



## EFFECT OF SOLVENTS ON STABILITY CONSTANTS OF LANTHANIDES METAL COMPLEXES WITH SOME SUBSTITUTED PYRAZOLES

Gopalkrushna H. Murhekar, Arun R. Raut, Noor Mohammad

Organic synthesis Division, PG Department of Chemistry, Government Vidarbha  
Institute of Science And Humanities, Amravati, 444604 (M.S.), India.

*gopalmurhekar@gmail.com*

### ABSTRACT

The reaction of Pr (III) and Nd (III) metal ions with  $L_1$ : 3 (2'-chlorophenyl) - 4-benzoyl - 5 (2-hydroxy phenyl) pyrazole,  $L_2$ : 3 (2'-chlorophenyl) - 4-pyridoyl - 5 (2-hydroxy phenyl) pyrazole,  $L_3$ : 3 (2'-aminophenyl)- 4-pyridoyl - 5 (2-hydroxyl phenyl) pyrazole and  $L_4$ : 3 (4'-chlorophenyl) - 4-Benzoyl - 5(2-hydroxy-phenyl) pyrazole, at 0.1M ionic strength at  $28 \pm 0.1^\circ\text{C}$  in 70% ethanol -water mixture and 70% dioxane-water mixture have been studied pH-metrically. The data obtained were used to estimate the values of proton-ligand (pK) and metal-ligand (logK) stability constants in different solvents mixture. It is observed that the pK and logK values in 70% dioxane-water mixture are greater than in 70% ethanol -water mixture. Pr (III) and Nd (III) metal ions formed 1:1 and 1:2 complexes with all the ligands in both solvent medium.

**Key words** – Substituted pyrazole, solvent effect, stability constants, chelates.

### INTRODUCTION

Pyrazoles are fall in the class of aromatic heterocyclic compounds, and unique structural feature involving pyrazolic nitrogen and make them interesting ligands. Pyrazoles are the good complexing agent<sup>1,3</sup>. The formation constants of transition metal ion complexes with some



substituted pyrazoles and pyrazolines have been reported <sup>4</sup>. The influence of ionic strength on the stability constants of transition and lanthanide metal ions complexes with substituted pyrazoles were also reported <sup>5</sup>. Sawalkahe et al<sup>6</sup> have studied the interaction on metal ions with 1,3 diketones, pyrazoles and pyrazoline spectrophotometrically. Lanthanide (III) metal complexes with nitrogen donor ligands including Schiff bases were reported <sup>7</sup>. The interactions of some lanthanide metal ions with substituted isoxazolines at 0.1M ionic strength have been reported pH metrically <sup>8,11</sup>.

Recently ultrasound promoted synthesis of substituted pyrazoles and isoxazoles were studied <sup>12</sup>. The effect of various mixed aqueous solvents on the stability constants of Cu (II) chelates with piperidine-2- carboxylic acid have been studied<sup>13</sup>.

The study of proton-ligand stability constants and metal-ligand stability constants of Pr (III) and Nd(III) complexes with some substituted pyrazoles at different solvent medium have been focus due to their wide range application in various field of human interest. In present research work we have undertaken the study of chelating properties of some substituted pyrazoles (mentioned above) with lanthanide metals like Pr(III), Nd(III) under suitable condition, in 70% ethanol-water mixture and 70% dioxane-water mixture pH metrically.

## EXPERIMENTAL

Substituted pyrazoles were synthesized in our laboratory by standard method <sup>14</sup>. The substituted pyrazoles are insoluble in water; hence 70% ethanol-water (v/v) and 70% dioxane-water (v/v) mixture was used as solvent. Lanthanide metal nitrates were dissolved in double distilled water and their concentration estimated by standard method <sup>15</sup>. The chemical used in this work where reagent grade including, Sodium hydroxide (Merck, 99.99%), potassium nitrate (Merck, 99.99%) and nitric acid (Merck, 99.98%), were used. Ethanol and dioxane was purified by standard method <sup>16</sup>. pH measurement were carried out with ELICO pH meter (accuracy  $\pm 0.05$  units) using combined electrode at  $28 \pm 0.1^{\circ}\text{C}$ .



## Calvin Bjerrum Titration Technique

The titrations were carried out in an inert atmosphere of nitrogen. The ionic strength of solution was maintained constant by adding an appropriate amount of 1M potassium nitrate solution. The values were recorded by pH meter. These values converted to  $[H^+]$  values by applying the correction proposed by Van Uitert and Hass<sup>17</sup>. The contribution of the other ions in addition to  $K^+$  and  $NO_3^-$  also taken into consideration. The overall 0.1 ionic strength of solution was calculated by expression -

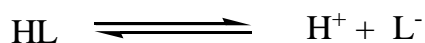
$$\mu = \frac{1}{2} \sum_{i=1} C_i Z_i^2 \text{ ----- (1)}$$

## RESULTS AND DISCUSSION

The titration data were used to construct the curve between volumes of *NaOH Vs pH*. They are called as acid titration curve, ligand titration curve and metal titration curve. The pK values of ligand and logK values of Pr (III) and Nd (III) complexes at various ionic strength were calculated by Irving and Rossotti's method<sup>18</sup>. (**Figure-1 and 2**)

### i) Proton – ligand stability constants (pK)

Substituted pyrazoles may be considered as monobasic acids having one replaceable  $H^+$  ion from phenolic  $OH^-$  group and can therefore be represented as HL



The titrations data in 70% ethanol-water mixture were used to construct the curve between volumes of *NaOH Vs pH*. It is observed from the titration curve that the ligand curves



start deviating from free acids curve at about pH – 3.50 for L<sub>1</sub>, at about pH 2.80 for L<sub>2</sub> , at about pH 3.45 for L<sub>3</sub> and at about pH 2.88 for L<sub>4</sub>. The deviation increased continuously up to pH 12.50. It indicated that OH<sup>-</sup> group start to dissociated at about 2.80 and complete its dissociation at about pH 12.50. (*Table-1*)

The titrations data in 70% dioxane-water mixture were used to construct the curve between volumes of NaOH Vs pH. It is observed from the titration curve that the ligand curves start deviating from free acids curve at about pH – 3.55 for L<sub>1</sub>, at about pH 2.90 for L<sub>2</sub>, at about pH 3.40 for L<sub>3</sub> and at about pH 2.96 for L<sub>4</sub>. The deviation increased continuously up to pH 12.56. It indicated that OH<sup>-</sup> group start to dissociated at about 2.90 and complete its dissociation at about pH 12.56. (*Table-2*)

The average number of proton associated with the ligand ( $\bar{n}_A$ ) was determined from ligand titration curves employing the Irving and Rossotti expression [18].

$$\bar{n}_A = \frac{2T_L^0 - \{(V_2 - V_1)(N + E^0) / (V^0 + V_1)\}}{T_L^0} \text{----- (2)}$$

Where,

V<sup>0</sup>- is the initial volume of the solution,

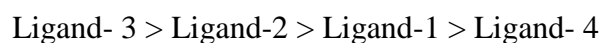
E<sup>0</sup> and T<sub>L</sub><sup>0</sup> - are initial concentrations of acid and ligand respectively,

V<sub>1</sub> and V<sub>2</sub> -are the volumes of alkali of normality,



N -during the acid and ligand titration at given pH and

$\gamma$  -is the replaceable proton from the ligand. The pK values were estimated from formation curves ( $\bar{n}_A$  Vs pH) by noting the pH, at which  $\bar{n}_A = 0.5$ . The accurate values of pK were estimated by pointwise calculations. The pK values of ligands increases in the following order in both the solvents. (*Table -1 and 2*)



It could be seen from the values, the more reduction in pK values of ligand  $L_4$  may be due to presence of chlorophenyl and benzoyl groups which act as stronger electron withdrawing groups. **ii) Metal – ligand stability constants ( logK ) :**

Metal ligand stability constants of Pr (III) and Nd (III) complexes with some substituted pyrazoles were determined by employing Calvin-Bjerrum pH-metric titration technique<sup>19-20</sup> as adopted by Irving and Rossotti.

➤ *The formation of chelates between Pr(III) and Nd(III) with substituted pyrazoles in 70% ethanol-water mixture was indicated by,*

- 1) The significant departure starting from pH 2.95 for Pr (III) complex systems,
- 2) The significant departure starting from pH 2.90 for Nd (III) complex systems,
- 3) The change in colour from, colourless to yellow and then dark yellow as pH increased from 3.50 to 12.50. (*Figure-1*)

➤ The formation of chelates between Pr(III) and Nd (III) with substituted pyrazoles in 70% dioxane-water mixture was indicated by,



- 1) The significant departure starting from pH 2.92 for Nd(III) complex system,
- 2) The change in colour from, colorless to yellow and then dark yellow as pH increased from 2.99 to 12.55 (**Figure-2**).

The logK values were directly read from the formation curves ( $\bar{n}$  Vs PL) using half integral method.  $\bar{n}$  can be calculated by using following expression

$$\bar{n} = \frac{(V_3 - V_2) - \{N + E^0 + T_L^0 (\gamma - \bar{n}_A)\}}{(V^0 + V_2) \bar{n}_A T_M^0} \text{ ----- (3)}$$

Where N,  $E^0$  and  $T_L^0$  have same significance as per the ligand titrations and  $V_3$  represents the volume of alkali required to obtain the same pH as the ligand and acid titration. The logK values were directly read from the formation curves ( $\bar{n}$  Vs PL) using half integral method. The most accurate logK values were calculated by pointwise calculation method, for all the systems and in 70% ethanol-water mixture and 70% dioxane-water mixture (**Table -3 and 4**). The  $\log K_1$  and  $\log K_2$  values follow the order as



It could be seen that logK values follow increasing trend. This is due to the electron withdrawing group. The values of logK, ( $\log K_1 - \log K_2$ ), and ( $\log K_1 / \log K_2$ ) are in good agreement with expected values. It is observed that the similar difference may be due to " *trans structure*".



The results show that, the ratio  $\log K_1 / \log K_2$  is positive in all cases. This implies that there is little or no steric hindrance to the additions of secondary ligand molecule. The different values of pK and logK in various solvents are due to the solubility of restrictions. The pK values of all the ligands and logK values of Pr(III) and Nd (III) metal ions chelates with L<sub>1</sub> : 3 (2'-chlorophenyl) - 4- benzoyl - 5 (2-hydroxy phenyl) pyrazole, L<sub>2</sub>: 3 (2'-chlorophenyl) - 4- pyridoyl -5 (2-hydroxy phenyl) pyrazole , L<sub>3</sub>: 3 (2'-aminophenyl)- 4-pyridoyl - 5 (2- hydroxyl phenyl) pyrazole and L<sub>4</sub>: 3 (4'-chlorophenyl) - 4- Benzoyl - 5 (2-hydroxy-phenyl) pyrazole, at 0.1M ionic strength at  $28 \pm 0.1^\circ\text{C}$  is greater in 70% dioxane-water mixture than 70% ethanol-water mixture, this is due to the change in dielectric constants of water in the presence of organic solvent, change in structure and hydrogen bonding in water, relative solvent basicity and proton solvation by organic solvent.

### iii) Validity of $\log K = a \text{ pK} + b$

The linear relationship  $\log K = a \text{ pK} + b$  has been found<sup>21</sup>, to hold good for transition metal complex of series of closely related ligands. The stability of the metal complexes of substituted pyrazoles follows the order Pr (III) < Nd (III). The plot of  $\log K_1$  Vs pK and  $\log K_2$  Vs pK show satisfactory linear relationship giving slope values of 1.00 and 1.05 respectively. The partial molar free energies of metal ligand and proton ligand complexes exactly compensate with each other. When  $\log K$  Vs pK plot is linear with a slope of unity. Pr (III) and Nd (III) metal ions formed 1:1 and 1:2 complexes with all the ligands. (**Table-3**)



**Table-1 : Determination of proton ligand stability constants (pK) of ligands at**

**0.1M ionic strength in 70% Ethanol-water mixture .**

Ligand	pH of deviation	Proton ligand stability constants (pK)	
		Half integral method	Pointwise method
L <sub>1</sub>	3.55	8.40	8.45 ± 0.03
L <sub>2</sub>	2.90	10.50	10.20 ± 0.05
L <sub>3</sub>	3.40	10.54	10.68 ± 0.03
L <sub>4</sub>	2.95	7.00	7.18 ± 0.04

**Table-2: Determination of proton ligand stability constants (pK) of ligands at**

**0.1M ionic strength in 70% Dioxane-water mixture .**

Ligand	pH of deviation	Proton ligand stability constants (pK)	
		Half integral method	Point wise method
L <sub>1</sub>	3.50	8.90	8.95 ± 0.03
L <sub>2</sub>	2.80	10.85	10.80 ± 0.05
L <sub>3</sub>	3.45	10.97	10.95 ± 0.03
L <sub>4</sub>	2.88	8.32	8.44 ± 0.04





**Table-3 : Metal ligand stability constants of Pr (III) Nd (III) complexes with ligands  
at 0.1M ionic strength in 70% ethanol-water mixture**

System	M-L stability Constants		$\log K_1 - \log K_2$	$\log K_1 / \log K_2$
	$\log K_1$	$\log K_2$		
Pr(III)-L <sub>1</sub>	5.94	0.253	5.68	2.34
-L <sub>2</sub>	9.85	2.96	6.89	3.33
-L <sub>3</sub>	7.74	2.45	5.29	3.16
-L <sub>4</sub>	6.70	2.75	3.95	2.43
Nd(III)-L <sub>1</sub>	5.97	0.346	5.62	1.72
-L <sub>2</sub>	9.96	6.16	3.80	1.62
-L <sub>3</sub>	8.24	4.85	3.39	1.70
-L <sub>4</sub>	6.74	2.92	3.82	2.31

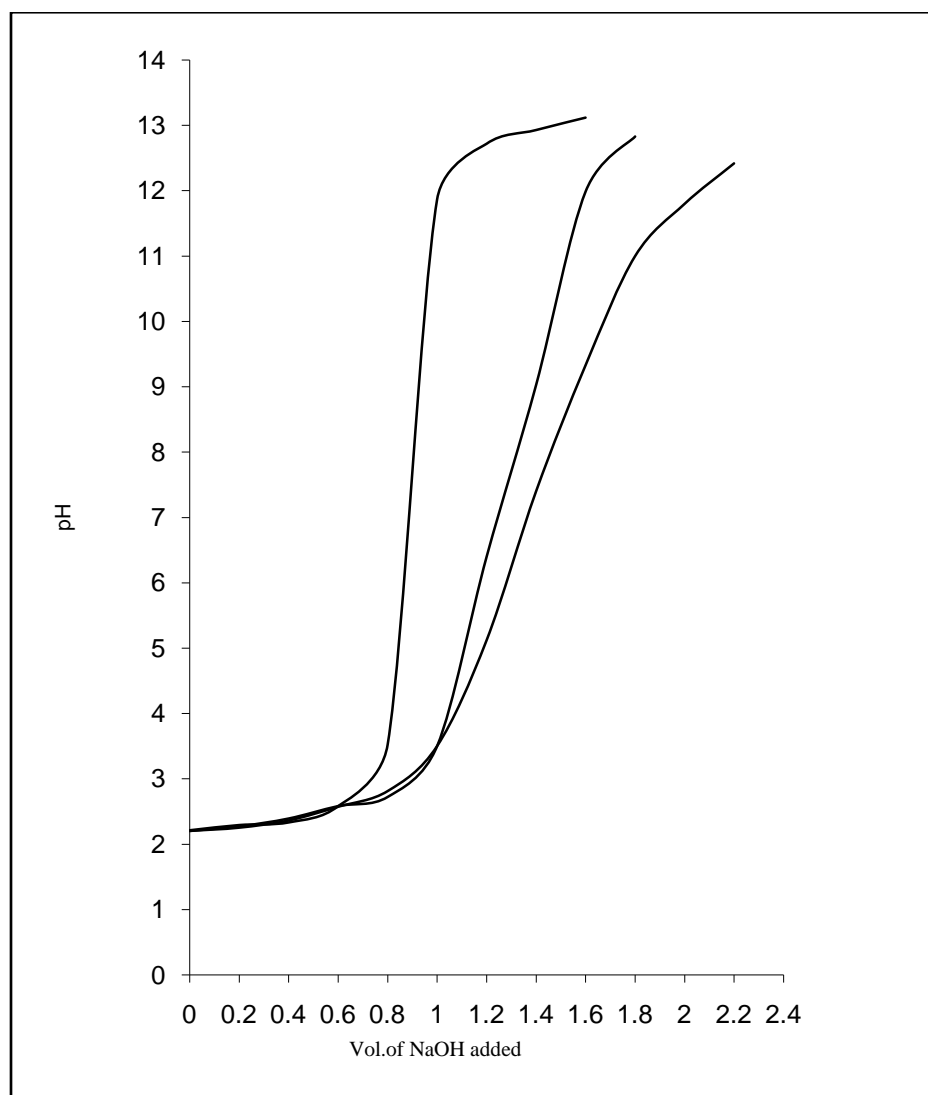


**Table-4 : Metal ligand stability constants of Pr (III) Nd(III) complexes with ligands  
at 0.1M ionic strength 70% Dioxane-water mixture**

System	M-L stability Constants		$\log K_1 - \log K_2$	$\log K_1 / \log K_2$
	$\log K_1$	$\log K_2$		
Pr(III)-L <sub>1</sub>	6.00	2.54	3.46	2.36
-L <sub>2</sub>	9.97	3.00	6.97	3.32
-L <sub>3</sub>	8.82	2.64	6.18	3.34
-L <sub>4</sub>	6.87	2.83	4.04	2.42
Nd(III)-L <sub>1</sub>	6.01	2.79	3.22	2.15
-L <sub>2</sub>	10.00	6.27	3.73	1.59
-L <sub>3</sub>	8.84	4.92	3.52	1.71
-L <sub>4</sub>	7.03	2.86	4.17	2.46

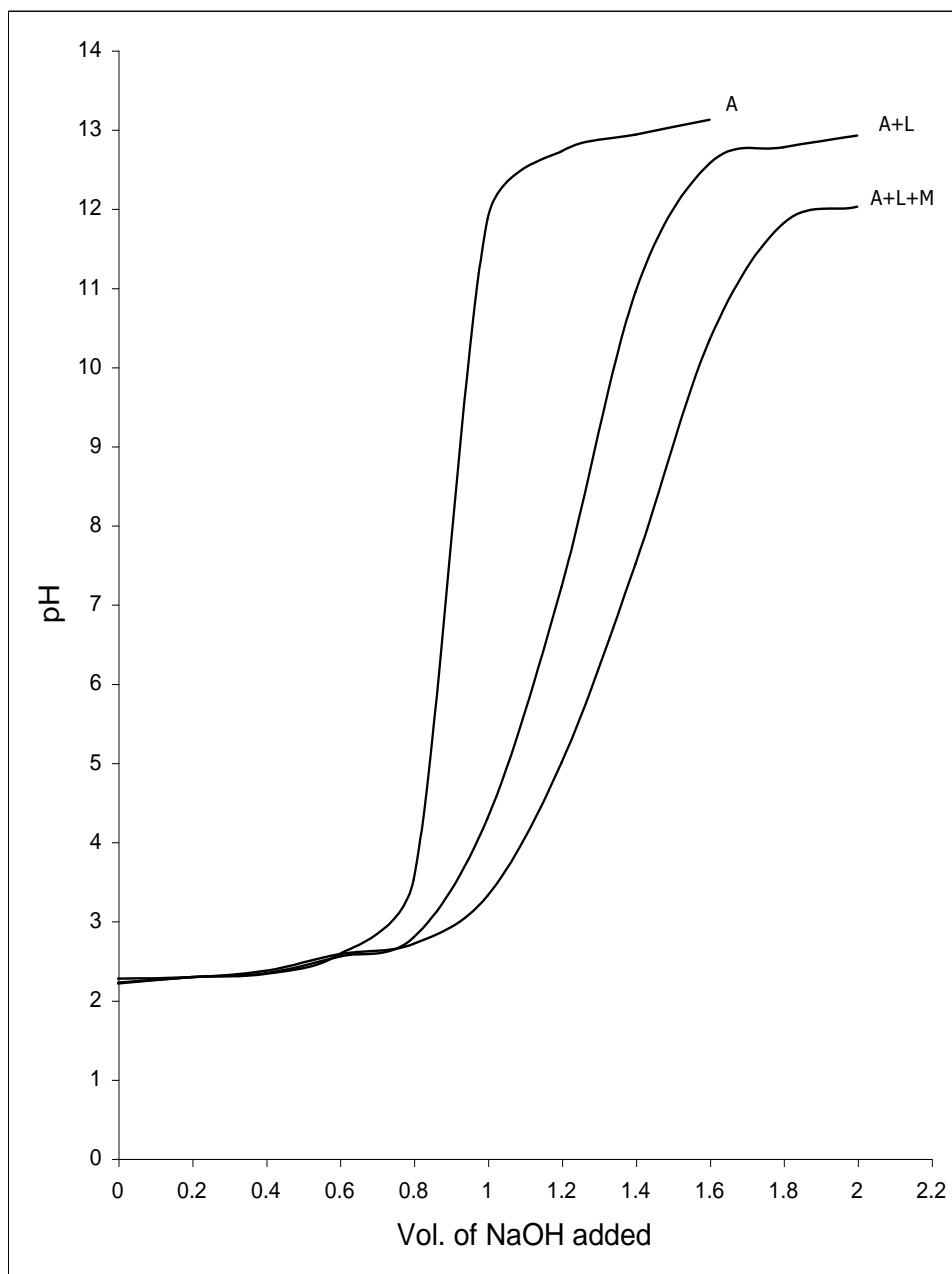


**Figure-1 : a) Formation of chelates between Pr (III) with substituted pyrazoles in 70% ethanol-water mixture**



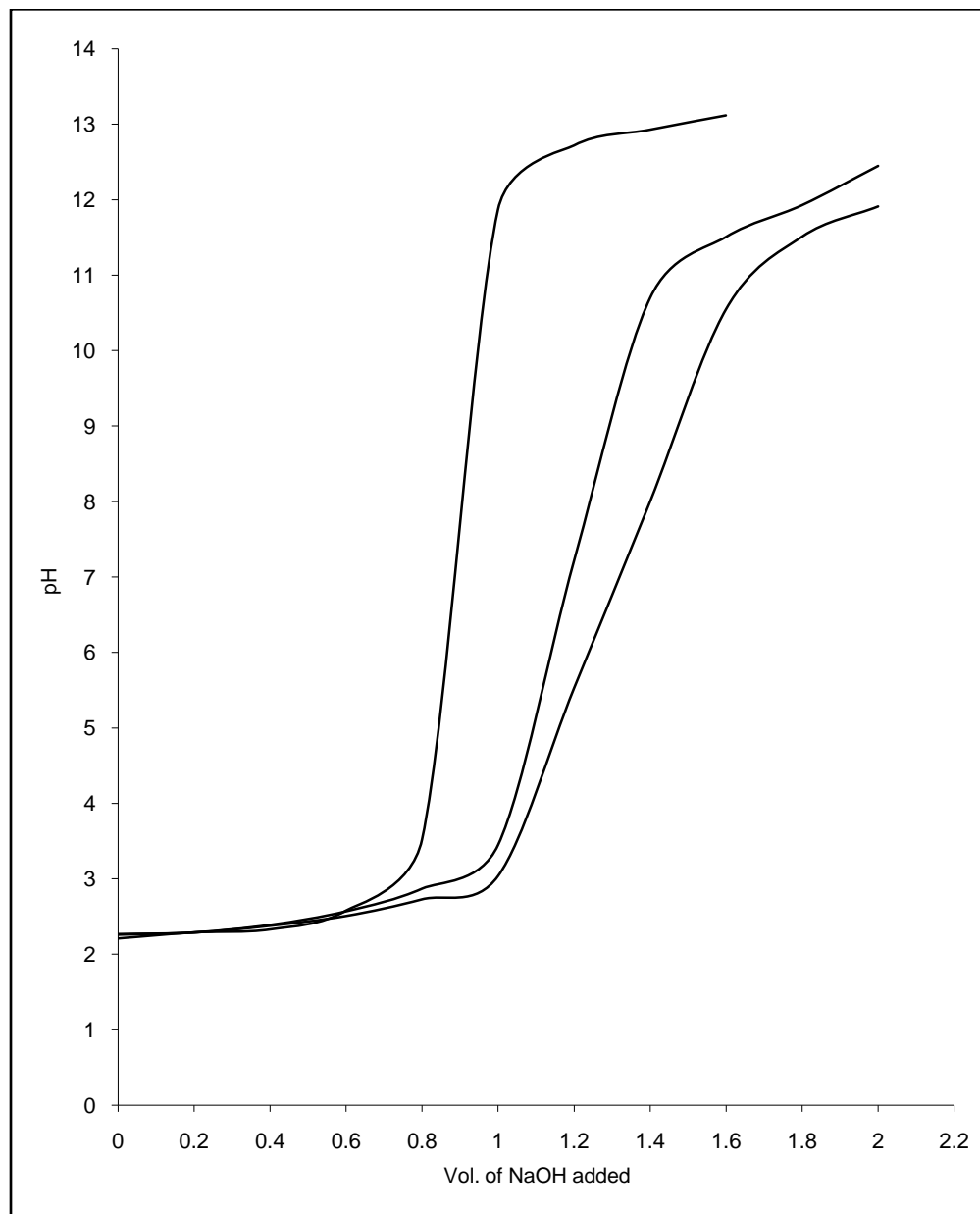


**b) : Formation of chelates between Nd (III) with substituted pyrazoles in 70% ethanol-water mixture**



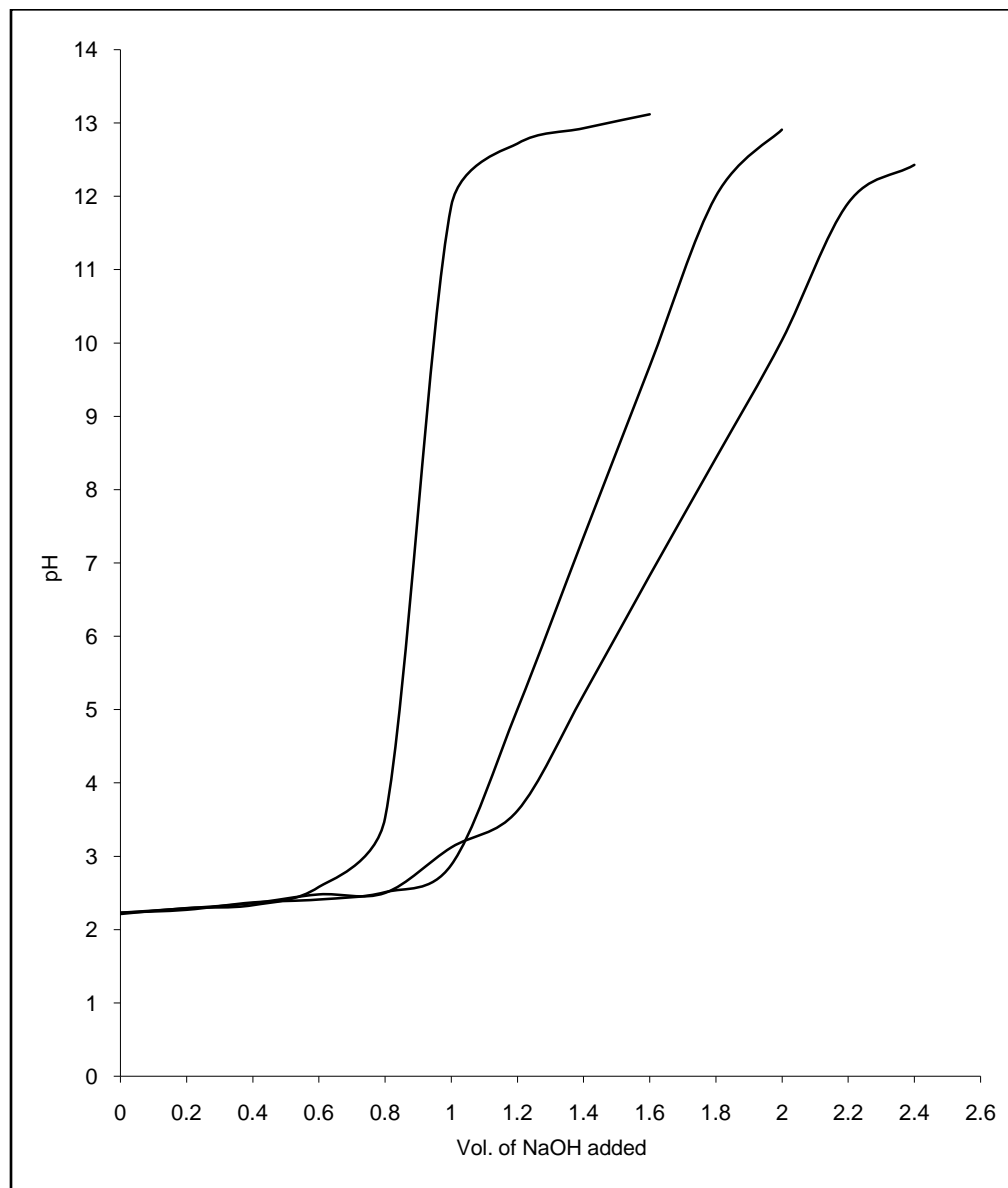


**Figure-2 : a) Formation of chelates between Pr (III) with substituted pyrazoles 70%  
Dioxane-water mixture**





**b) Formation of chelates between Nd (III) with substituted pyrazoles in 70%  
Dioxane-water mixture**





## REFERENCE

- 1) Jain S.C. Gill M.S. and Roo G.S., *Ind. J. Chem.* Lx III, 1986, 195.
- 2) Rossi R. and Ruvedda E., *ARKIVOC*; X, 2003, 209.
- 3) Lukic S.R., Leovac V.M. , *Mano metal org. Chem*; 31(05), 2002, 873.
- 4) Sawalakhe P.D. and Narwade M.L., *J Ind. Chem. Soc.*; 71, 1994, 49.
- 5) Agrawal P.B., Burghate A.S, and Narwade M.L, *Orent J. Chem.*; 17 (1), 2001.
- 6) Sawalakhe P.D. Narwade M.L. *XXXVIII Calogium spectroscopicum international laughs Borough*, (U.K), P.-29, 1993.
- 7) Komatsu Mitsuo and Oderaotoshi Yoji, *Congress of Hetro. Chem.*, 31, 2000, 13,
- 8) Mashram Y.K. Narwade M. L. , *Asian J. Chem.* 19(1), 2000, 493.
- 9) Singhal R. Tiwari V. and Limaye S.N., *J. Ind Chem. Soc* 81, 2004, 207.
- 10) Graham M. D., Harry A. and Michael D. W., *Acta cryst*, C- 61, 2005, 221.
- 11) Kishor Arora and Kiran Burman, *Orent J. Chem.* 22 (2), 2006.
- 12) Salah TS, ET- Rahaman NMA, *Ultrasonic Sonachem.*, 16(02), 2009.
- 13) Rebello C., Shashikala G. and Reddy M.G. ; *Ind. Acad.Sci.*, 95, 1985, 541-545.
- 14) Murhekar G. H. *M. Phil. Dissertation*, SGB Amravati University Amravati, 2008.
- 15) Vogel A.I. *A text book of quantitative inorganic analysis*, logmans Green, Landon, P - 589, 1975.
- 16) Vogel A.I., *Text book of practical organic chemistry*, P-177, 1956.
- 17) Van L.G., Vitert and Hass C., *J Am Chem. Soc.* 75, 1953, 451.



- 18) Irving H. M. and Rossotti H.S, *J Chem. Soc.*, 3397, 1953.
- 19) Bjerrum J, *Chem Rev*, 46, 1950, 381.
- 20) Calvin M and Melchior N C, *J. Am Chem Soc*, 70, 1948, 3270
- 21) Hones J.G. Tomkinson J.B., Poole and Williams J. P., *J. Chem. Soc.*, 3125, 1958.