

# Studies Thermodynamical Stability of Complexes of Rare Earth Metal Ions with Substituted Pyrazole

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**Abstract** The stability constants of 1-phenyl-3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole (PHMPMPz) and their complexes with Pr (III) and Sm (III) metal ions have been determined in 70% v/v dioxane-water media at different ionic strength (0.02, 0.04, 0.06, 0.08, 0.1) mol.dm<sup>-3</sup> at 300.15K by pH metry method. The pK and logK values decrease with increase in ionic strength of medium, which indicated the opposite charges on reacting species. The values of stability constants for Sm (III) were greater than Pr (III) metal ion. The thermodynamic stability constants at zero ionic strength have also been determined.

**Keywords** Pyrazole, ionic strength, stability constant, pH

## 1. Introduction

Dissociation of organic acids and their interaction with metal ions (complex formation) may be extremely sensitive to ionic strength of the medium [1]. If charges on the reacting species are opposite then there is a decrease in the reaction rate with increasing ionic strength (IS) whereas if the charges are identical, an increase in the reaction rate will occur while one of the reactant charge is less the reaction rate does affect by ionic strength of the medium [2]. Ionic strength measures the intensity of an electric field of solution due to the presence of ions in a solution. Ionic strength of medium affects the rate at which ions react with each other and to extent the reaction occurs [3]. High ionic strength reactions are found all around us, from industrial reactions that are carried out at high concentrations to ensure increased productivity to biochemical processes that occur at low or high pH. Indeed, practically every solution based reaction of importance deviates from ideality to some extent. The ionic strength data also used to study the correct mechanism of the complexation reaction [4]. The thermodynamic properties of electrolyte solutions can be studied from long range interactions between ion and solvent molecules. Number of workers [5, 6] reported the influence of ionic strength on the

organic compounds with metal ions.

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 [7]. The pyrazole moiety is present in a large number of biologically active compounds which find wide applications in pharmaceuticals [8] and agro- chemical industries [9]. Numerous compounds containing pyrazole moiety have shown exhibit analgesic, anti-inflammatory, antihelmintic, anti- bacterial, hypoglycemic, antiluekemic and anti- fungal activity [10-13]. The rare earth elements play a significant role in the development of our scientific, everyday life and industrial life [14]. More explicitly, in the previous decades their use in various organic technical processes led to a rapid growth especially in the field of complexes. In recent years the luminescence properties of rare metal complexes with different  $\beta$ -diketones have been widely studied due to their use in fabrication of polymer light emitting diodes to enable low cost, full color, flat panel displays. The pyrazoles and its derivatives have long been known for their strong complex forming ability. The studies on complex formation by tripositive rare earth ions with biologically important ligands are in progress because of their role in biological processes.

To the best of our knowledge, we explicitly study the effect of ionic strength on complex equilibria and ascertain the thermodynamic association and dissociation stability constants of the metal-ligand complex with rare earth metal ions. The interaction between rare earth metal cations viz. Sm (III), Pr (III) and PHMPMPz anion showed a complexation reaction.

## 2. Materials and Methods

The stock solution of PHMPMPz ( $4.0 \times 10^{-2}$  mol.dm<sup>-3</sup>) was prepared by dissolving the requisite amount of ligand in the minimum volume of dioxane subsequently diluted to the final volume. Nitrates of rare earth metal ions (Sigma-Aldrich) were used to prepared metal solutions ( $1.0 \times 10^{-2}$  mol.dm<sup>-3</sup>) and were standard- ized by the EDTA

titration method [15]. The stock solution of perchloric acid was prepared and used after standardization [16]. The ionic strength (0.02, 0.04, 0.06, 0.08 and 0.1) mol. dm<sup>-3</sup> was maintained constant by using sodium perchlorate solutions. The carbonate free sodium hydroxide solution (0.1071 mol. dm<sup>-3</sup>) was prepared by Vogel's method [17].

The pH of solution was measured with EQUIP-TRONICS (Model EQ-614) equipped with combined electrode and magnetic stirrer pH meter model (accuracy  $\pm$  0.005 units) with a combined glass electrode assembly. The instrument could read pH in the range 0.00 to 14.00 in steps of 0.005. This pH meter has a built an internal electronic voltage supply with temperature compensator covering the range 0 to 100 °C. The Instrument was calibrated before each titration with an aqueous standard buffer solution of pH, 4.20 (phthalate buffer), 7.00 and 9.10 (borate buffer) prepared from a 'Qualigens' buffer tablets.

The pH metric titration of acid, ligands and metal complexes against standard carbonate free sodium hydroxide (0.1071 mol. dm<sup>-3</sup>) using Calvin-Bjerrum [18] and Calvin-Wilson pH titration techniques already reported [19]. The proton-ligand constants were calculated by using the Irving-Rossotti method [20, 21]

The proton-ligand stability constants for the system were determined at various ionic strengths are shown in table 1. It may be inferred from experimental data that the pK values decreases with rise in ionic strength of the medium which in accordance with Debye-Hukel theory [22]. It indicates that, there is increase in hydrogen ion concentration upon increase in ionic strength of medium. Table 1. Proton-ligand stability constants of PHMPMPz at various Ionic strengths.

The pK and log K are employed to calculate the thermodynamic constant at zero ionic strength by using Bronsted equation;

$$pK = pK^0 - A\Delta Z^2\sqrt{\mu} \quad (1)$$

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

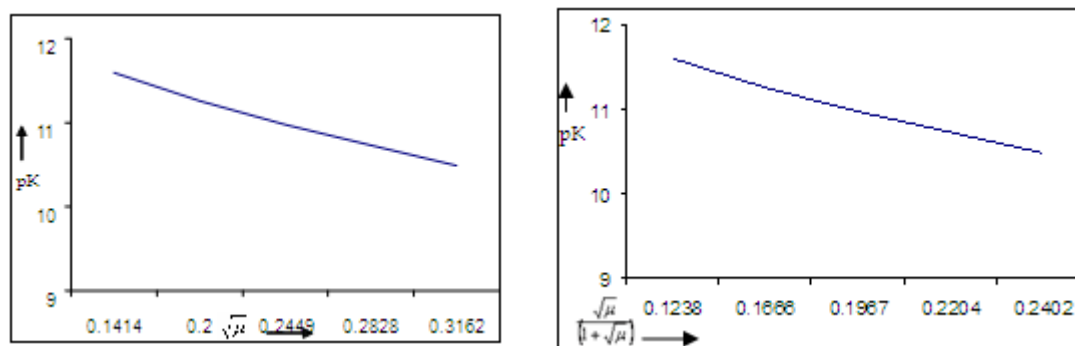
Where  $\Delta Z^2$  = difference in the square of the charges of product and reactant ion. The value of A was taken equal to 0.5161[23].

Thermodynamic proton-ligand stability constants, pK<sup>0</sup> (shown in table 2) were determined at zero ionic strength from the plot of pK versus  $\sqrt{\mu}$  and  $\sqrt{\mu}/(1+\sqrt{\mu})$  by extrapolating the curves to zero ionic strength in fig. 1.

### 3. Result and Discussion

**Table 1.** Proton-ligand stability constants of PHMPMPz at various Ionic strengths

IS	$\sqrt{\mu}$	$\sqrt{\mu}/(1+\sqrt{\mu})$	$\sqrt{\mu}/(1+\sqrt{\mu})-0.3\sqrt{\mu}$	pK
0.02	0.1414	0.1238	0.0813	11.60
0.04	0.2000	0.1666	0.1066	11.26
0.06	0.2449	0.1967	0.1232	10.97
0.08	0.2828	0.2204	0.1355	10.73
0.10	0.3162	0.2402	0.1453	10.48



**Figure 1.** Thermodynamic proton-ligand stability constant pK Vs  $\sqrt{\mu}$  and  $\sqrt{\mu}/(1+\sqrt{\mu})$

**Table 2.** Thermodynamic Dissociation Constants (pK<sup>0</sup>) at Zero Ionic strength

Plots	pK <sup>0</sup> for PHMPMPz
pK Vs $\sqrt{\mu}$	11.66
pK Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	11.80
pK Vs $\sqrt{\mu}/(1+\sqrt{\mu})-0.3\sqrt{\mu}$	11.98

**Table 3.** Thermodynamic Association constants ( $\log K^0$ ) from various plots

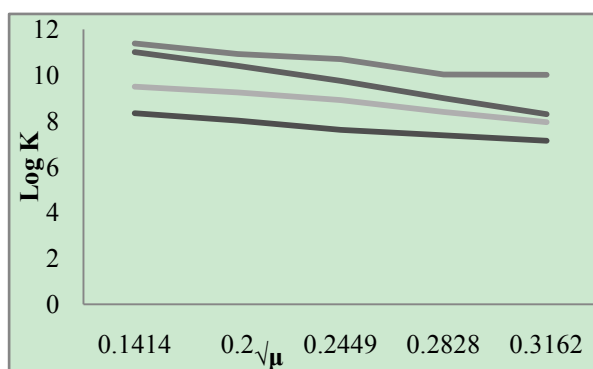
Plots	$\log K^0$	
	Pr (III)-PHMPMPz	Sm (III)-PHMPMPz
$\log K_1 \text{ Vs } \sqrt{\mu}$	12.60	11.20
$\log K_1 \text{ Vs } \sqrt{\mu}/(1+\sqrt{\mu})$	11.95	11.00
$\log K_1 \text{ Vs } \sqrt{\mu}/(1+\sqrt{\mu})-0.3\sqrt{\mu}$	11.60	10.75
$\log K_2 \text{ Vs } \sqrt{\mu}$	10.40	8.40
$\log K_2 \text{ Vs } \sqrt{\mu}/(1+\sqrt{\mu})$	9.35	7.60
$\log K_2 \text{ Vs } \sqrt{\mu}/(1+\sqrt{\mu})-0.3\sqrt{\mu}$	8.00	7.30

**Table 4.** System of  $\text{pK Vs } \sqrt{\mu}$  and  $\text{pK Vs } \sqrt{\mu}/(1+\sqrt{\mu})$ 

System	System	$\text{pK Vs } \sqrt{\mu}$		$\text{pK Vs } \sqrt{\mu}/(1+\sqrt{\mu})$	
		Slope	$\Delta Z^2$	Slope	$\Delta Z^2$
Pr(III)-PHMPMPz	$\log K_1$	17.81	34.50	26.69	51.72
	$\log K_2$	31.33	61.71	48.01	93.04
Sm (III)-PHMPMPz	$\log K_1$	10.55	20.44	15.62	30.27
	$\log K_2$	11.39	22.07	40.40	78.29

**Table 5.** Probable Reaction Mechanism and  $\Delta Z^2$  Values

System	Constant	Reaction Equilibria	Observed $\Delta Z^2$	
			Expected	Observed
PHMPMPz	pK	$HL^- \leftrightarrow H^+ + L^-$	2.0	-14.18
Pr(III)-PHMPMPz	$\log K_1$	$\text{Pr}^{3+} + L^- \leftrightarrow (\text{Pr}L)^{2+}$	-6.0	-32.29
Pr(III)-PHMPMPz	$\log K_2$	$(\text{Pr}L)^{2+} + L^- \leftrightarrow (\text{Pr}L_2)^+$	-4.0	-45.21
Sm(III)-PHMPMPz	$\log K_1$	$\text{Sm}^{3+} + L^- \leftrightarrow (\text{Sm}L)^{2+}$	-6.0	-35.98
Sm(III)-PHMPMPz	$\log K_2$	$(\text{Sm}L)^{2+} + L^- \leftrightarrow (\text{Sm}L_2)^+$	-4.0	-1.72


**Figure 2.**  $\log K$  versus  $\sqrt{\mu}$ 

The plot of  $\log K$  versus  $\sqrt{\mu}$  gave straight line over the entire range of ionic strengths for metal complexes are shown in fig. 2. The  $\log K$  values decreases with increase ionic strength of the medium [24, 25] which is concordance

with Debye-Hukel limiting law. It means that Bronsted relationship is valid for the dissociation of ligand and complex equilibria of chelates. The difference in the  $\log K_1$  and  $\log K_2$  is small which is due to the simultaneous formation of complexes. The thermodynamic metal-ligand stability constants are reported in Table 3. Literature survey reveals that  $\log K$  versus  $\sqrt{\mu}$  plots are generally linear up to 0.1 M ionic strength.

The values  $\Delta Z^2$  were calculated from the slopes of the straight lines. The different possible reactions observed and expected values of  $\Delta Z^2$  for corresponding dissociation or association equilibria are represented in table 4. The observed  $\Delta Z^2$  values, in all these cases are different than expected. These values do not interfere, give conclusion evidence regarding to the magnitude of charge of reacting species except the information that these are oppositely charged.

## 4. Conclusions

The stability constants of complexes were determined pH metrically in 70% dioxane-water media at 300.15 K with varying the ionic strengths (0.02, 0.04, 0.06, 0.08 and 0.1) mol.dm<sup>-3</sup> NaClO<sub>4</sub>. The Calculated values of stability constant at various ionic strengths are high. The complexes of PHMPMPz with Pr(III) and Sm(III) is quite stable at entire range of ionic strength. The values of thermodynamic parameters are nearly same from all plots was good agreement of results.

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