

## pH metric studies of synthesized ligands 1-(2'-hydroxy phenyl )-3-phenyl propane-1,3-dione with Fe(III),Cd(II), Co(II), Ni(II), Zn(II) cations at 0.1 M ionic strength

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### ABSTRACT

The binary complex of 1-(2'-hydroxy Phenyl )-3-Phenyl Propane-1,3-dione(  $\beta$ -diketone) prepared from 2'-hydroxy acetophenone were studied in presence of iron(III),Cadmium(II), Cobalt(II), Nickel(II), Zinc(II) cations in various aquo-organic media using pH metric measurements at 298K and 0.1M ionic strength. The effect of substituent was studied from estimated data (pK & log k).The proton ligand and metal ligand stability constant were discussed light of the nature of the binding site of  $\beta$ -diketone. The effect of ionic strength explains with reference to interaction of cation of transition metal ion with ligand  $\beta$ -diketone.

**Keywords:**  $\beta$ -diketone, Ionic strength, pH metry, Proton ligand stability constant, Metal ligand stability constant.

### 1. INTRODUCTION

$\beta$ -diketone have gained a lot of interest due to their importance as good ligands and its complexes have been widely used in diverse areas because of their unique structural features, chemical functionalities [1]. It shows chelating behavior towards transition metal ion. 1,3-diketone are very important compound in organic synthesis, because they exhibits some biological activity such as antioxidant, antitumor, antibacterial activities and are also key intermediation to various heterocyclic compound [2-5].  $\beta$ -diketone and its keto- enol form is also importance pharmacophores of HIV-1 integrease inhibitors [6].

The studies in metal ligand complexes in solution of a number of metal ion with carboxylic acids, oximes, phenol etc. Would be interesting which throw light on the mode of storage and transport of metal ions in biological Kingdom. Metal with the view to understand the bio-inorganic chemistry of metal ions, Banergee et al [7] have synthesized a no. of mixed ligand alkaline earth metal complexes. Bjerrums [8] dissertation has taken the initiative to develop field. Metal complexation not only brings the reacting molecules together to give activated complex [9] but also polarized electrons from the ligand towards the metal. The relation between stability and basicity of ligands is indicated by the formation constant and free energy change value

Bulkier group increases the basicity of ligands as well as stability. The stability of complexes is determined by the nature of central metal atom and ligands. Tekade et al [10] investigated stability constants of some substituted pyrazolines, isoxaline and diketone Shivaraj et al [11] have studied formation constants and thermodynamic parameters of bivalent metal ion complexes with 3-amino-5-ethyl isoxazole Schiff bases and N,N,N,O and O,O donar ligands in solution. Recently Tihile [12] studies on interaction between cu (II), Cr(II), Nd (II) and Pr(II) metal ions and substituted hydroxyl chalcones at 0.1 M ionic strength pH metrically. Thakur et al [13,14] have studies the influence of dielectric constants of medium on the complex equilibrium of substituted hydroxyl-1,3- propandiones with Cr(II) metal ions and studies on interaction between Cu(II), Cr(II) and Ni(II) metal ions at 0.1 M ionic strength pH metrically.

In present work an attempt has been made to study the interactions between Fe(III),Cd(II), Co(II), Ni(II), Zn(II) Cations At 0.1 M Ionic Strength with Ligand at 0.1 ionic strength, pH metrically in 60% ethanol-water mixture.

### 2. MATERIALS AND METHODS

All the chemicals used were Analar grade (India make). Metal ion Concentration were determined by using EDTE with suitable indicator and used as chelating reagent.  $\beta$ -diketone were synthesized by using Baker Venkatraman

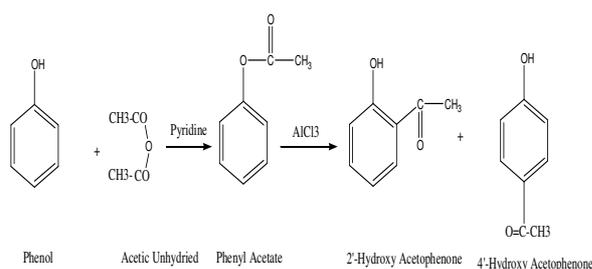
Transformation method. Synthesized compounds were checked by their M.P. coloration, IR, on silica gel by TLC.

### 2.1. Synthesis of 1-(2'-hydroxy Phenyl )-3-Phenyl Propane-1,3-dione ( $\beta$ -diketone):

It is prepared in three steps:

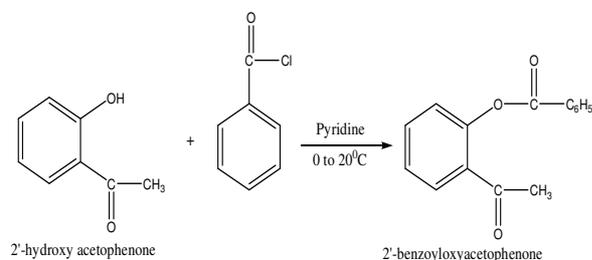
#### 2.1.1. Preparation of 2'-hydroxy acetophenone

Fries rearrangement of phenyl acetate in presence of anhydrous Aluminum Chloride, obtained 2'-hydroxy acetophenone and 4'-hydroxy acetophenone. Both are separated by steam distillation. Reaction starting from Phenol as;



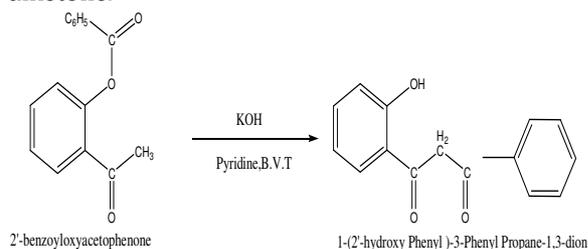
#### 2.1.2. Preparation of 2'-benzoyloxyacetophenone

Benzoyl Chloride added to a mixture of 2'-hydroxy acetophenone and pyridine slowly with stirring under temperature  $20^\circ C$ . The reaction mixture was kept overnight at room temperature and poured on crushed ice and concentrated HCl. It was then filtered and crystallized from alcohol colorless needle.



#### 2.1.3. Synthesis of 1-(2'-hydroxy Phenyl )-3-Phenyl Propane-1,3-dione

2'-benzoyloxyacetophenone was dissolved in Pyridine to which added powdered Potassium Hydroxide. The reaction mixture was stirred for 20 minutes, with thick yellow paste formed. It was decomposed by crushed ice and concentrated HCl. The yellow product obtained is the  $\beta$ -diketone.



### 3. pH metric analysis

Eleco -120 model instrument with accuracy in 0.01 unit with glass and saturated calomel electrode was used for the titrations. It was calibrated with the buffer solution of pH 7.00 and 9.20 at  $28 \pm 0.1^\circ C$  before titrations. Titrations were carried out in an inert atmosphere by bubbling a constant flow of nitrogen gas.

The binary system were studied by following pH metric titration

- Free acid  $HNO_3$  (0.04 M) = A
- Free acid  $HNO_3$  (0.04 M) and ligand ( $20 \times 10^{-4}$ ) = A+R
- Free acid  $HNO_3$  (0.04 M) and ligand ( $20 \times 10^{-4}$ ) and metal ion ( $4 \times 10^{-4}$  M) = A+R+M

The ionic strength of all the solution was maintained constant (0.1 M) by adding appropriate amount of  $NaClO_4$  solution. All the titrations were carried out in 60 % ethanol-water mixture by addition of sodium hydroxide. The graph of volume of alkali (NaOH) against pH were plotted (Figure 1-5: shows graph of pH vs volume of NaOH of  $\beta$ DK and metal ions.).

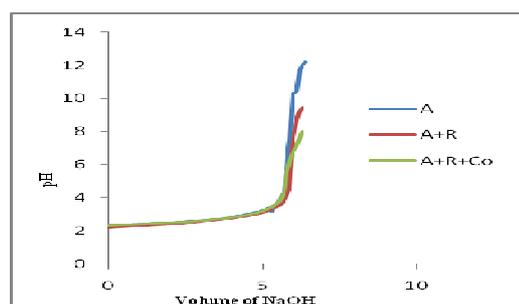


Figure - 1

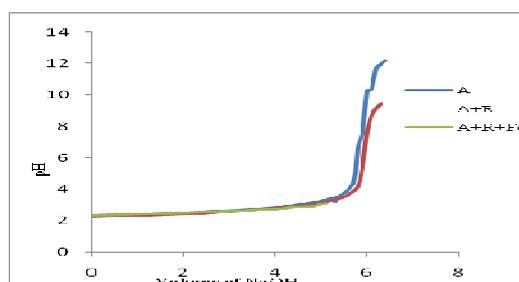


Figure - 2

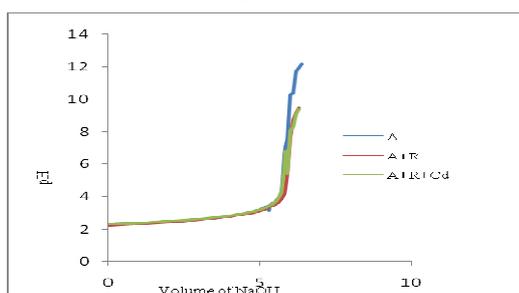


Figure - 3

**Table - 1: pH Titration of  $\beta$ DK in the presence of Metal ion Fe (III), Cd(II), Co(II), Ni(II), Zn(II), 60 % EtOH Mixture**

Volume of NaOH	pH Of Solution						
	HNO <sub>3</sub> (A)	HNO <sub>3</sub> +R	HNO <sub>3</sub> +R+ Fe(III)	HNO <sub>3</sub> +R+ Cd(II)	HNO <sub>3</sub> +R+ Co(II)	HNO <sub>3</sub> +R +Ni(II)	HNO <sub>3</sub> +R+ Zn(II)
0	2.35	2.25	2.35	2.35	2.35	2.31	2.33
1.2	2.43	2.36	2.43	2.44	2.41	2.4	2.4
2.4	2.55	2.5	2.54	2.58	2.54	2.52	2.53
2.8	2.61	2.58	2.6	2.62	2.6	2.58	2.59
3.2	2.68	2.63	2.64	2.69	2.65	2.66	2.65
3.6	2.73	2.71	2.7	2.76	2.74	2.72	2.72
4	2.82	2.8	2.72	2.85	2.83	2.82	2.8
4.4	2.97	2.91	2.86	2.96	2.94	2.93	2.93
4.8	3.12	3.04	2.92	3.12	3.1	3.11	3.11
5	3.25	3.15	3.05	3.24	3.2	3.26	3.2
5.1	3.31	3.2	3.1	3.29	3.3	3.3	3.28
5.2	3.39	3.25	PPT	3.38	3.36	3.39	3.36
5.25	3.44	3.28		3.42	3.42	3.44	3.43
5.3	3.17	3.38		3.44	3.45	3.49	3.47
5.35	3.52	3.42		3.51	3.51	3.54	3.54
5.4	3.58	3.43		3.56	3.55	3.6	3.62
5.45	3.65	3.46		3.63	3.65	3.68	3.68
5.5	3.73	3.53		3.7	3.7	3.75	3.8
5.55	3.82	3.59		3.8	3.8	3.84	3.91
5.6	3.94	3.66		3.93	3.9	3.96	4.06
5.63	4.08	3.73		4.06	4.04	4.14	4.32
5.7	4.34	3.83		4.31	4.32	4.4	4.8
5.75	4.96	3.98		4.77	4.78	5	5.7
5.8	6.64	4.16		5.88	5.6	5.6	6.2
5.85	7.09	4.5		6.82	5.95	5.95	6.5
5.9	7.56	5.4		5.44	6.22	6.25	6.75
6	10.3	7.65		8.1	6.78	6.85	7.17
6.1	10.38	8.7		8.3	7.17	7.35	7.63
6.2	11.74	9.15		9.1	7.5	7.72	8.13
6.3	11.97	9.45		9.41	PPT	8.14	PPT
6.4	12.2			PPT		PPT	

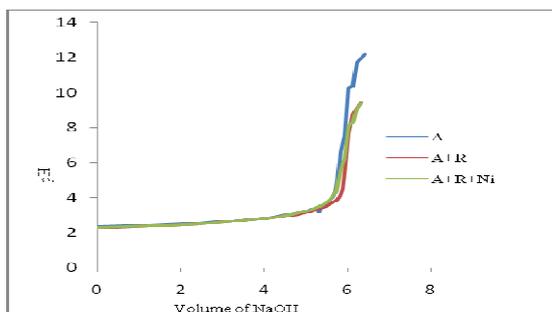


Figure - 4

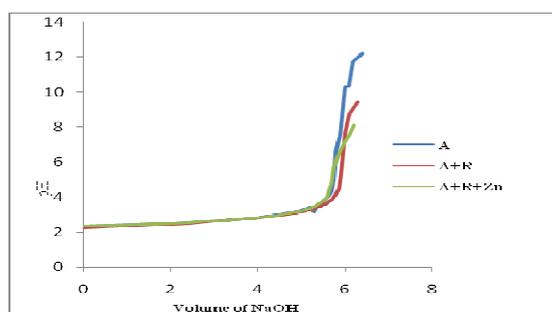
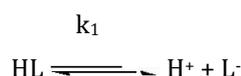


Figure - 5

#### 4. RESULTS AND DISCUSSION

Proton-ligand stability constants:

The binary complex of 1-(2'-hydroxy Phenyl)-3-Phenyl Propane-1,3-dione prepared from 2'-hydroxy acetophenone were studied in aquo-organic media in presence of Fe(III), Cd(II), Co(II), Ni(II), Zn(II) metal ions by pH metric measurements at various temperature at 0.1 M ionic strength. The 1-(2'-hydroxy Phenyl)-3-Phenyl Propane-1,3-dione ( $\beta$ -diketone) was monobasic acids having only one dissociable H<sup>+</sup> ion from OH group. It can therefore, be represented as HL



Proton ligand stability constant  $k_1$  is represented as;

$$K_1^H = \frac{a_{H^+} a_{L^-}}{a_{HL}}$$

The proton-ligand formation number ( $n_A$ ) were calculated by Irving and Rossotti expression.

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

Where,

- $V^0$  = Initial volume of solution
- $E^0$  = Initial concentration of free acid
- $T_L^0$  = Concentration of ligand
- $\gamma$  = Number of replaceable protons
- $N$  = Avagadros Number
- $(V_2 - V_1)$  = Volume of alkali N, consumed by acid and ligand on the given pH.

pH titration data was utilized for determination of, Proton ligand stability constant, metal ligand stability constants. The respective pH metric data given in table 1-4. The plot of pH vs volume of NaOH given in table. Dissociation constant and stability constant were evaluated by Irving-Rossotti Methods and by computer pregame (SCOSS).  $pK_1$  and  $pK_2$  values were determine by adopting half-Integral and point wise calculation methods shown in table 2.

**Table - 2: Dissociation constant metal chelate of  $\beta$  diketone in EtOH at 298 k at 0.1 M ionic strength**

% $\rightarrow$	60%	70%
$pK_1$	4.13	4.23
$pK_2$	10.31	10.71

**Table - 3: Stepwise stability constant  $\beta$ -diketone in EtOH at 298 k at 0.1 M ionic strength**

% $\rightarrow$	60%		70%	
Metal $\downarrow$	Log $K_1$	Log $K_2$	Log $K_1$	Log $K_2$
Fe(III)	12.10	12.06	12.22	2.85
Cd(II)	12.11	11.74	11.25	2.89
Co(II)	12.45	12.02	11.20	3.30
Ni(II)	11.59	3.20	11.19	3.42
Zn(II)	11.84	2.96	11.32	3.67

**Table - 4: Effect of temperature on Stepwise stability constant  $\beta$ -diketone in Et-OH at 298 K<sup>0</sup> at 0.1 M ionic Strength**

Metal	298		308		318	
	Log $K_1$	Log $K_2$	Log $K_1$	Log $K_2$	Log $K_1$	Log $K_2$
Fe(III)	12.10	12.06	10.53		11.75	
Cd(II)	12.11	11.74	10.36	3.87	9.37	4.77
Co(II)	12.45	12.02	10.63	3.56	10.42	
Ni(II)	11.59	3.20	11.08	7.32	10.71	7.77
Zn(II)	11.84	2.90	11.61	3.51	11.16	9.26

It could be seen that  $pK_a$  and  $\log K$  decreases. The  $pK_a$  value influence by intrinsic basicity of the solvent.

It can be account towards the fact that the increase in ions of the solution, decrease dielectric constant of medium. The effect of ionic strength may be explain with reference to cation  $k^+$  of the added salt with the ligand and anion  $NO_3^-$  with the metal ion under study. Which may be more as compared with the actual interaction of metal ion with the ligands.

#### 5. CONCLUSION

Titration curves for all systems started from pH =2.0. This indicated the complex formation. The value  $pK_a$  and  $\log K$  obtained in the present work are explain in the view of the dissociation of the acid proton at pH 2-3 and second proton which dissociates at higher pH 10-11.

#### 6. REFERENCES

- Pooja N Varma JJ and Shaikh D. Juneja. **World applied Science Journal**, 2011; 14(8): 1154-1157.
- Manuel A, Silva R and Luis M. Santos. **J. Chem. Thermodynamics**, 2005; 38: 817.
- Bennett IJ and Broom R. **Boinorganic Medicinal chemistry Lett.**, 9; 1847-1852.
- Nishiyama, Shiotsu TB and Sujita HT. 2002; 76: 435-439.

5. Sato K, Yamazoa S, Yamamoto R and Sohataand A Ando. **Organic Latter**, 2008; 10: 2405-2408.
6. Tchertanov L and Mouscaded J. **J. Med. Chem.**, 2007; 50: 1133-1145.
7. Banerjee AK and Rao TVR. **J. Indian Chem. Soc.**, 1968; 63: 480.
8. Bjerrum J, Hasse P and Sons. **Copenhagn**, 1941.
9. Florene AT, and Attwood D. **Physical Principle of pharmacy , Macmillan Londen**, 1981.
10. Poddar SN, Dey K and Poddai NG. **J. Indian Chem. Soc.**, 1999; 11: 420.
11. Karalmai K, Prashanthi Y and Chatyala V. **J.Chem.Pharm.Res.**, 2011; 3: 226-233.
12. Thile MS. **J.Chem.Pharm.Res.**, 2012; 4: 2233-2227.
13. Thakur SD, Munot KP, Mahajan DT, Deshmukh RD and Thile MS. **J.Chem.Pharm.Res.**, 2012; 4: 450-455.
14. Thakur SD, Deshmukh RD and Thile MS. **J.Chem.Pharm.Res.**, 2012; 4: 456-459.