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Metal-Ligand Stability Constants and Thermodynamic Study of Mn(II) and Cd(II) Metal Ion Complexes with the ligand 2-Oxo-2H-Chromene-3-Carbohydrazide

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ABSTRACT

In this study simple, economic and rapid potentiometric method was used to calculated proton-ligand stability constant of [2-oxo-2H-chromene-3-carbohydrazide] and metal-ligand stability constant of its complexes with metal ion (Mn^{+2} and Cd^{+2}).

This method has been employed at three different temperatures 298k, 308k and 318k and at an ionic strength of 1N NaCl. The thermodynamic parameters △G, △H and △S were studied from logk at three different temperatures.

KEY WORDS: Potentiometric, proton-ligand stability constant, metal-ligand stability constant, Coumarin derivatives and calvin-bjerrums equation.

1. INTRODUCTION

Coumarin derivatives are used in the field of polymer, medicine and biology sciences. They are also present in the actions of plant growth hormones (Abdel-Wahab, 2014; Cavar, 2012), and used in cosmetics (Haiwei, 2015), lasyer dyes (Mohamed, 1997), perfumes (Kadhum, 2011) and cigarettes (Vahdat, 2015). Various techniques have been developed to determine coumarin and its derivatives, such as spectro fluorimetric (Mirian, 2011), HPLC (Constanze, 2008; Izquierdo, 2000), capillary gas chromatography (Wisneski, 2001) and fluorescent probes (Frenette, 2005). The aim of this study was developed simple potentiometric method for the determination coumarin derivative [2-oxo-2H-chromene-3-carbohydrazide] (fig.1) and its complexes with Mn^{+2} and Cd^{+2}.

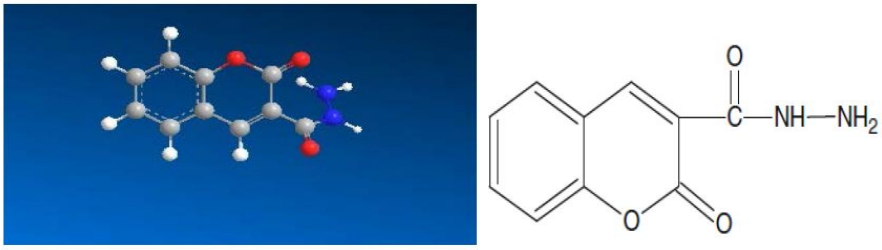


Fig.1. 3D and 2D structure of the ligand [2-oxo-2H-chromene-3-carbohydrazide]

2. MATERIAL AND METHOD

pH metric titration were carried out with jenway 3020 pH meter, Varian UV–Vis spectrophotometer and all chemicals were analytical grade supplied by BDH and Fluka.

Procedure of ligand [2-oxo-2H-chromene-3-carbohydrazide]: Cumarin-3-carboxylic acid ethyl ester (1mol) was mixed with 50 ml hydrazine hydrate and the mixture was refluxed at 25^0C for 2 h. The white solid product formed was separated by filtration and wash with ethanol (purity 99%) and dried.

Procedure of potentiometric method: This method involved titration of the following solution (total volume 50 ml) against (0.1N) NaOH solution at three temperatures 25^0C, 35^0C and 45^0C keeping ionic strength of the solution constant (1N) NaCl:

a) 5ml of (0.1N) HCl + 5ml (1N)NaCl+ 20 ml ethanol+ 20ml distilled water.

b) 5ml of (0.1N) HCl + 5ml(1N)NaCl+ 15 ml ethanol+ 20ml distilled water+ 5ml (0.002N) ligand [2-oxo-2H-chromene-3-carbohydrazide]

c) 5ml of (0.1N) HCl + 5ml(1N)NaCl+ 15 ml ethanol+ 15ml distilled water+ 5ml (0.002N) ligand [2-oxo-2H-chromene-3-carbohydrazide] + 5 ml (0.002N) Mn^{+2} and Cd^{+2} ions.

3. RESULTS AND DISCUSSION

The ligand [2-oxo-2H-chromene-3-carbohydrazide] was monobasic acid having only one dissociable (H^+) ion from (OH^-) group, it can therefore, be expressed as HL:

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

It was scanned between 200-600 nm in Uv-Visable spectrophotometer (fig.2) against absolute ethanol as a blank.

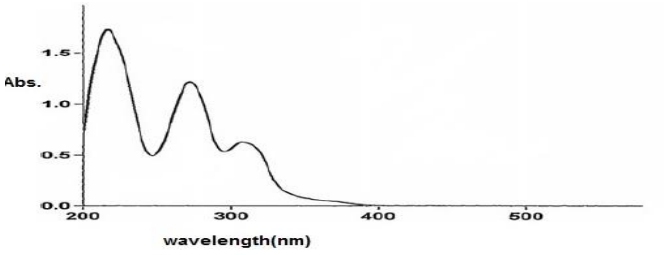


Fig.2. UV-Visible spectrum of the ligand [2-oxo-2H-chromene-3-carbohydrazide]

On plotting the observed pH against the volume (0.1N) NaOH, we get different trends in titration curve, HCl curve (A), the ligand [2-oxo-2H-chromene-3-carbohydrazide] curve(B) and metal complex titration curve for (Mn^{+2} and Cd^{+2}) metal ion (C) shows in figures.3, 4.

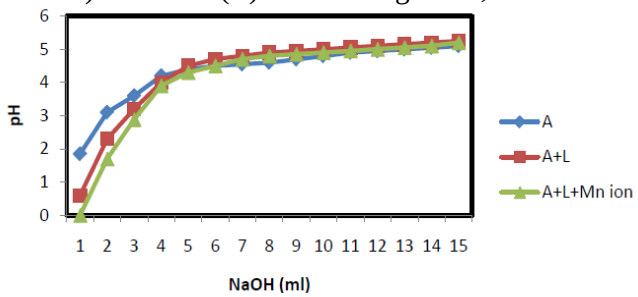


Fig.3. System Mn^{+2}-ligand[2-oxo-2H-chromene-3-carbohydrazide] pH metric titration

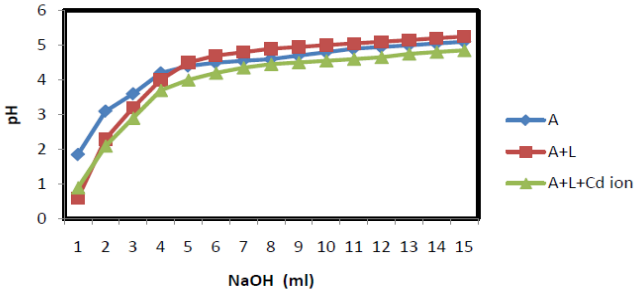


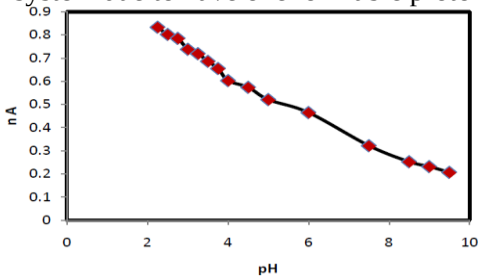
Fig.4. System Cd^{+2}-ligand[2-oxo-2H-chromene-3-carbohydrazide] pH metric titration

The average number of the protons associated $\tilde{n}_A$ at different pH values was calculated from the titration curves by Iriving and Rossotti equation (Maldhure, 2012):

$$\tilde{n}_A = Y - \frac{(V_1 - V_2)(N^0 - E^0)}{(V_0 + V_1)T^0\, CL} \qquad (1)$$

Where N^0 = is the concentration of NaOH (0.15N), E^0 = the concentration of HCl (0.1N), V^0 = the total volume (50ml), T^0cl = the concentration of ligand [2-oxo-2H-chromene-3-arbohydrazide] (0.002N), V_1 and V_2 = the volume of (0.15N) NaOH calculated by (0.1N) HCl and (0.002N) ligand [2-oxo-2H-chromene-3- carbohydrazide] on the same pH, Y = the number of dissociable protons from the ligand.

Thus, proton-ligand system was found between 0.2-0.8 in $\tilde{n}_A$ scale, this means that $\tilde{n}_A$ values decreased with increasing pH of the solution system due to have one ionizable proton (fig.5).



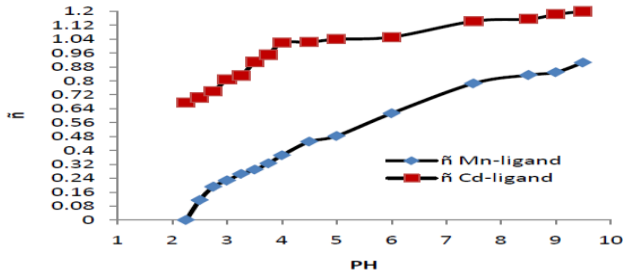
Ph	n A
2.25	0.832
2.5	0.801
2.75	0.784
3	0.737
3.25	0.718
3.5	0.685
3.75	0.654
4	0.602
4.5	0.573
5	0.52
6	0.464
7.5	0.321
8.5	0.252
9	0.231
9.5	0.206

Fig.5. The relationship between $\tilde{n}_A$ and pH for the ligand [2-oxo-2H-chromene-3-carbohydrazide]

The metal-ligand formation number ñ fig.6, was given by calvin-bjerrums equation (Nimbalkar, 2012):

$$\tilde{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2)\, \tilde{n}A\, T^0 CM} \qquad (2)$$

Where, T^0_{CM} = the total concentration of Cd^{+2} and Mn^{+2} ion (0.002N), V^0 = the total volume (50 ml), V_2 = the volumes of (0.15N) NaOH calculated by (0.002N) organic ligand, V_3 = the volumes of (0.15N) NaOH calculated by (0.002N) Cd^{+2} and (0.002N) Mn^{+2}.



ph	ñ Cd-ligand	ñ Mn-ligand
2.25	0.677	0
2.5	0.704	0.113
2.75	0.741	0.19
3	0.807	0.226
3.25	0.83	0.264
3.5	0.91	0.29
3.75	0.95	0.325
4	1.02	0.372
4.5	1.023	0.45
5	1.04	0.483
6	1.053	0.613
7.5	1.144	0.786
8.5	1.156	0.833
9	1.183	0.85
9.5	1.2	0.906

Fig.6. The relationship between ñ and pH for the Mn^{+2}-ligand and Cd^{+2} -ligand

The proton-ligand stability constant (PK) and metal-ligand stability constant were estimation using point wise method. The volume of PK_1 and PK_2 were expression by the following equations:

For mono basic: $PK_1 = \log \frac{\tilde{n}A}{1-\tilde{n}A} + PH$ . . . .(0.2-0.8 = $\tilde{n}_A$)…(3)

For di basic: $PK2 = \log \frac{\tilde{n}A - 1}{2-\tilde{n}A} + PH$ . . . .(1.2-0.8 = $\tilde{n}_A$)…(4)

Since we get $\tilde{n}_A$ between 0.2-0.8 indicating (1:1) complex formations. Table.1, shows PK_1 and logk for the proton-ligand stability constant values decreases with increase temperatures.

Table.1. Proton-ligand stability constant PK_1 and $logk_1$ for the ligand [2-oxo-2-Hchromene-3-carbohydrazide]

Ligand [2-oxo-2H-chromene-3-carbohydrazide]	298.15 k		308.15k		318.15k	
	PK_1	$Logk_1$	PK_1	$Logk_1$	PK_1	$Logk_1$
	0.330	2.138	0.275	1.886	0.211	1.629

Table.2, shows the values of logk1 for Mn^{+2}-ligand which indicate that the range of the ñ values between 0.2-0.8, this suggest that the Mn^{+2} form (1:1) complex in solution, but logk1 and logk2 for Cd^{+2}-ligand indicate that the range of the ñ values between 0.2-0.8 and 1.2-1.8 this suggest that Cd^{+2} ion form (1:1) and (1:2) complexes with the ligand [2-oxo-2H-chromene-3-arbohydrazide] and the values of stability constant for the same complexes decreases with an increase in temperature, thus rise in temperature is not good for the complex formation in these system.

Table.2. The stability constant logk1 for Mn^{+2}-ligand and logk1 and logk2 for Cd^{+2}-ligand

	$logk_1$			$logk_2$		
complex	298.15k	308.15k	318.15k	298.15k	308.15k	318.15k
Mn^{+2}-ligand	3.009	2.680	2.271	-	-	-
Cd^{+2}-ligand	3.645	3.355	2.975	2.943	2.617	2.321

Thermodynamic Study: The thermodynamic parameters such as △G, △H and △S for the ligand [2-oxo-2H-chromene-3-arbohydrazide] and it is complex with Mn^{+2} and Cd^{+2} were determined. The free Gippes energy of the ligand and complexes is calculated by the following equation:

△G = -2.303RTlogk…(5)

The enthalpy △H was calculated from Van't Hoff equation by plot logk versus 1/T using graphical representation as shown in fig.7:

Slope = $\frac{\triangle H}{2.303\ R}$ …… (6)

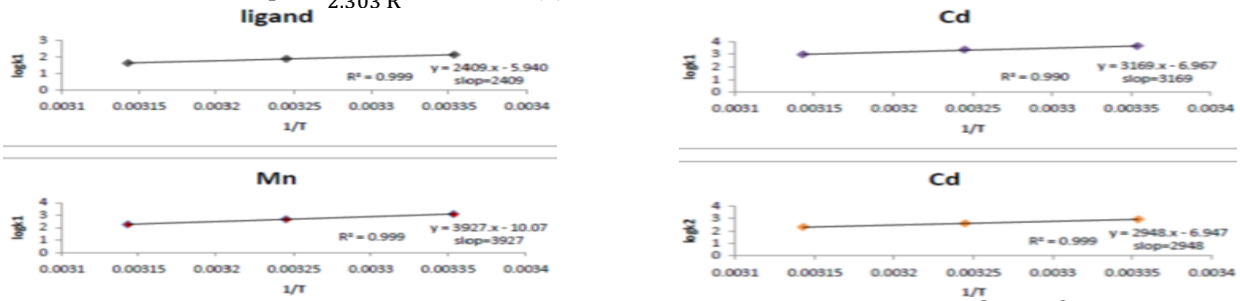


Fig.7. Van't Hoff plot logk1 and logk2 of ligand and it is complexes with Mn^{+2} , Cd^{+2} against 1/T

The changes in entropy △S for the ligand and it is complex is done by the following equation:

△G = △H - T△S….(7)

Table.3. Thermodynamic parameters for ligand and its complexes

compound	T (K)	Gibbs energy change (J. mol^{-1})		Enthalpy change (J. mol^{-1})		Entropy change (J. mol^{-1}. K^{-1})	
		$-\triangle G_1$	$-\triangle G_2$	$\triangle H_1$	$\triangle H_2$	$\triangle S_1$	$\triangle S_2$
ligand	298.15	9350.883	-	55603.300		155.131	-
	308.15	9357.704	-			150.079	-
	318.15	9314.153	-			145.494	-
Mn^{+2}-ligand	298.15	17695.189	-	75190.826		192.841	-
	308.15	15812.396	-			192.693	-
	318.15	13827.972	-			192.873	-
Cd^{+2}-ligand	298.15	20808.459	16983.443	60677.292	56445.770	133.720	132.357
	308.18	19794.996	15440.801			132.671	133.068
	318.15	18122.563	14138.750			133.756	132.978

The values in table.5, of the thermodynamic parameters are found that the process of formation of ligand [2-oxo-2-Hchromene-3-carbohydrazide] and it is complexes is exothermic and spontaneous.

4. CONCLUSION

The sensitive, accurate and precise potentiometric method was shown PKa values for proton-ligand stability constants was decreased with increased temperatures.

(logk1) for Mn^{+2}-ligand complex and (logk1 and logk2) for Cd^{+2}-ligand complex values were decreased with an increased in temperatures, thus rise in temperatures is not good for the complex formation in these system. The proposed method was shown. The interaction process between the ligand [2-oxo-2H-chromene-3-carbohydrazide] and metal ions (Mn^{+2} and Cd^{+2}) is exothermic and spontaneous.

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