.8998	0.2668	0.6039
9.35	3.6660	3.9329	0.2669	0.6037
9.70	3.7661	4.0661	0.3000	0.5534
9.84	3.7907	4.1248	0.3340	0.5024
10.00	3.8000	4.1660	0.3660	0.4557
10.35	3.9000	4.2988	0.3988	0.4081
10.70	4.0330	4.5316	0.4986	0.2617

Table 2: Proton Ligand Stability Constant p^K

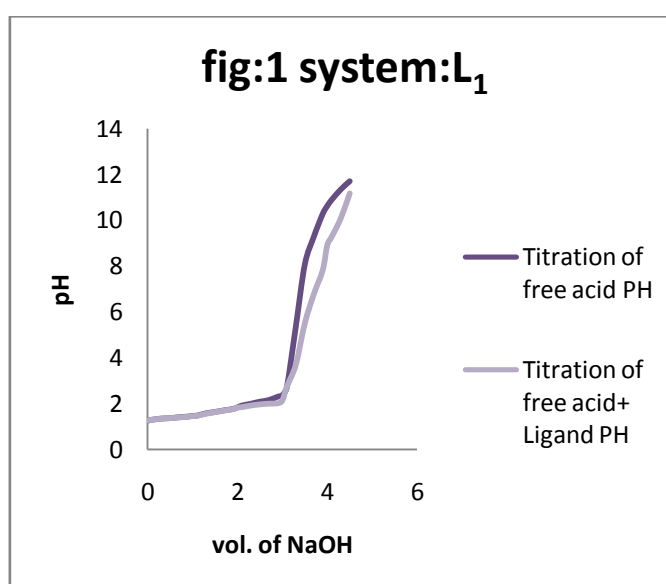
System	p^K	
	Half integral method	Pointwise calculation method
HNMP2EI (L_1)	7.0028	7.0014
HBNM3NI(L_2)	9.8442	9.7267

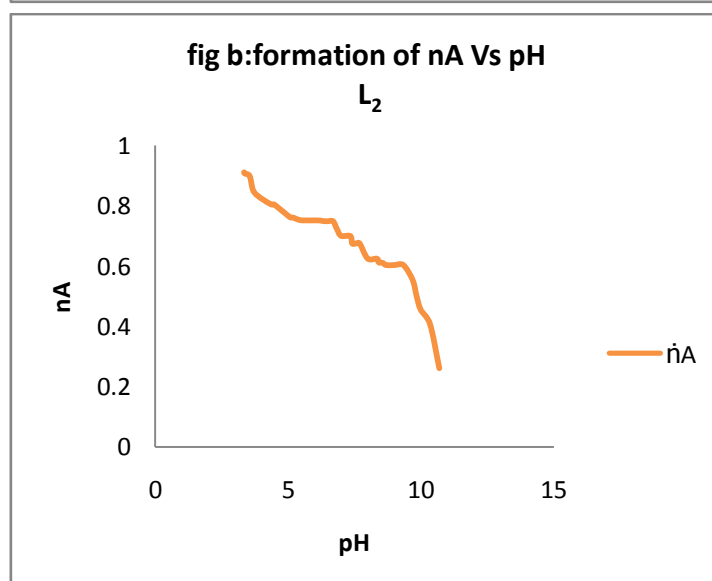
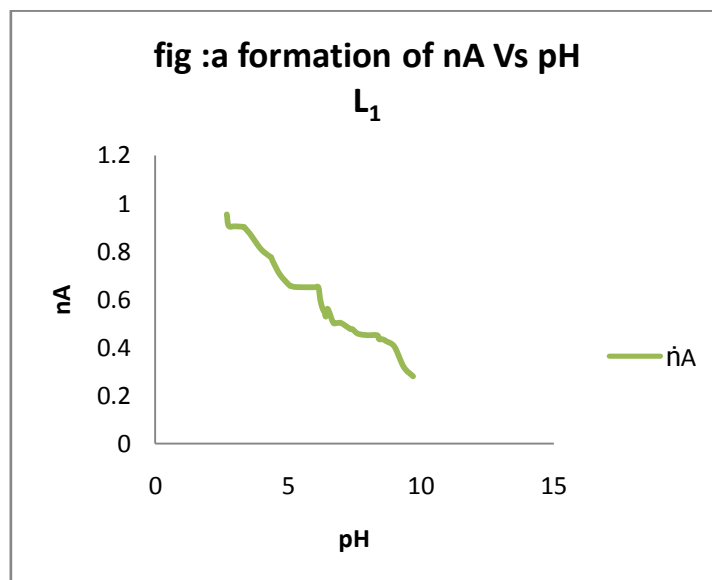
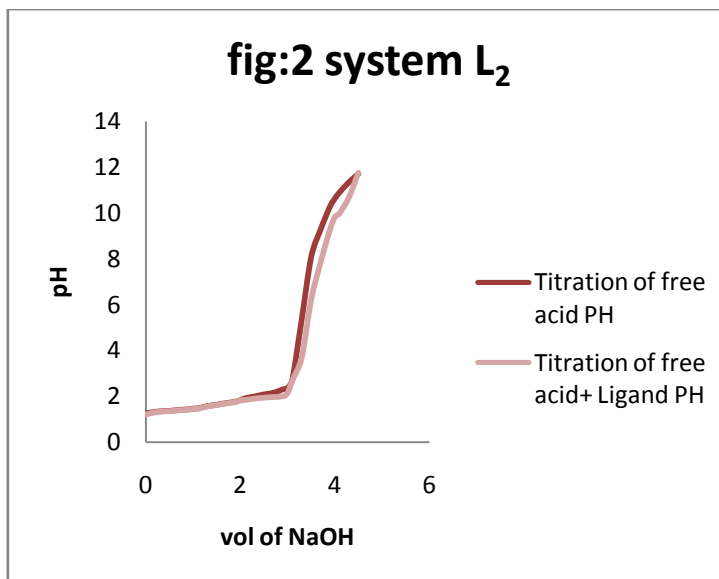
Table 3: Metal Ligand Stability Constant(Log K)a) HNMP2EI (L_1)

System	Log K_1	Log K_2	Log $K_1 - \text{Log} K_2$	Log $K_1/\text{Log}K_2$
Cr(III)	5.2467	2.5621	2.6846	2.0478
Th(III)	8.8731	5.7694	3.1037	1.5379
Nd(III)	6.9310	4.1066	2.8244	1.6878

b) HBNM3NI(L_2)

System	Log K_1	Log K_2	Log $K_1 - \text{Log} K_2$	Log $K_1/\text{Log}K_2$
Cr(III)	9.4366	7.9238	1.5128	1.1909
Th(III)	9.0159	5.9807	3.0352	1.5075
Nd(III)	8.5708	5.7870	2.7838	1.4810





CONCLUSION

From the titration curve, it is observed that the departure between (Acid + Ligand) curve & (Acid+Ligand +Metal) Curve for all system of L₁ & L₂ started from pH=2.12 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 10.00 during the titration showed the complex formation between Metal & Ligand.

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