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Determination of Stability Constant of The Complexes of Metal Ion Fe(III), Mn(II) And Cr(III) With Some Substituted 2-Oxo-2H-Chromene-3-Carbohydrazide Derivatives at 0.1 M Ionic Strength at 42°C

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I. INTRODUCTION

Proton ligand and metal ligand stability constant are measured for Fe(III) and 1, 2-dihydroxy benzene and 1, 5-disulphonic acid complexes[i]. Determination of stability constant of substituted of pyrazoles with rare earth metals form complexes are reported[ii]. Effect of temperature on formation constants of 2 acetylpyridine(N benzoyl)glycine hydrazone with lanthanide(III) ions at different ionic strengths are reported. Irving and Rossotti, Herson and Gilbert[iii], Wilkins and Lewis[iv] and Rossotti and Rossotti[v] have determined stability constant by Bjerrum-Calvin titration technique[vi]. Kabadi[vii], Jahagirdar[viii] and Narwade[ix] have determined pK values of salicylaldehyde, salicylic acid and sulphonic acid respectively by similar procedure. The metal ligand stability constant of some β-diketones are reported[x]. Stability constants have investigated for some substituted pyrazolines, isoxalline and diketone[xi]. The method most frequently applied for study of complex equilibria is pH-metric titration technique[xii]. Stepwise formation of mononuclear binary complexes is described by set of equilibrium constants. For pH-metric measurements an electrode must be selected. According to Bjerrum, Martell and Calvin[xiii], the formation of complex ML_N is stepwise process and one has to deal with a series of equilibria of the type:

Irving and Rossotti, Herson and Gilbert[xiv], Wilkins and Lewis[xv] and Rossotti and Rossotti[xvi] have determined stability constant by Calvin-Bjerrum titration technique[xvii]. The value of $\bar{n}_A$, $\bar{n}$, pK, log K_1 and log K_2 are evaluated by Irving and Rossotti's equation. The stability constant and thermodynamic parameters of complexes containing lighter lanthanides[xviii], copper(II)[xix], calcium and magnesium[xx] are reported. It is also important in environmental studies[xxi], medicinal[xxii] and industrial chemistry[xxiii]. Effects of transition metal on stability constant of complexes have studied by pH metric method[xxiv]. Bendi[xxv], Janrao[xxvi] and Ramteke[xxvii] have studied stability constant of ligands with lanthanide metals complexes.The present work involves pH metric study of substituted 2-oxo-2*H*-chromene-3-carbohydrazide derivatives with metal ions Fe(III), Mn(II), Cr(III) and Ti(III) at temperature42°C. The Bjerrum-Calvin titration technique as modified by Irving and Rossotti has been employed in the present study. The following three sets of titrations are carried out in sequence.

II. METAL IONS AND LIGANDS.

2.1 Metal Ions

Metal Ions Following metals in the form of their salts are used for complexing with chelating agents (Ligands): 1. Fe(III) 2. Mn(II) 3. Cr(III)

2.2 Ligands

Ligand (L_A) = N-[(E)-1-(3,5-dichloro-2-hydroxy-phenyl)ethylideneamino]-2-oxo-chromene-3-carboxamide
Ligand (L_B) = N-[(E)-1-(2-hydroxy-5-methyl-phenyl)ethylideneamino]-2-oxo-chromene-3-carboxamide
In the present work, following substituted 2-oxo-2*H*-chromene-3-carbohydrazide derivatives compound have synthesized by standard method[xxviii].

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III. EXPERIMENTAL WORK

The ligands used in present work considered as monobasic acid containing only one dissociable H^+ ion from -OH group.

$$HL \rightleftharpoons H^+ + L^-$$

Calculation of Proton-Ligand Formation Number ($\bar{n}_A$)

The values of $\bar{n}_A$ are calculated by Irving Rossotti's expression

$$\bar{n}_A = y - \frac{(V_2 - V_1)(N + E^o)}{(V_o + V_1)T_L} \quad (1)$$

Where V^0 is the initial volume of solution,
E^0 and T_L are initial concentrations of mineral acid and ligand respectively,
V_1 and V_2 volumes of alkali required during acid and ligand titration at given pH,
y is the no. of replaceable protons from the ligand.

The difference $(V_2 - V_1)$ is estimated from the plot between volume of NaOH and pH of solution. The values of $\bar{n}_A$ calculated along with the values of $(V_2 - V_1)$ at various pH.

Calculation of Metal-Ligand Stability Constant ($\bar{n}$)

The metal ligand formation number is estimated by Irving-Rossotti expression

$$\bar{n} = \frac{(V_3 - V_2)(N + E^o)}{(V_o + V_2)\bar{n}_A T_M} \quad (2)$$

The horizontal difference (V_3-V_2) between metal curve (A+L+M) and ligand curve (A+L) is used to evaluate the value of $\bar{n}$ using Irving-Rossotti expression. The pH at which turbidity starts developing in (A+L+M) titrations indicates metal hydroxide formation.

a) Half Integral Method

The graphs are plotted between $\bar{n}$ vs pH and the values of log K_1 and log K_2 are determined. The values of log K_1 and log K_2 are determined from the formation curves by knowing the values of pH at which $\bar{n}$ = 0.5 and $\bar{n}$ = 1.5 respectively.

b) Point wise Calculations Method

For value of $\bar{n}$ < 1.0, metal ligand stability constants for 1:1 complex formations are calculated by using[xxix].

$$\log\left(\frac{\bar{n}}{1-\bar{n}}\right) = \log K_1 - pH \quad (3)$$

For value in the region 1< $\bar{n}$ <2, metal ligand stability constants for 1:2 complex are calculated by using equation.

$$\log\frac{(\bar{n}-1)}{(2-\bar{n})} = \log K_2 - pH \quad (4)$$

The values of $\log K_1$ and $\log K_2$ are shown in table no. 2. The values of logK calculated by point wise calculation methods are good agreement with the values obtained by the half integral method.

The experimental procedure involves following titration:

The following three sets of titrations are carried out in sequence.

i) *Acid titration*: Nitric acid (1 x 10^{-2} M)

ii) *Ligand titration*: Nitric acid (1 x 10^{-2} M) and ligand (20 x 10^{-4} M)

iii) *Metal titration*: Nitric acid (1 x 10^{-2} M), ligand (20 x 10^{-4} M) and metal salt (4 x 10^{-4} M) againststandard sodium hydroxide solution (0.09803 to 0.106 N) are carried out in 70% DMF-watermedium. Ionic strength of the solution is maintained constant by adding an appropriate amount of1M KNO_3 solution. Following constants are determined in the present work.

a) pK values of substituted 2-oxo-2*H*-chromene-3-carbohydrazide ligands in 70% DMF-water medium.

b) logK values of complexes of metal ions Fe(III), Mn(II), Cr(III) and Ti(III) with ligands are determined.

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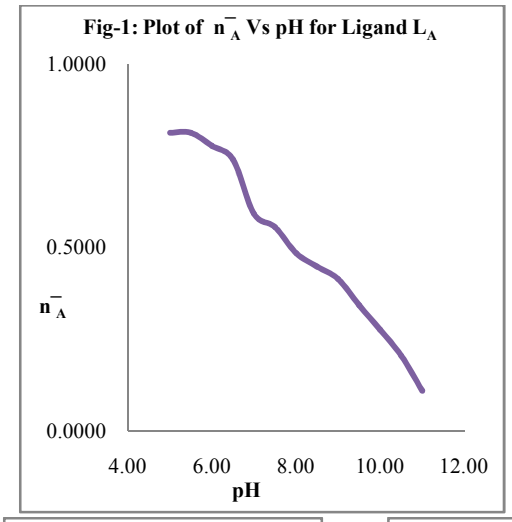
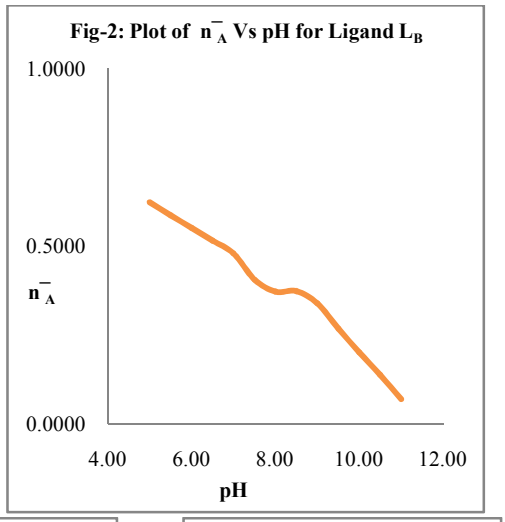
III. Result and Discussion

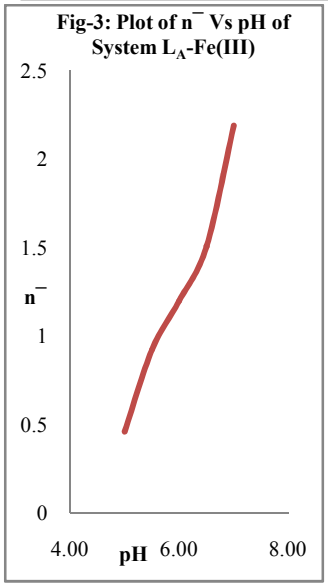
Simultaneous and stepwise complex formation are fiend out from the difference between $\log K_1$ and $\log K_2$. It is observed that if the difference is less than 2.5 then simultaneous complex formation of 1:1 and 1:2 takes place and if it is more than 2.5 then stepwise complex formations occurs. In the present work it is observed that the difference is less than 2.5 then simultaneous complex take place. Also ratio $\log K_1 / \log K_2$ give the information that if it is less than 1.5 simultaneous complex formation takes place. In this work it is less than 1.5 so simultaneous complex formation take place.

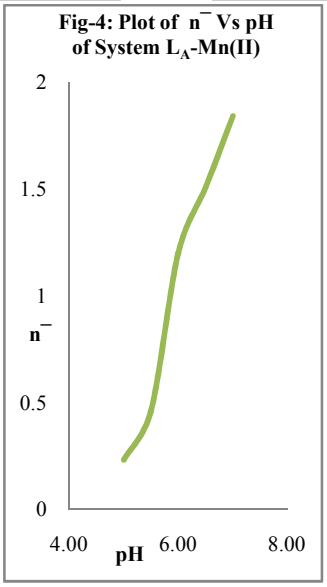
IV. Conclusion

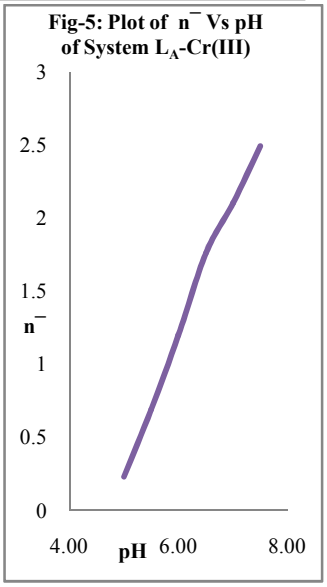
In this study the complex formation of Fe(III), Mn(II) and Cr(III) with substituted-2-oxo-2H-chromene-3-carbohydrazide derivatives at temperatures 42°C is favorable Process. The Point wise calculation method and Half integral method gives this information that complex formation is favorable.











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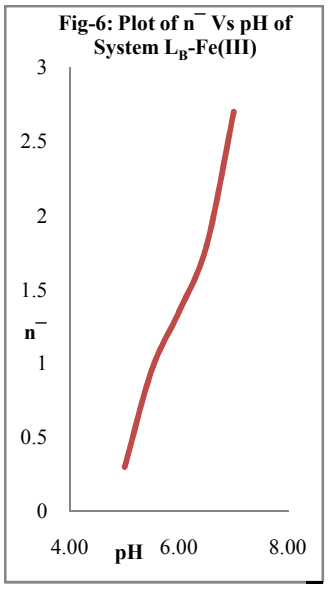

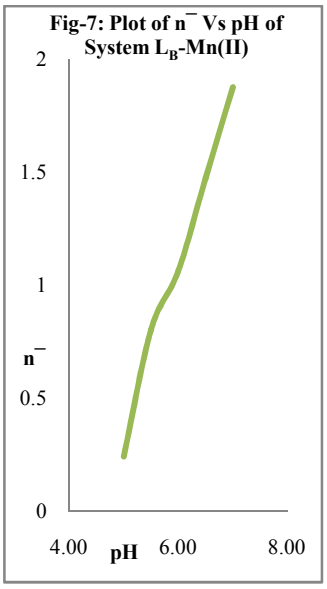

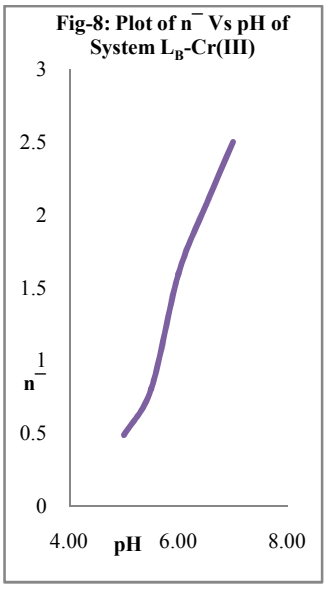

Table – 1: pK Values of Various Ligands

Temp. = 42+ 0.1^{0}C μ = 0.1 M

Ligands	pK (Point wise Calculation Method)	pK (Half Integral Method)
L_A	7.83	7.71
L_B	7.36	6.70

Table –2: Data of logK_1 and logK_2, Difference and Ratio between them at 42^{o}C

Ligand	Metal	logK_1	logK_2	logK_1/logK_2	logK_1-logK_2
L_A	Fe(III)	5.4047	4.2638	1.2675	1.1409
	Mn(II)	5.1047	4.0638	1.2561	1.0409
	Cr(III)	5.2047	4.2538	1.1906	0.9509
L_B	Fe(III)	4.4447	3.4538	1.2869	0.9909
	Mn(II)	4.1747	3.0538	1.3670	1.1209
	Cr(III)	4.3447	3.5538	1.2225	0.7909

Table-3: Metal-ligand Stability Constants by Different Methods

Ligand	Metal	Half integral method	Point wise calculation method
		logK	logK
L_A	Fe(III)	5.4047	5.5593
	Mn(II)	5.1047	5.1412
	Cr(III)	5.2047	5.2710
L_B	Fe(III)	4.4447	4.5720
	Mn(II)	4.1747	4.2716
	Cr(III)	4.3447	4.4793

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