

## pH-metric study on determination of proton- ligand stability constants of some substituted pyrazolines

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### ABSTRACT

Proton - ligand stability constant ( $pK$ ) of 1-H-3 - (2'' - hydroxy-3'' -nitro -5'' -methylphenyl) -5-phenyl -  $\Delta^2$  - pyrazolines ( $L_1$ ), 1-H-3 (2'' - hydroxy - 3'' -nitro -5'' - methylphenyl) -5 - (4' - methoxyphenyl) -  $\Delta^2$  - pyrazonine ( $L_2$ ), 1-H-3 - (2'' - hydroxy-3'' -nitro -5'' -methylphenyl) -5 - (3' nitrophenyl)  $\Delta^2$  - pyrazonine and 1-H-3- (2'' - Hydroxy - 3'' - nitro - 5'' - methylphenyl -5 - (3',4' - methylenedioxyphenyl) -  $\Delta^2$  - pyrazonine ( $L_4$ ) have been investigated pH- metrically in 70% dioxane - water mixture as a solvent by Calvin- Bjerrum titration technique at 0.1 M ionic strength and at ( $27 \pm 0.1^\circ C$ ) temperature. The Proton - ligand stability constants for above ligands are found to be more than  $pH = 8.0$ . This showed dissociation of phenolic - OH group. The data obtained were used to determine the standard deviation ( $\sigma$ ) by using different values of  $\bar{n}$  A of same ligand except the difference in concentration of alkali NaOH.

**Key words:** Synthesis, pyrazolines, pH-metric study.

### INTRODUCTION

Pyrazolines are good chelating agents due to the presence of nitrogen as the electron donor atom. Narwade *et. al.*,<sup>1</sup> studied the formation constants and stability constants of Th (IV) complexes with some substituted Pyrazolines. Pawar *et.al*<sup>2</sup> have studied proton- ligand and metal - ligand stability constants of transition metal ions with some substituted pyrazolines pH- metrically. Natrajan *et.al*<sup>3</sup> have synthesised and characterised complexes of some substituted pyrazolines with Cu(II) and Co (II). Narwade *et. al.*,<sup>4</sup> studied the formation constants and stability constants of thorium (IV) complexes with some substituted pyrazolines. The study of stability constants of Th (IV) complexes with some substituted pyrazolines was reported by Gudadhe *et. al.*,<sup>5</sup>. Khadikar *et. al.*,<sup>6</sup> have reported the metal chelates of Be (II), Mn (II),

Co (II), Ni (II), Cu (II), Zn (II) & Cd (II) metal ions with 3- (2- hydroxyphenyl) - 5 - phenyl isoxazolines. Metal chelates of some substituted isoxazolines have been reported by Meshram *et. al.*, Acostical study of some substituted azoles in N, N-dimethylformamide at different temperature have been done by Gulwade *et. al.*,<sup>8</sup>. Metal ligand stability of lanthanides with some substituted pyrazolines and diketones has been studied<sup>9</sup>. Some pyrazolines are found to be bactericidal<sup>10</sup> of fungicidal<sup>11</sup> agents.

In view of analytical applications and for the sake of curiosity, it is worthwhile to know the dissociation of phenolic - OH group and effect of substitutes on proton- ligand stability constants. Therefore the present work is undertaken to make a systematic study for determining proton- ligand stability constants pH- metrically at 0.1M ionic strength in 70% dioxane water mixture.

### EXPERIMENTAL

In the present investigation, chemicals such as sodium hydroxide, perchloric acid, sodium perchlorate used were of AR grade. Ligands  $L_1$ ,  $L_2$ ,  $L_3$  &  $L_4$  were prepared according to literature method. All ligands were crystallized and their purity were checked by TLC before use. The solution of ligands were prepared in pure dioxane and 70% dioxane water as a solvent. The other solutions were prepared in double distilled water. pH-measurements are carried out by Equip - Tronics

pH- meter with model EQ 614 ( accuracy + 0.05 unit) using combined glass and calomel electrode at  $27^\circ\text{C} \pm 0.1^\circ\text{C}$ . The practical values ( B.Values) are converted into real values of pH of solution by applying the correction proposed by Van - Uitert and Hass<sup>12</sup>.

### RESULTS AND DISCUSSION

#### Proton - Ligand Stability Constants ( pK)

Substituted ligands  $L_1$ ,  $L_2$ ,  $L_3$  &  $L_4$  may be considered as a mono basic acids having only one

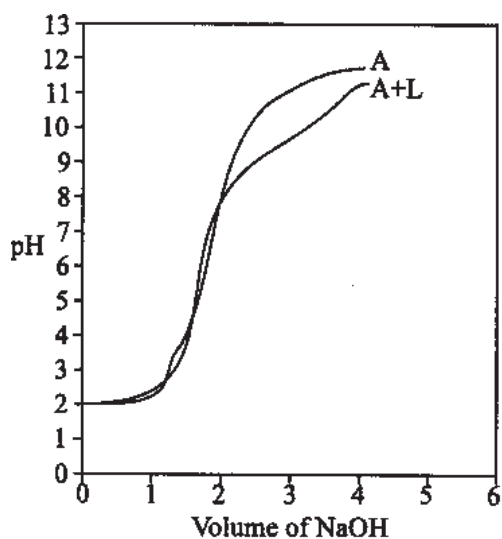


Fig. 1: Ligand  $L_4$  : Volume of NaOH vs pH

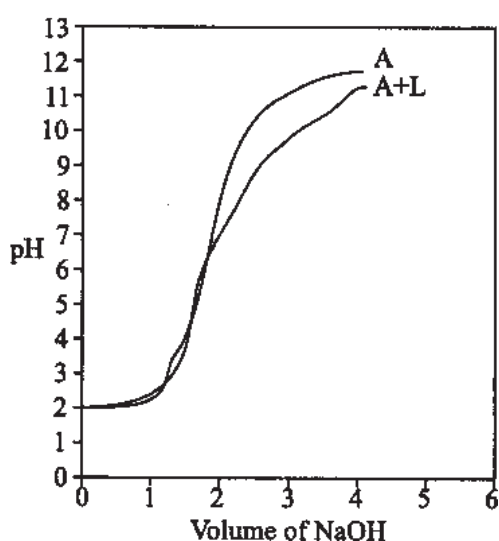


Fig. 2: Ligand  $L_2$  : Volume of NaOH vs pH

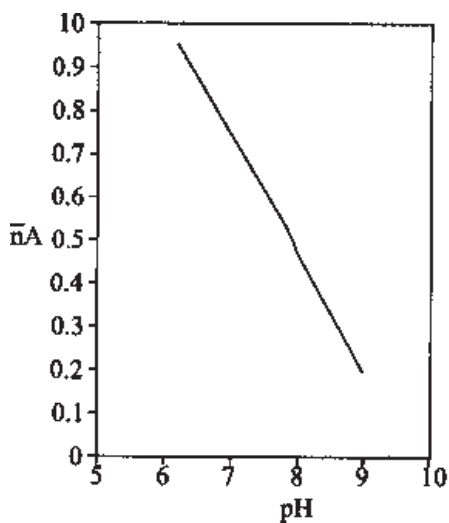


Fig. 3: Plot between  $nA$  vs pH Ligand  $L_4$

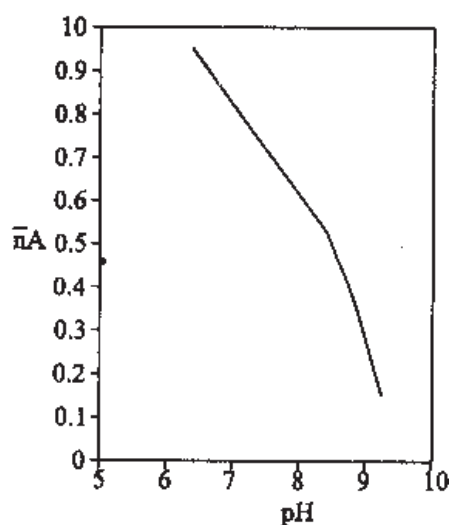


Fig. 4: Plot between  $nA$  vs pH Ligand  $L_1$

replaceable H<sup>+</sup> ion: From OH<sup>-</sup> group and that OH<sup>-</sup> group generally dissociates completely above pH 9.0 and can therefore be represented as HL i.e. HL = H<sup>+</sup> + L<sup>-</sup>. Two types of titrations are carried out using calvin - Bjerrum process.

#### Free acid titration

5 ml HClO<sub>4</sub> ( 0.1M ) + 5 ml NaClO<sub>4</sub> ( 1M ) + 35 ml dioxane + 5 ml water ( V<sup>o</sup> = 50 ml ) and

#### Free acid + Ligand titration

5 ml HClO<sub>4</sub> ( 0.1 M ) + 5 ml NaClO<sub>4</sub> ( 1M ) + 10 ml ligand + 25 ml dioxane + 5 ml water ( V<sup>o</sup> = 50 ml ) are titrated with standard alkali solution pH-metrically by bubbling nitrogen gas to avoid oxidation. The ionic strength 0.1M is maintained constant by adding an appropriate amount of 1 M NaClO<sub>4</sub> solution. Titration curves for all the systems were constructed by plotting the graph between volume

**Table 1: Determination of A values (Ligand L<sub>1</sub>)**

S. No	pH	V <sub>1</sub>	V <sub>2</sub>	ΔV=V <sub>2</sub> -V <sub>1</sub>	$\bar{n}A = V \cdot \frac{(E^o + N)(\Delta V)}{(V^o + V)(TL^o)}$
1.	7.0	2.20	2.25	0.05	0.9473
2.	7.2	2.25	2.35	0.10	0.8947
3.	7.4	2.25	2.40	0.15	0.8421
4.	7.6	2.30	2.50	0.20	0.7896
5.	7.8	2.35	2.60	0.25	0.7373
6.	8.0	2.40	2.70	0.30	0.6821
7.	8.2	2.45	2.80	0.35	0.6329
8.	8.4	2.45	2.90	0.40	0.5805
9.	8.6	2.50	2.95	0.45	0.5285
10.	8.8	2.50	3.00	0.50	0.4761
11.	9.0	2.55	3.20	0.60	0.3720
12.	9.2	2.60	3.30	0.70	0.2680
13.	9.4	2.65	3.50	0.80	0.1642

**Table 2: Determination of A values (Ligand L<sub>2</sub>)**

S. No	pH	V <sub>1</sub>	V <sub>2</sub>	ΔV=V <sub>2</sub> -V <sub>1</sub>	$\bar{n}A = V \cdot \frac{(E^o + N)(\Delta V)}{(V^o + V)(TL^o)}$
1.	6.5	2.20	2.30	0.10	0.8964
2.	7.0	2.25	2.40	0.15	0.8421
3.	7.2	2.25	2.50	0.25	0.7368
4.	7.4	2.30	2.60	0.30	0.6845
5.	7.6	2.30	2.65	0.35	0.6319
6.	7.8	2.30	2.70	0.40	0.5793
7.	8.0	2.35	2.80	0.45	0.5276
8.	8.2	2.40	2.90	0.50	0.4727
9.	8.4	2.50	3.05	0.55	0.4238
10.	8.6	2.50	3.10	0.60	0.3741
11.	8.8	2.50	3.20	0.70	0.2666
12.	9.0	2.55	3.30	0.75	0.2150
13.	9.2	2.60	3.40	0.80	0.1635

of NaOH and pH. Some representative graphs are presented in figure 1 & 2. It is observed from graphical curves that the dissociation starts at above pH 6.5. This indicates the dissociation of -OH group of the ligand. This deviation increased continuously upto 10.00. This may be due to the complete dissociation of phenolic -OH group from ligand. This indicated the presence of -OH group in the ligand.

#### Calculation of Proton - Ligand Formulation Number ( A ) :

The values of nA are evaluated by applying an expression of Irving and Rossotti.<sup>13</sup>

$$\bar{n}A = \sqrt{\frac{(E^{\circ}+N)(V_2-V_1)}{(V^{\circ}-V_1)TL^{\circ}}}$$

Where,

$\sqrt{\phantom{x}}$  = replaceable H<sup>+</sup> ions from OH<sup>-</sup> group ( $\sqrt{-1}$ )

E<sup>o</sup> = Initial concentration of free acid solution (0.01 M)

N = Normality of NaOH solution ( 0.1M - 0.2 M )

V<sup>o</sup> = Initial volume of solution ( 50 ml )

V<sub>1</sub> = Volume of free acid with respect to pH of the solution.

**Table 3: Determination of A values (Ligand L<sub>3</sub>)**

S. No	pH	V <sub>1</sub>	V <sub>2</sub>	$\Delta V = V_2 - V_1$	$\bar{n}A = \sqrt{\frac{(E^{\circ}+N)(\Delta V)}{(V^{\circ}+V_1)(TL^{\circ})}}$
1.	6.5	2.20	2.30	0.10	0.8946
2.	7.0	2.25	2.40	0.15	0.8421
3.	7.5	2.35	2.55	0.20	0.7798
4.	8.0	2.40	2.70	0.30	0.6851
5.	8.2	2.45	2.80	0.35	0.6333
6.	8.4	2.50	3.00	0.50	0.4761
7.	8.6	2.50	3.10	0.60	0.3714
8.	8.8	2.50	3.20	0.70	0.2666
9.	9.0	2.55	3.30	0.75	0.2150
10.	9.2	2.60	3.45	0.85	0.1112

**Table 4: Determination of A values (Ligand L<sub>4</sub>)**

S. No	pH	V <sub>1</sub>	V <sub>2</sub>	$\Delta V = V_2 - V_1$	$\bar{n}A = \sqrt{\frac{(E^{\circ}+N)(\Delta V)}{(V^{\circ}+V_1)(TL^{\circ})}}$
1.	6.6	2.15	2.20	0.05	0.9472
2.	6.8	2.15	2.25	0.10	0.8945
3.	7.0	2.20	2.35	0.15	0.8419
4.	7.2	2.20	2.40	0.20	0.7892
5.	7.4	2.25	2.50	0.25	0.7368
6.	7.6	2.25	2.55	0.30	0.6842
7.	7.8	2.30	2.65	0.35	0.6319
8.	8.0	2.30	2.70	0.40	0.5793
9.	8.2	2.35	2.85	0.50	0.5412
10.	8.4	2.40	2.90	0.50	0.4751
11.	8.6	2.45	3.00	0.55	0.4227
12.	8.8	2.50	3.10	0.60	0.3714
13.	9.0	2.55	3.20	0.65	0.3196
14.	9.2	2.60	3.30	0.70	0.2680

TL° = Total concentration of ligand solution (2x10<sup>-3</sup> M)

of A and it is given for one of the system L<sub>2</sub> as shown in Table - 6.

The values of A obtained are presented in Table 1 to 4 along with volume V<sub>1</sub> & V<sub>2</sub>

**DISCUSSION**

**Formation curves**

The formation curves are prepared by plotting the values of pH and A for all the systems. The representative formation curves for two systems are given in figure 3 & 4. The proton-ligand stability constants (pK values) are calculated at nA = 0.5. This is called half integral method. The proton-ligand stability constants are also determined by pointwise calculations. The values of pK from both methods are presented in Table -5. The standard deviation (σ) is also calculated to the value

In above ligand systems there is a steric hindrance due to electron releasing -CH<sub>3</sub> group and electron withdrawing -NO<sub>2</sub> group. It could be seen from above Table -5 that, there is no appreciable change in proton-ligand constant (pK) because steric hindrance effect is compensated due to electron withdrawing effect of -NO<sub>2</sub> group and electron releasing effect of -CH<sub>3</sub> group. There is reduction in pK values of the ligands L<sub>2</sub> as compared to the pK values of Ligand L<sub>1</sub>, L<sub>2</sub> & L<sub>4</sub>. This may be due to the fact of the presence of methoxy as an electron withdrawing group in ligand

**Table 5: Proton-ligand stability constants (pK) of ligands L<sub>1</sub> to L<sub>4</sub>**

S. No	System	Half integral value of pK	Pointwise calculation value of pK
1.	Ligand L <sub>1</sub>	8.67 $\bar{n}$	8.69 ± 0.03
2.	Ligand L <sub>2</sub>	8.40	8.39 ± 0.02
3.	Ligand L <sub>3</sub>	8.22	8.19 ± 0.03
4.	Ligand L <sub>4</sub>	8.52	8.50 ± 0.04

**Table 6: Determination of standard deviation (σ) of Ligand L<sub>2</sub>**

S. No.	pH	Conc. NaOH 0.13M A	Conc. NaOH 0.13M A	Δ A	(Δ A) <sup>2</sup>	$\left[ \frac{\sum (\Delta nA)^2}{n-1} \right]$
1.	6.5	0.8946	0.8900	+4.6 x 10 <sup>-3</sup>	21.16 x 10 <sup>-6</sup>	0.00413
2.	7.0	0.8421	0.8451	-3.0 x 10 <sup>-3</sup>	9.00 x 10 <sup>-6</sup>	
3.	7.2	0.7368	0.7293	+7.5 x 10 <sup>-3</sup>	56.25 x 10 <sup>-6</sup>	
4.	7.4	0.6845	0.6862	+1.7 x 10 <sup>-3</sup>	2.89 x 10 <sup>-6</sup>	
5.	7.6	0.6319	0.6330	+2.1 x 10 <sup>-3</sup>	4.41 x 10 <sup>-6</sup>	
6.	7.8	0.5793	0.5821	-2.8 x 10 <sup>-3</sup>	7.84 x 10 <sup>-6</sup>	
7.	8.0	0.5276	0.5300	-2.4 x 10 <sup>-3</sup>	5.76 x 10 <sup>-6</sup>	
8.	8.2	0.4727	0.4782	-5.5 x 10 <sup>-3</sup>	30.25 x 10 <sup>-6</sup>	
9.	8.4	0.4228	0.4782	-2.2 x 10 <sup>-3</sup>	4.84 x 10 <sup>-6</sup>	
10.	8.6	0.3741	0.3731	+1.5 x 10 <sup>-3</sup>	1.00 x 10 <sup>-6</sup>	
11.	8.8	0.2666	0.2600	+6.6 x 10 <sup>-3</sup>	43.56 x 10 <sup>-6</sup>	
12.	9.0	0.2150	0.2160	+1.0 x 10 <sup>-3</sup>	1.00 x 10 <sup>-6</sup>	

$L_2$ . The electron withdrawing group reduces the pK value of the ligand. The deviation between free and curve & ligand curve indicates the dissociation of -OH group of the ligand .

The standard deviation ( $\delta$ ) is calculated by keeping all the same conditions except the concentration of alkali NaOH. The value of standard deviation is found to be very low. ( i.e.  $\delta = 0.00413$  ) this clearly indicates that the value of  $A$  evaluated are found to be correct .

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