Study of Stability Constant of Complexes of the metal ions Fe(III), Mn(II), Cr(III) and Ti(III) with substituted 2-oxo-2*H*-chromene-3-Carbohydrazide derivatives in 70% DMF-Water solvent at 32^0 C

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ABSTRACT

The interaction of metal ions Fe(III), Mn(II), Cr(III) and Ti(III) with substituted 2-oxo-2*H*-chromene-3-Carbohydrazide derivatives at 0.1 M ionic strength are determine by pH metric technique. Calvin Bjerrum titration technique are use to study proton ligand and metal ligand stability constant. It is observed that there is formation of 1:1 and 1:2 complexes. The log K^1 and log K^2 values are find out for simultaneous complex formation.

Key Words- pH metric study, substituted 2-oxo-2*H*-chromene-3-Carbohydrazide derivatives and stability constant.

I. INTRODUCTION

Considerable research work has done on coordination compounds and information concerning complex equilibrium has published. In the manufacture of dyes like alizarin red dye[1] and aureolin[2] coordination compounds are used. Coordination compound is used in polymerization of ethylene[3]. Aluminium and titanium coordination complexes are used as catalyst for the manufacture of various dyes[4]. Organic light-emitting devices are fabricated using the complex of iridium(III)[5]. Stability constant is well known tool for solution chemist and biochemist. There are two terms expressing the stability constant. They are metal ligand stability constant and proton ligand stability constant. The determination of metal ligand stability constant requires the knowledge of reliable and accurate values of proton ligand stability constant because both are correlated with each other. Stability constant and biological activities are determined for reaction in water[6]. Determination of stability constant is also important in environmental studies[7], medicinal[8] and industrial chemistry[9]. Determination of stability constant of complexes of Cu(II) and Ni(II)[10], Cd(II) and Pb(II)[11] with high molecular weight poly(acrylic acids) are studied. Metal ligand stability constant of substituted diketones have reported[12]. Stability constant is investigated for substituted pyrazolines, isoxazolines and diketone[13]. Study of stability constant and basicity of metal complexes of β-diketone is reported[14]. The stability constant of Al(III), Cr(III) and Fe(III) metal ions with substituted sulphonic acid have reported[15].

II. EXPERIMENTAL SECTION

Pointwise calculation and half integral method were used to calculate proton ligand and metal ligand stability constant.

This shows the dissociation of ligands giving H^+. The ligands used in present work considered as monobasic acid containing only one dissociable H^+ ion from -OH group.

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

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

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

$$\bar{n}_A = y - \frac{(V_2 - V_1)(N + E^0)}{(V_o + V_1)T_L} \quad (1)$$

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.

The values of $\bar{n}_A$ obtained at various pH along with the horizontal difference for different systems are present. This horizontal difference measured is between formation curve of acid + ligand (V_2) and acid (V_1). The formation curves are constructed by plotting the values of $\bar{n}_A$ against pH of solution. The dissociation constant pK of ligands are calculated from formation curves.

b) Metal ligand stability constant $\bar{n}$

The metal ligand stability constant is also called as association or formation constant. The metal ligand formation number is estimated by Irving-Rossotti expression

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

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 values of $\bar{n}$ are calculated for Fe(III), Mn(II), Cr(III) and Ti(III) metal ion complexes with substituted 2-oxo-2*H*-chromene-3-carbohydrazide derivatives using Irving-Rossotti's expression and the values of $\bar{n}$ for all systems.

For the calculation of metal-ligand stability constant considers the titration curve of acid + ligand and acid + ligand + metal ion. The values of V_2 and V_3 are determined from the graph of pH versus volume of alkali added (Fig. no. 1 to 3). The values of V_2 and V_3 are used for determination of the values of $\bar{n}$ at different pH. The values of $\bar{n}$ are calculated by using expression. The values of $\log K_1$ and $\log K_2$ are determined from the formation curves by knowing values of pH at which $\bar{n}$ = 0.5 and $\bar{n}$ = 1.5 respectively.

c) 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.

d) Pointwise Calculations Method

For value of $\bar{n} < 1.0$, metal ligand stability constants for 1:1 complex formations are calculated by using[16].

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

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

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

The values of $\log K_1$ and $\log K_2$ are shown in table. The values of logK calculated by point wise calculation methods are good agreement with the values obtained by the half integral method.

Irving and Rossotti, Herson and Gilbert[17], Wilkins and Lewis[18] and Rossotti and Rossotti[19] have determined stability constant by Calvin-Bjerrum titration technique[20]. 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 experimental procedure involves following titration:

I. *Acid titration*: Nitric acid (A) (1.00×10^{-2} M)
II. *Ligand titration*: Nitric acid (1.00×10^{-2} M) and ligand (20.00×10^{-4} M), (A + L)
III. *Metal titration*: Nitric acid (1.00×10^{-2} M), the ligand (20.00×10^{-4} M) and the metal salt (4.00×10^{-4} M), (A + L+ M) against standard NaOH solution.

The ionic strength of all the solutions is first adjusted to constant value of 0.1M by addition of appropriate amount of 1M KNO_3 solution. The titrations are carried out in 100 ml borosil glass double jacket beaker at constant room temperature. The temperature is adjusted by circulating water from thermostatic bath. The pH meter readings are taken after every addition of alkali solution. Titrations are continued up to the constant pH value.

In the present work, following substituted 2-oxo-2*H*-chromene-3-carbohydrazide derivatives compound have synthesized by standard method[21]. All this work is done in 70% DMF-Water at 32°C. All pH-metric titrations and pH-measurements are carried out with EQIP-TRONIC DIGITAL pH meter model EQ-610 (accuracy $\pm$ 0.05 units) with a glass and calomel electrodes assembly. The instrument could read pH in the range 0.00 to 14.00 in steps of 0.01. The readings are recorded only when the instrument registered a steady value for at least one minute. The pH meter is standardized before each titration with a buffer solution of pH = 4.01, 7.00 and 9.11.

III. RESULT AND DISCUSSION

All the two ligand are use in present work are monobasic. The graph are plotted between pH against $\bar{n}_A$. Pointwise calculation method and half integral method are use for the calculation of proton ligand stability constant (pK). The metal titration curve and ligand titration curve are used to calculate ligand molecules attach per metal ion $\bar{n}$ by using the equation 2. The $\bar{n}$ is generally known as degree of formation constant. If the ratio of log K1 and log K2 is less than 1.5 then simultaneous and greater than 1.5 than stepwise complex formation take place. The difference between log K1 and log K2 are generally positive[22]. If difference between log K1 and log K2 is less than 2.5, simultaneous formation of 1:1 and 1:2 complex take place and if it is more than 2.5 than stepwise complex formation occurs[23]. In the present case all the system shows less than 2.5. This indicates simultaneous formation of 1:1 and 1:2 complexes. The difference and ratio gives the same result.

IV. CONCLUSION

In the present work 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 temperature 32°C. Pointwise calculation method and half integral method shows that there is simultaneous complex formation. The metal ligand stability constant for all the system shows that there is stable complex formation.

pK Values of Ligands

Temp = 32 + 0.1°C μ = 0.1 M

Ligands	pK (Pointwise Calculation Method)	pK (Half Integral Method)
L_A	8.12	7.90
L_B	7.92	7.50

Table-1

Metal-ligand Stability Constants by Different Methods

Ligand	Metal	Half integral method	Pointwise calculation method
		logK	logK
L_A	Fe(III)	5.1847	5.2562
	Mn(II)	5.3447	5.6843
	Cr(III)	5.2847	5.4208
	Ti(III)	5.5247	5.6033
L_B	Fe(III)	5.1947	5.3905
	Mn(II)	5.1247	5.4739
	Cr(III)	4.9647	4.4702
	Ti(III)	5.2447	5.4068

Table – 2

Data of $\log K_1$ and $\log K_2$, difference and ratio between them at 32°C

Ligand	Metal	$\log K_1$	$\log K_2$	$\log K_1/\log K_2$	$\log K_1-\log K_2$
L_A	Fe(III)	5.1847	4.1538	1.2481	1.0309
	Mn(II)	5.3447	4.5538	1.1736	0.7909
	Cr(III)	5.2847	4.2038	1.2571	1.0809
	Ti(III)	5.5247	4.3338	1.2747	1.1909
L_B	Fe(III)	5.1947	4.1138	1.2627	1.0809
	Mn(II)	5.1247	4.2538	1.2047	0.8709
	Cr(III)	4.9647	4.3938	1.1299	0.5709

	Ti(III)	5.2447	4.5238	1.1593	0.7209

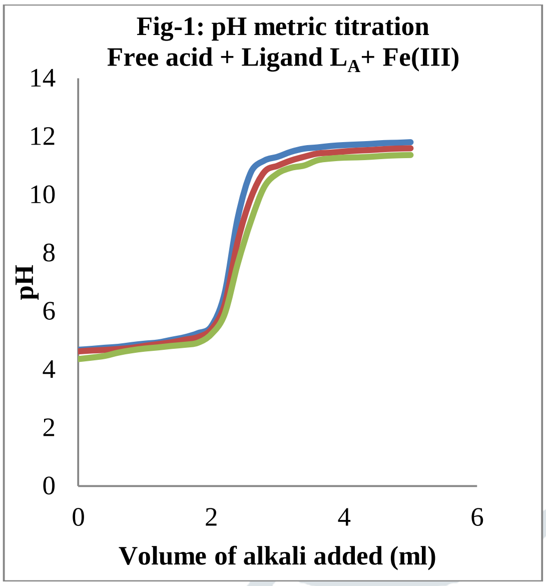

Figure no. 1: pH metric titration curve

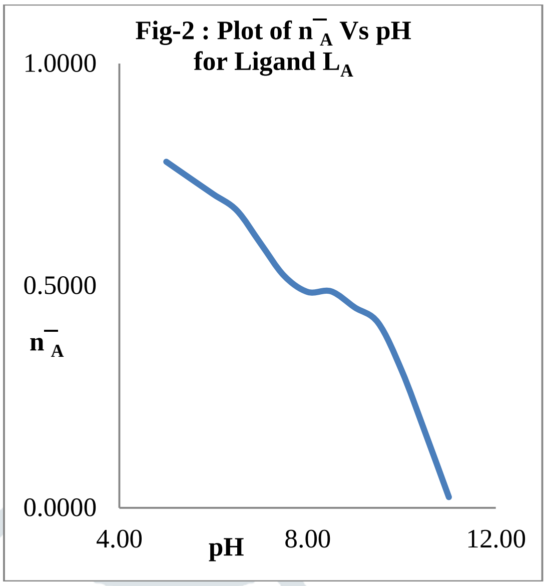

Figure no. 2: Proton ligand Stability Constant

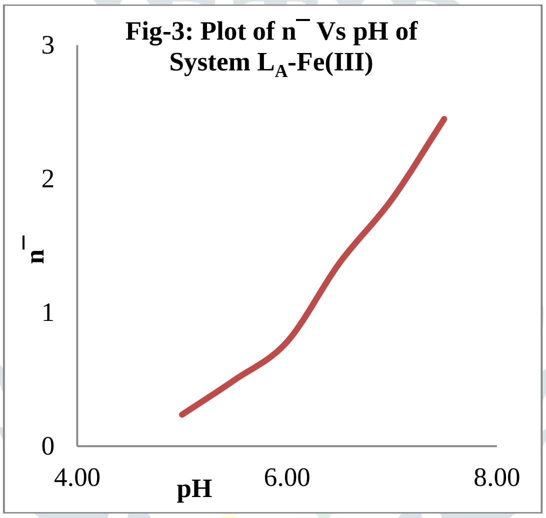

Figure no. 3: Metal ligand stability Constant

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