



Formation Constants of Lanthanide Metal Ions Chelates With Some Substituted Pyrazoles in Different Solvent Composition

Gopalkrushna Haribhau Murhekar*, Arun R. Raut

*Department of Chemistry, Government Vidarbha Institute of Science and Humanities,
Amravati (M.S.), India*

Abstract

The proton-ligand and metal-ligand stability constants of Pr (III) and Nd (III) metal ions with L_1 : 3 (2'-chlorophenyl)-4-benzoyl-5(2-hydroxy phenyl) pyrazoles and L_2 :3 (2'-chlorophenyl)-4-pyridoyl-5(2-hydroxy phenyl) pyrazole have been studied pH-metrically at 0.1M ionic strength at $30 \pm 0.1^\circ\text{C}$ by varying the proportions of ethanol -water mixture. The data obtained were used to study the effect of solvent composition on pK and logK values in terms of solubility restrictions. It is observe that pK and logK values increases as the proportion ethanol in ethanol-water mixture increases.

Key words: Solvent Composition, pyrazoles, stability constants, chelates,

Introduction

Substituted "azoles" have played an important role in many biological systems and used as a antibiotic, anticancer drugs. Substituted pyrazoles play an important role in chelation and stability of complexes 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 [1-3]. The metal ligand stability constants of transition metal ions complexes with some substituted pyrazoles and pyrazolines have been reported [4]. The influence of ionic strength on the stability constants of transition and lanthanide metal ions complexes with substituted pyrazoles reported [5]. The interaction on metal ions with 1, 3 diketones, pyrazoles and pyrazoline spectrophotometrically have studied [6]. Stability constants of transition metal ion complexes with substituted pyrazoles was studied and observed that, ligand L_1 is better chelating agent than the ligand L_2 [7]. The interactions of some lanthanide metal ions with substituted isoxazolines at 0.1M ionic strength have been reported pH metrically [8-11]. Recently ultrasound promoted synthesis of substituted pyrazoles and isoxazoles have reported [12]. Effect of acetone-water solvent on the stability constants of Cu (II) and Ni (II) complexes of nicotinamide have been studied [13]. Influence of ionic strength and stability constants of substituted pyrazoles with lanthanides metals ions have recently studies in our laboratory [14-15].The study of proton-ligand stability constants and metal-ligand stability constants of Pr (III) and Nd (III)

complexes with substituted pyrazoles at different solvent composition that is 0%, 20%, 30%, 40%, 50%, 60%, and 70% ethanol- water mixture is still remaining. It was therefore thought interest to study the chelating properties of L₁: 3 (2'- chlorophenyl) - 4- benzoyl - 5 (2-hydroxy phenyl) pyrazole, L₂: 3 (2'-chlorophenyl) - 4- pyridoyl -5 (2-hydroxy phenyl) pyrazole at different composition of solvent and 0.1 M ionic strength pH metrically.

Materials and Methods

Experimental

Substituted pyrazoles were synthesized in the laboratory by standard method (16). 0%, 20%, 30%, 40%, 50%, 60%, and 70% ethanol-water (v/v) was used as solvent. Lanthanide metal nitrates were dissolved in double distilled water and their concentration estimated by standard method [17]. Sodium hydroxide, KNO₃, and nitric acid, used were of AR grade. Ethanol was purified by standard method [18]. pH measurements were carried out with ELICO pH meter (accuracy ± 0.05 units) using combined electrode at $30 \pm 0.1^{\circ}\text{C}$.

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 KNO₃ solution. The values were recorded by pH meter. These values converted to [H⁺] values by applying the correction proposed by Van Uitert & Hass [19].

The overall 0.1 ionic strength of solution was calculated by expression

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

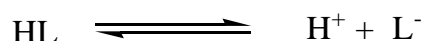
The contribution of the other ions in addition to K⁺ and NO₃⁻ also taken into consideration.

Results and Discussion

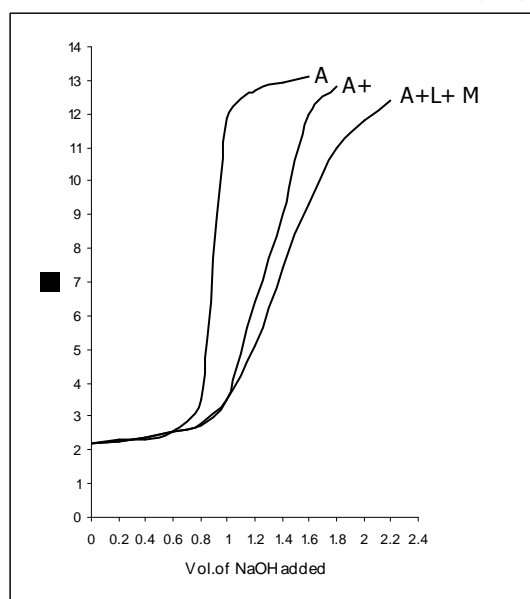
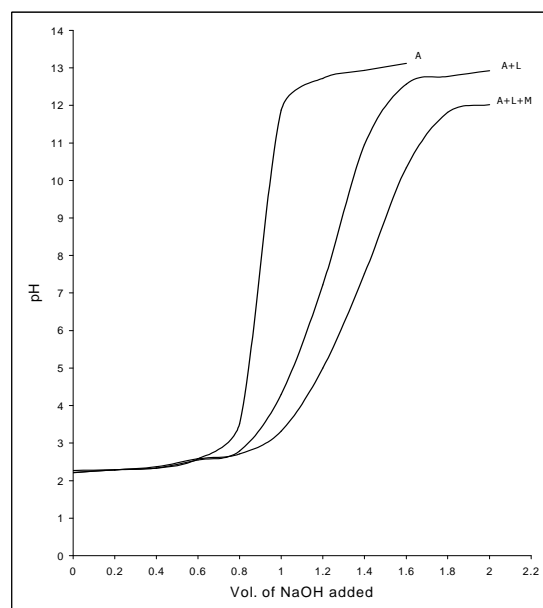
The titration data were used to construct the curve between volumes of NaOH vs pH. They are called as acid titration curve, ligand titration curve and metal titration curve. The pK values of ligand and logK values of Pr (III) and Nd(III) complexes at various compositions of solvent were calculated by Irving and Rossotti's method [20].

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 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 L₁, and at about pH 2.80 for L₂. The deviation increased continuously up to pH 12.50. It indicated that OH⁻ group start to dissociated at about 2.80 and complete its dissociation at about pH 12.50. As indicated by titration curve.

Figure- 1 :- Titration curve of L₁ - Pr (III) system**Figure-02 :- Titration curve of L₂ - Pr (III) system****Table 01 : Determination of proton- ligand stability constants (pK) of ligand L₁ at different solvent composition**

Ligand	Solvent Composition(v/v)	Mole Fraction	Proton ligand stability constants (pK)	
			Half integral method	Pointwise method
L ₁	0% ethanol- water	0.000	00.00	00.00± 0.03
	20 %	0.109	10.47	10.48 ± 0.05
	30 %	0.116	10.54	10.55 ± 0.03
	40 %	0.169	10.63	10.65 ± 0.04
	50 %	0.231	10.67	10.68 ± 0.03
	60 %	0.318	10.73	10.75 ± 0.03
	70 %	0.355	10.78	10.80 ± 0.02

Table 02: Determination of proton- ligand stability constants (pK) of ligand L₂ at different solvent composition

Ligand	Solvent Composition(v/v)	Mole Fraction	Proton ligand stability constants (pK)	
			Half integral method	Pointwise method
L ₂	0% ethanol-water	0.000	00.00	00.00± 0.03
	20	0.109	10.45	10.44 ± 0.05
	30	0.116	10.52	10.54 ± 0.03
	40	0.169	10.57	10.58 ± 0.04
	50	0.231	10.59	10.60 ± 0.03
	60	0.318	10.65	10.64 ± 0.03
	70	0.355	10.71	10.72 ± 0.02

It is observed from values represented in table 01 and 02, the pK values of both ligands are increases as the proportion of solvent increases; which is due to solubility restrictions and polarity of solvent. The reduction in pK values of ligand L₂ than L₁ may be due to presence of chlorophenyl and benzoyl, groups which act as stronger electron withdrawing groups. The

average number of proton associated with the ligand (\bar{n} A) was determined from ligand titration curves by employing the equation of Irving and Rossotti [20]. 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 method at different solvent composition, are presented in table -01 and 02. The pK values of ligands increases in the following order for all proportion of solvents. *Ligand 01 > Ligand02*

Table-03 : Metal-ligand stability constants of Pr (III) complexes with ligand L₁ at 0.1M ionic strength

System	Solvent composition(v/v)	Mole fraction	M-L stability Constants		logK ₁ -logK ₂	logK ₁ /logK ₂
			logK ₁	logK ₂		
Pr(III)-L ₁	0 % ethanol-water	0.000	0.00	0.00	0.00	0.00
	20%	0.109	7.50	6.07	1.43	1.24
	30%	0.116	8.52	6.92	1.60	1.23
	40%	0.169	8.65	6.96	1.69	1.24
	50%	0.231	8.79	7.12	1.67	1.23
	60%	0.318	8.98	7.24	1.74	1.24
	70%	0.355	9.18	7.88	1.30	1.66

ii) Metal – ligand stability constants (logK)

Metal ligand stability constants of Pr (III) and Nd (III) complexes with L₁: 3 (2'-chlorophenyl) - 4- benzoyl - 5 (2-hydroxy phenyl) pyrazole were determined by employing Calvin-Bjerrum pH-metric titration technique as adopted by Irving and Rossotti. The formation of chelates between Pr (III) and Nd (III) with substituted pyrazole was indicated by

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

The logK values were directly read from the formation curves (\bar{n} Vs PL) using half integral method.

Table-04 : Metal-ligand stability constants of Nd (III) complexes with ligand L₁ at 0.1M ionic strength

System	Solvent composition(v/v)	Mole fraction	M-L stability Constants		logK ₁ -logK ₂	logK ₁ /logK ₂
			logK ₁	logK ₂		
Nd(III)-L ₁	0 % ethanol-water	0.000	0.00	0.00	0.00	0.00
	20%	0.109	7.68	6.82	0.86	1.13
	30%	0.116	8.59	6.97	1.62	1.23
	40%	0.169	8.72	7.05	1.67	1.24
	50%	0.231	8.92	7.26	1.72	1.24
	60%	0.318	9.03	7.62	1.73	1.24
	70 %	0.355	9.27	7.97	1.85	1.25

Conclusion

Data cited in table-03 and 04, logK values are increases as the solvent composition increases. It is due to solubility restrictions and polarity of solvent. As the solvent proportion increases solubility of the ligand increases, greater is the solubility greater is the stability constants. Change in dielectric constant of water in presence of different composition solvent and different solvents. Change in structure and hydrogen bonding in water. Relative solvent basicity and proton solvation by the organic solvent also affect the stability constants. The most accurate logK values were calculated by pointwise calculation method are presented in table -03 and 04 for all the systems. The logK₁ and logK₂ values in 0%, 20%, 30%, 40%, 50%, 60%, and 70% ethanol-water follow the order as **Pr (III) < Nd (III)**.

The logK values follow increasing trend. This is may be due to the electron withdrawing group (Cl⁻, Br⁻ and I⁻). The values of logK, (logK₁ – logK₂), and (logK₁ / logK₂) are in good

agreement with expected values. It is observed that the similar difference may be due to trans effect. 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 linear relationship $\log K = a \text{pK} + b$ has been found [21], 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.

Acknowledgements

The authors are very thankful to the UGC for financial support and Director, Govt. Vidarbha Institute of Science and Humanities, Amravati for providing necessary research facilities.

Reference

- [1] Jain S.C., Gill M.S. and Roo G.S.,; *Ind. J. Chem.* **1986**, Lx III: 195.
- [2] Rossi R. and Ruvedda E, ; *ARKIVOC*, **2003**, X, 209-219.
- [3] Lukic S.R., Leovac V. M. ; *Mano metal org. Chem.* **2002**, 31(05), 873-884.
- [4] Sawalakhe P.D. and Narwade M.L.; *J. Ind. Chem. Soc.* **1994**, 71, 49-51.
- [5] Agrawal P.B., Burghate A.S, and Narwade M.L; *Orient J. Chem.* **2001**, 17(1).
- [6] Sawalakhe P.D. Narwade M.L.; *XXXVIII Calogium spectroscopicum international laugh Borough (U.K)*, **1993**, 29
- [7] Jamode V.S and Kale A.S., *Asian J. Chem.*; **2007**, 12 (1), 787-789.
- [8] Mashram Y.K. Narwade M.L.; *Asian J. Chem.*, **2000**, 19(1) 493.
- [9] Singhal R. Tiwari V. and Limaye S. N.; *J. Ind Chem. Soc.* **2004**, 81,207.
- [10] Graham M. D., Harry A. and Michael D. W.; *Acta cryst.*, **2005**, 61, 221 -223.
- [11] Kishor Arora and Kiran Burman; *Orent J. Chem.* **2006**, 22(2).
- [12] Salah TS, ET- Rahaman NMA ; *Ultrasonic Sonachem*, **2009**, 16(02).
- [13] Isaeva V.A., Gesse Z.F. and Sharnin; *Russion J. Coord. Chem.*, **2006**, 32(5), 325-328.
- [14] Murhekar G.H. Raut A.R. and banewar V.W.; *Oriental J. Chem.* **2009**, 25(4), 1093-1096.
- [15] Murhekar G.H., Raut A. R., Narwade N.L.; *Vidarbha J. Sci.*; **2009**, 4 (3-4), 69-74.
- [16] Murhekar G. H. *M. Phil. Dissertation*, S.G.B. University (Amravati, India, **2008**).
- [17] Vogel A.I. *A text book of quantitative inorganic analysis*, Landon, **1975**, 589.
- [18] Vogel A.I., *Text book of practical organic chemistry*, **1956**, P-177.
- [19] Van L.G., Vitert and Hass C.; *J. Am. Chem. Soc.* **1953**, 75, 451.
- [20] Irving H. M. and Rossotti H.S.; *J. Chem. Soc.*, **1953**, 3397.
- [21] Hones J.G. Tomkinson J.B., Poole and Williams J.P.; *J. Chem. Soc.*, **1958**, 3125.