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## **pH-METRIC STUDY OF SUBSTITUTED 3,5-DIARYL ISOXAZOLINES COMPLEXES IN 70% DIOXANE SOLVENT MEDIA**

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Substituted 3,5-  
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water mixture, stability  
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### **ABSTRACT**

The complex formation between Pr(III)&Sm(III) metal ions and 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(2-phenylethenyl)isoxazoline [HNMP2EI]L<sub>1</sub>, 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(phenyl) isoxazoline [HNMP5PI]L<sub>2</sub>, 3-(2-hydroxy-3-bromo-4-nitro-5-methyl)-5-(3-nitrophenyl)isoxazoline [HBNM3NI]L<sub>3</sub> 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 Pr(III)&Sm(III) metal ions form 1:1 & 1:2 complexes with ligand L<sub>1</sub>,L<sub>2</sub>&L<sub>3</sub>.The data obtained were used to estimate & compare the values of proton ligand stability constant (p<sup>K</sup>) & metal ligand stability constant (log K).From estimated data (p<sup>K</sup> & log K),the effect of substituents were studied.

## 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. Metal with the view to understand the bioinorganic chemistry of metal ions, Agrawal et al<sup>[1]</sup> have studied thermodynamic & ionisation constant of 2,5-diaminopentanoic acid. Wadekar et al<sup>[2]</sup> have studied stability constant of substituted thiopyrimidine. Khambre et al<sup>[3]</sup> have studied proton and metal ligand stability constant of some substituted Schiff's bases and dibromo chalcone. Meshram et al<sup>[4]</sup> have studied the formation constant of Co(II), Ni(II), Cr(III) & Fe(III) ion complexes with some heterocycles by pH metrically. Recently Sonkamble<sup>[5]</sup> have studied stability constant of some synthesized ligand at 0.1M ionic strength. Recently Tihile<sup>[6]</sup> studies on interaction between Cu(II), Cr(II), Nd(II) and Pr(II) metal ions and substituted hydroxyl chalcones at 0.1 M ionic strength pH metrically. Thakur et al<sup>[7,8]</sup> have studied the influence of dielectric constants of medium on the complex equilibrium of substituted hydroxyl-1,3- propanediones with Cr(II) metal ions and studies on interaction between Cu(II), Cr(II) and Ni(II) metal ions at 0.1M ionic strength pH metrically. Isoxazolines possess medicinal activities such as anti-inflammatory<sup>[9]</sup>, antibacterial, anticonvulsant<sup>[10]</sup>, antibiotic<sup>[11]</sup>, antitubercular<sup>[12]</sup>, antifungal<sup>[13]</sup> and anxiolytic activity<sup>[14]</sup>.

In present work an attempt has been made to study the interactions between Pr(III) & Sm(III) Cations At 0.1 M Ionic Strength with Ligand at 0.1 ionic strength, pH metrically in 70% Dioxane-water mixture.

## 2. MATERIALS AND METHODS

The ligands L<sub>1</sub>, L<sub>2</sub>, & L<sub>3</sub> 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.

## 2.1. 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.

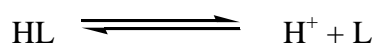
## 2.2. Procedure

The experimental procedure involved the titrations of

- i. Free acid  $\text{HClO}_4$  ( $0.01 \text{ mol.dm}^{-3}$ )
- ii. Free acid  $\text{HClO}_4$  ( $0.01 \text{ mol.dm}^{-3}$ ) and ligand ( $20 \times 10^{-4} \text{ mol.dm}^{-3}$ )
- iii. Free acid  $\text{HClO}_4$  ( $0.01 \text{ mole dm}^{-3}$ ) 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 ( $0.15 \text{ mol.dm}^{-3}$ ) 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  $\text{NaClO}_4$  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 1-3). 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) .

## 3. 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] $\text{L}_1$ , 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(phenyl)isoxazoline [HNMP5PI] $\text{L}_2$ , 3-(2-hydroxy-3-bromo-4-nitro-5-methyl)-5-(3-nitrophenyl)isoxazoline[HBNM3NI] $\text{L}_3$  may be considered as a monobasic acid having one replaceable  $\text{H}^+$  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).

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

Where  $\gamma$  denotes the number of dissociable protons,  $N$  is the concentration of sodium hydroxide (0.15 mol.dm<sup>-3</sup>),  $(V_2 - V_1)$  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<sup>3</sup>). 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

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

Where  $N$ ,  $E^0$ ,  $V_0$  and  $V_2$  have 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  $T_M^0$  ( $4 \times 10^{-4}$  mol dm<sup>-3</sup>) is the concentration of metal ion in reaction mixture. The stability constants for various binary complexes have been calculated (Table 3).

### 3.1. Metal Ligand Stability Constant (Log K)

It is observed that (Table 3 a-c) sufficiently large difference between  $\log K_1$  &  $\log K_2$  values of Sm(III) for ligand  $L_1$  &  $L_2$  & Pr(III) for ligand  $L_1$  &  $L_3$  indicates the stepwise formation of complex between metal ion and ligand except Pr(III) for ligand  $-L_2$  & Sm(III) for ligand  $L_3$ . 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 Pr(III)-Ligand- $L_1$  &  $L_3$  & Sm(III)-ligand- $L_1$  &  $L_2$  complex indicates the more stable stepwise complex formation as compared to Sm(III)-Ligand- $L_3$  & Pr(III)-Ligand  $L_2$  complexes.

### 3.2. Proton-Ligand stability constant (pK):-

It is observed from titration curve in (fig.1,2,3) shows that the ligand curves start deviating from free acid (HClO<sub>4</sub>) curves at  $pH > 2.12, 2.14, \& 2.0$  respectively. The extent of deviation may be the dissociation of  $-OH$  group completely.

#### 4. CONCLUSION

From the titration curve, it is observed that the departure between (Acid + Ligand) curve & (Acid+Ligand +Metal) Curve for all system of  $L_1, L_2, \& L_3$  started from pH=2.12 to 3.38, this indicate the commencement of complex formation. Also change in color from yellow to brown in pH range from 3.35 to 10.07 during the titration showed the complex formation between Metal & Ligand.

**Table no.1** :Proton Ligand Formation number ( $\bar{n}_A$ ) at  $(26 \pm 0.1)^\circ\text{C}$  and at ionic strength  $\mu=0.1$  moldm<sup>-3</sup> NaClO<sub>4</sub> in 70%Dioxane-Water mixture.

**a)System : HBMP2EI( $L_1$ )**

$P^H$	$V_1$	$V_2$	$V_2 - V_1$	$\bar{n}_A$
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 : HNMP5PI( $L_2$ )**

$P^H$	$V_1$	$V_2$	$V_2 - V_1$	$\bar{n}_A$
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

**c)System : HBNM3NI(L<sub>3</sub>)**

$P^H$	$V_1$	$V_2$	$V_2 - V_1$	$\dot{n}_A$
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
<b>HNMP2EI (<math>L_1</math>)</b>	7.0027	7.3487
<b>HNMP5PI(<math>L_2</math>)</b>	6.6507	6.5728
<b>HBNM3NI(<math>L_3</math>)</b>	9.8442	9.2987

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

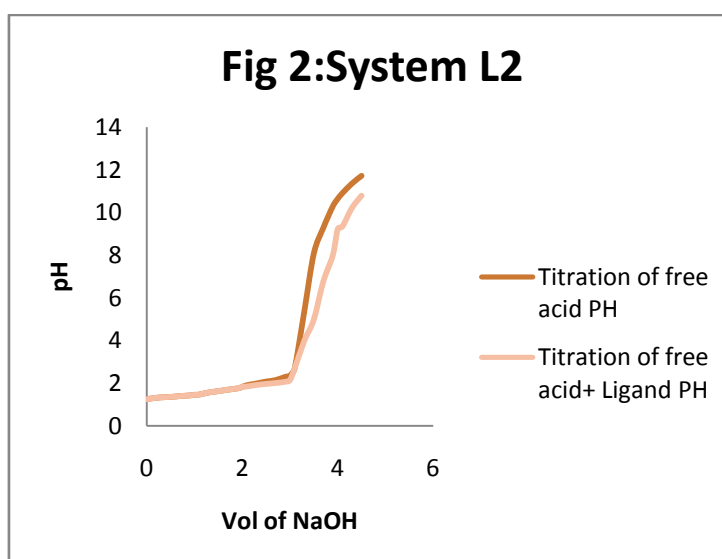
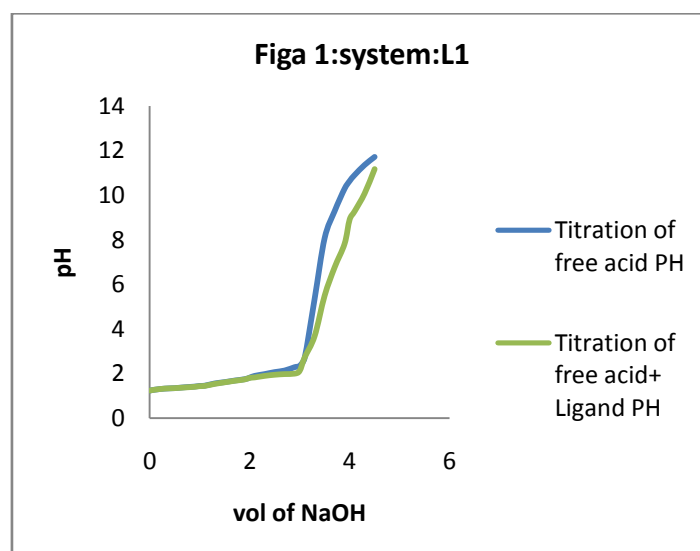
System	Log $K_1$	Log $K_2$	Log $K_1$ -Log $K_2$	Log $K_1$ /Log $K_2$
<b>Pr(III)</b>	6.5807	3.8465	2.7342	1.7108
<b>Sm(III)</b>	6.7926	3.9788	2.8138	1.7071

**b) HNMP5PI(L<sub>2</sub>)**

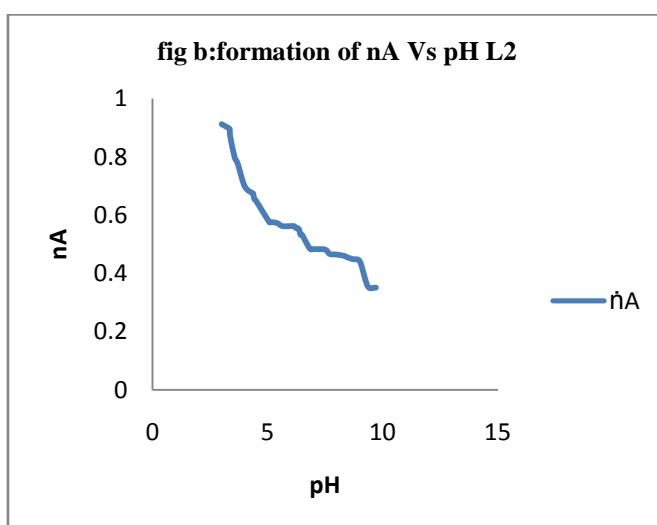
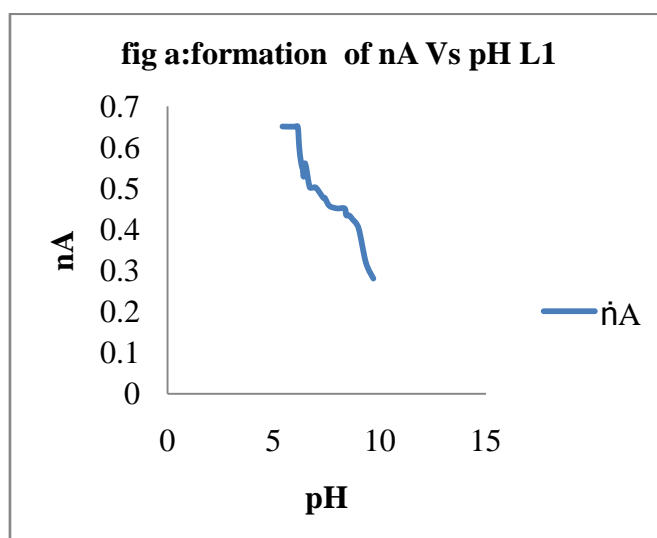
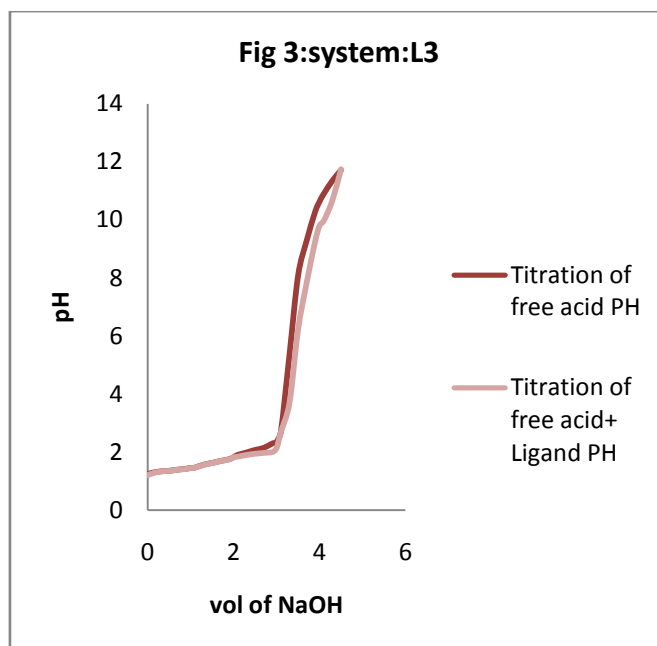
System	Log K <sub>1</sub>	Log K <sub>2</sub>	LogK <sub>1</sub> -LogK <sub>2</sub>	LogK <sub>1</sub> /LogK <sub>2</sub>
<b>Pr(III)</b>	7.3972	5.7815	1.6157	1.2795
<b>Sm(III)</b>	7.7559	4.8924	2.8635	1.5853

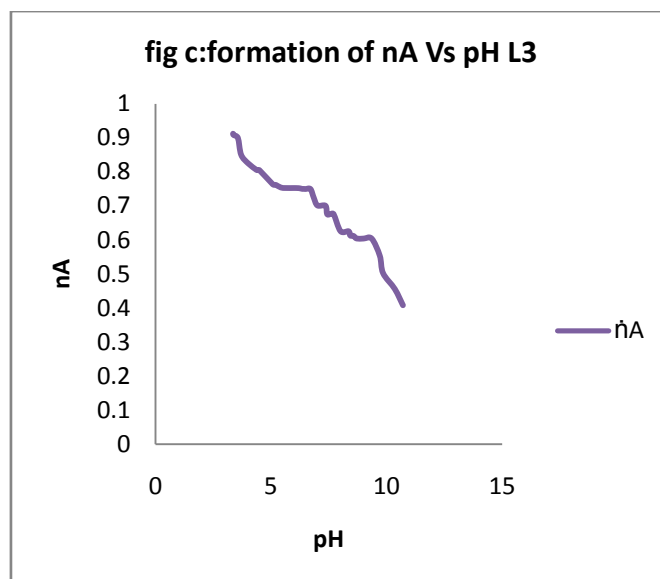
**c) HBNM3NI(L<sub>3</sub>)**

System	Log K <sub>1</sub>	Log K <sub>2</sub>	Log K <sub>1</sub> - LogK <sub>2</sub>	LogK <sub>1</sub> /LogK <sub>2</sub>
<b>Pr(III)</b>	9.9990	7.4911	2.5079	1.3347
<b>Sm(III)</b>	9.7658	7.4891	2.2767	1.3040









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