

# Study the Effect of Ionic Strengths on Complex Equilibrium between Actinide Metal Ions with Substituted Pyrazole in Organic Solvent

## Abstract

The proton ligand stability constants of 3(2 -Chloro phenyl)-4 benzoyl - 5(2- hydroxyl phehyl) pyrazole (L) and metal ligand stability constants of Pr (III) &Nd (III) complexes have been investigated at 0.03, 0.06, 0.08, 0.09 and 0.1 M ionic strength, pH metrically from the values of pK and logK the values of thermodynamic constants at zero ionic strength can be calculated. The value of pK and logK are found to be decreased with increasing ionic strengths.

**Keywords:** Stability Constants, Ionic Strength, Actinide Metal Ions, Pyrazoles.

## Introduction

Substituted pyrazoles have played an important role in many biological systems and used as a antibiotic, anticancer, drugs<sup>1-5</sup>, Substituted pyrazoles play an important role in chelation and stability of complexes, Pyrazoles differ strongly from pyrazoline in its remarkable stability and more basic character. The important physical property of pyrazoles in the existence of tautomerism. Stability constants of transition metal ions complex with substituted pyrazoles was studied<sup>6-7</sup>. The influence of ionic strength on stability constant of Co (II), Sr (III), and Pr (III) complexes with substituted pyrazoles was reported<sup>8</sup>. The complexes of Pr (III) with substituted pyrazoles were studied by Davies et al<sup>9</sup>. Determination of stability constants of transition metal ions with substituted pyrazoles and oxazoles reported pH-metrically<sup>10</sup>. Stability constants for the lanthanide metal complexes in aqueous Solution at 25<sup>o</sup>C and 0.5 M ionic strength has also reported<sup>11</sup>. Gupta et al<sup>12</sup> have determined the stability constants of transition metal ion complexes with disalicylamide at different ionic strength. Palaskar<sup>13</sup> have studied the effect of ionic strength and dielectric constant of Cu(II) 3-nitrophthalic acid, potentiometrically at different ionic strengths in aqueous medium. Ultrasonic promoted synthesis of substituted pyrazoles & studies on proton ligand stability constants of some substituted pyrazoles has reported recently<sup>14-15</sup>. Hence an attempt has been made to study the determination of proton-ligand stability constants and metal - ligand stability constants of Pr(III) &Nd(III) complexes with 3(2'-chloro phenyl)-4-benzoyl-5(2- hydroxyl phenyl) pyrazoles (L) at various ionic strength (i.e. 0.02, 0.04, 0.06, 0.08, 0.1M) at 28±0.01<sup>o</sup>C in 70% ethanol - water mixture pH metrically.

## Aim of study

from the survey of literature reveals that the study of effect of ionic strength on complex equilibrium between actinide metal ions with substituted Pyrazol in organic solvent have not been systematically investigated while they have many uses in academic field, technological and industries.

## Experimental

The work has been studied by Calvin - Bjerrum pH-metric titration technique. All pH measurements were carried out with ELICO - Li 10 pH meter (accuracy ± 0.05 units) using combined electrode assembly at 28± 0.1<sup>o</sup>C, Pr (III) and Nd (III) was used in the form of its nitrate and concentration was estimated by EDTA<sup>16</sup>. Ethanol, sodium hydroxide, and Potassium nitrate, were used are of A.R. Grade, The substituted pyrazoles is prepared by standard method<sup>17</sup>. It is insoluble in water and hence 70% ethanol water (v/v) was used as a solvent.

## Calvin-Bjerrum Titration Technique

The titrations were carried out in an inert atmosphere of nitrogen. The ionic strength of solution was maintained 0.02, 0.04, 0.06, 0.08, and 0.1M by adding an appropriate amount of 1M KNO<sub>3</sub> solution. The values were recorded by pH meter. These values converted to [H<sup>+</sup>] Values by applying the correction proposed by Van Uilert and Hass<sup>18</sup>.



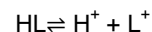
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**Results & Discussion**

Substituted pyrazoles may be considered as a monobasic acid having one replaceable H<sup>+</sup> ion from

phenolic. OH group and can therefore be represented as

**Table 1, pK and log K Values at various ionic strength for Pr(III) – L system.**

Ionic Strength ( $\mu$ )	$\sqrt{\mu}$	$\sqrt{\mu} / \sqrt{1 + \mu}$	$\sqrt{\mu-0.3} / \sqrt{1 + \mu}$	$\sqrt{\mu}$ pk	Log K <sub>1</sub>	Log K <sub>2</sub>
0.02	0.1412	0.1235	0.1451	10.41	8.60	2.85
0.04	0.2000	0.1665	0.1352	9.23	7.61	1.80
0.08	0.2445	0.1969	0.1232	8.95	6.95	1.02
0.08	0.2822	0.2202	0.1064	8.69	6.40	0.80
0.10	0.3160	0.2400	0.0811	8.35	5.90	0.23

**Table 2.pK and log K values at various ionic strength for Nd (III) – L system.**

IonicStrength ( $\mu$ )	$\sqrt{\mu}$	$\sqrt{\mu} / \sqrt{1 + \mu}$	$\sqrt{\mu-0.3} / \sqrt{1 + \mu}$	$\sqrt{\mu}$ pk	Log K <sub>1</sub>	Log K <sub>2</sub>
0.02	0.1412	0.1235	0.1451	10.41	8.65	2.92
0.04	0.2000	0.1665	0.1352	9.23	7.66	1.86
0.08	0.2445	0.1969	0.1232	8.95	7.00	1.08
0.08	0.2822	0.2202	0.1064	8.69	6.45	0.86
0.10	0.3160	0.2400	0.0811	8.35	5.94	0.27

**Table 3. Slopes and  $\Delta Z^2$  values from the plots of pK and logK Vs  $\sqrt{\mu}$** 

System	pKvs $\sqrt{\mu}$		logK <sub>1</sub> vs $\sqrt{\mu}$		logK <sub>2</sub> vs $\sqrt{\mu}$	
	Slope	$z^2$	Slope	$z^2$	Slope	$z^2$
L	0.52	0.25	-	-	-	-
L-Pr(III)	-	-	0.342	0.175	0.260	0.134
L-Nd (III)	-	-	0.146	0.0610	0.118	0.060

$$\log K = \log K^0 + A \Delta Z^2 - \sqrt{\mu}$$

.....(1) and

$$pK = pK^0 - A \Delta Z^2 - \sqrt{\mu}$$

.....(2)

Where, A – Debye-Huckel constant,  $\Delta Z^2$ - Difference in the square of the charges of product and reactant ions,  $K^0$ - is the formation constant at zero ionic strength  $\mu$  - ionic strength.

The values of pK<sub>1</sub>, logK<sub>1</sub>, and logK<sub>2</sub> were plotted against the values of  $\sqrt{\mu}$  the plot of logKvs $\sqrt{\mu}$  and pK, vs $\sqrt{\mu}$  gave straight lines.

The magnitude of  $\Delta Z^2$  and slope were calculated from graphs. The data obtained of pK and logK values could be utilized to know the mechanism of complex equilibria. The expected and observed values for  $\Delta Z^2$  values for the corresponding dissociation and association equilibria are given below.

It is observed from that the slope values of pK and are more than expected values, while the logK values are less than expected values. Those values do not give conclusive evidence regarding the magnitude of the charges of reacting species. The discrepancy may be due to the limited applicability of Bronsted equation.

The plots of pK, logK Vs  $\sqrt{\mu} / \sqrt{1 + \mu}$  and  $(\sqrt{\mu} - 0.3\sqrt{\mu}) / (1 + \sqrt{\mu})$  are also plotted and slopes values were determined. It shows that modified Debye - Huckel equation also not show much more improvement in the slope values. The discrepancy been observed and expected slope value was thought to be due to the concentration and did not activity terms used in the equation of stability constants.

**Thermodynamic Stability Constants**

The thermodynamic stability constants observed from various plots at zero ionic strength are presented.

It can be seen that there is good a agreement among thermodynamic constants obtained from various plots.

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**Endnotes**

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