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RESEARCH ARTICLE

POTENTIOMETRIC AND THERMODYNAMIC STUDIES OF [2-OXO-2H-CHROMENE-3-CARBOHYDRAZIDE] AND ITS METAL COMPLEXES

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ABSTRACT

In this research work the proton-ligand dissociation constant of [2-oxo-2H-chromene-3-carbo hydrazide] and metal-ligand stability constants of its complexes with metal ions (Ni^{+2} and Cu^{+2}) have been determined potentiometrically at 298, 308 and 318 K. The stability constants of the formed complexes increased in the order: $Ni^{+2} > Cu^{+2}$. The effect of temperature was studied and the thermodynamic parameters (ΔH, ΔS and ΔG) were derived and discussed. The dissociation process was endothermic and spontaneous. The formation of the metal complexes has been found to be spontaneous and endothermic.

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INTRODUCTION

The benzopyrones are a group of compounds whose members include coumarins and flavonoids. Dietary exposure to a benzopyrone is quite significant, as these compounds are found in vegetable, fruits, seeds, nuts, coffee and tea. It is estimated that the average western diet contains approximately 1 g / day of mixed benzopyrones (Lacy *et al*., 2004). Coumarin was first isolated in 1820 by vogel from the seeds of Tonka beans (coumarouna adorata) (Jain *et al*., 2012). Coumarin and its derivatives represent one of the most active classes of compounds possessing a wide spectrum of biological activity (Al-Haiza *et al*., 2005). The synthesis and biological activities of coumarin derivatives occupy an important position in heterocyclic chemistry as well as in medical chemistry. The compounds containing this heterocyclic motif are widely found as additives in food, cosmetic products, as pharmaceutical agents and as luminescent materials (Osman *et al*., 2012). In addition, their enzyme inhibition properties, antimicrobial and antioxidant activities (Borges *et al*., 2005). The transition metals have tendency to form co-ordination compounds with Lewis bases with groups which are able to donate an electron pair.

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Their chelating characteristics have long been observed and the bacteria static activity seems to be due to this chelating. The physic chemical studies of coumarins with chelating group at appropriate position and their metal complexes reveal that the ligand can be used as potential analytical reagents (VYAS *et al*., 2009).

MATERIALS AND METHODS

Materials

A ligand [2-oxo-2H-chromene-3-carbo hydrazide] (Figure 1) was prepared by refluxing a mixture of hot solution of [coumarin-3-ethyl carboxylate] (1mmol) and aqueous hydrazine (purity 99%) in ethanol (purity 99%) for two hours. The formed solid product was separated by filtration, purified by crystallization, washed with ethanol (purity 99%) and dried (Bayader, 2009)

Procedure

A ligand solution (0.001M) was prepared by dissolving an accurately weighed amount of the solid in ethanol. Metal ions solutions (0.0002M) were prepared from metal (Ni^{+2} and Cu^{+2}) in distilled water. Solutions of (0.001M) HCl and (1M) KCl were also prepared in distilled water. Sodium hydroxide solution in 30% (by volume) ethanol-water mixture was used as titrant.

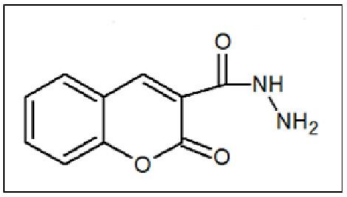

Figure 1. The structure of ligand

The apparatus, general conditions and methods of calculation were the same as in previous work. The following mixtures (i), (ii) and (iii) were prepared and titrated potentiometrically at 298K against standard (0.004M) NaOH in 30% (by volume) ethanol-water mixture:

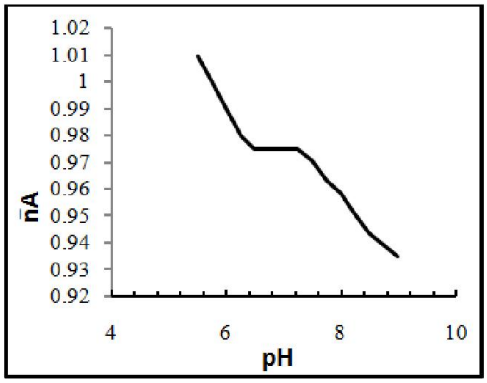

Figure 2. The relationship between n_A and pH

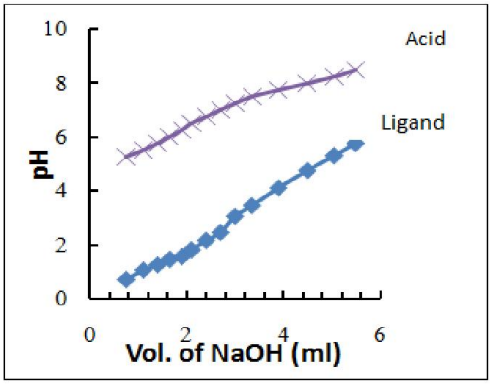

Figure 3. Potentiometric titration curve for acid and ligand in 30% ethanol-water mixture 298K

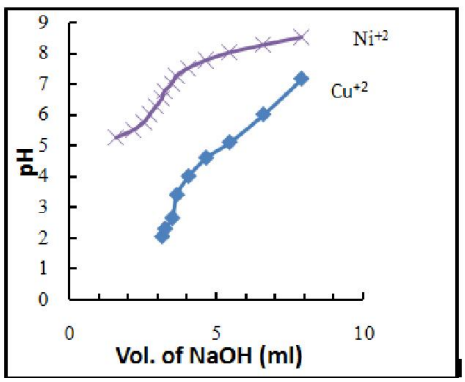

Figure 4. Potentiometric titration curve for Ni^{+2} and Cu^{+2} in 30% ethanol-water mixture at 298K

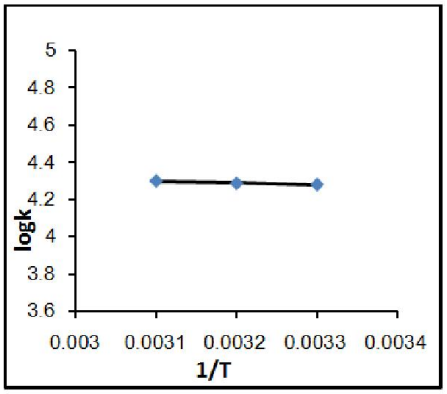

Figure 5. Van't Hoff plot logk of ligand against 1/T

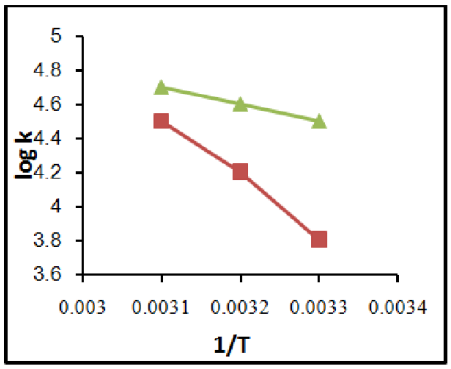

Figure 6. Van't Hoff plot logk of complexes against 1/T

- 5ml 0.001M HCl + 5ml 1M KCl + 20ml ethanol + 20ml water
- 5ml 0.001M HCl + 5ml 1M KCl + 5ml 0.001M ligand +15ml ethanol + 20ml water.
- 5ml 0.001M HCl + 5ml 1M KCl + 5ml 0.001M ligand + 5ml 0.0002M metal ion + 15ml ethanol +15ml water.

For each mixture, the volume was made up to 50ml before the titration (Mittal *et al*., 2010). These titrations were repeated for temperatures of 308 and 318K. The temperature was controlled by (magnetic stirrer RH basic). The pH measurements were performed with (pH-meter HANA) equipped with a combined electrode.

RESULTS AND DISCUSSION

The average number of the protons associated with ligand [2-oxo-2H-chromene-3-carbohydrazide] at different pH value, n_A was calculated from the titration curves of the acid in the absence and presence of ligand apply equation 1 :

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

where Y is the number of available protons in ligand (Y =1), V_1 and V_2 are the volume of alkali required to reach the same pH on the titration curve of hydrochloric acid and organic ligand, V_0 is the initial volume (50ml) of the mixture, T_{CL}^0 is the concentration of ligand, N^0 is the normality of sodium hydroxide solution and E^0 is the concentration of free acid (El-Sonbati *et al*., 2014).

Table 1. The dissociation constants of ligand in 30% ethanol-water mixture at different temperatures

pH	298(K)		_308(K)		318(K)	
	n_A	log k_2	n_A	log k_2	n_A	log k_2
5.25	1.0049	2.307	1.0148	3.427	1.0248	3.45
5.5	1.0048	2.316	1.0148	3.677	1.0049	3.193
5.75	1.014	1.847	0.99	3.746	0.995	3.447
6	1.0096	2.013	0.99	3.996	0.985	4.17
6.25	1.033	1.466	0.98	4.543	0.975	4.638
6.5	1.028	1.54	0.98	4.793	0.975	4.888
6.75	1.0238	1.612	0.98	5.043	0.975	5.138
7	1.0237	1.614	0.985	5.17	0.975	5.388
	Average $logk_2$=4.285		Average $logk_2$=4.299		Average $logk_2$=4.31	

Table 2. The dissociation constants of ligand in 30% ethanol-water mixture at different temperatures

	298(K)		308(K)		318(K)	
pH	n_A	log k_1	n_A	log k_1	n_A	log k_1
7.25	0.995	9.575	0.99	9.245	0.980	8.953
7.5	0.99	9.527	0.98	9.19	0.971	9.024
7.75	0.981	9.474	0.975	9.341	0.966	9.206
8	0.9771	9.63	0.97	9.509	0.961	9.396
8.25	0.9773	9.884	0.971	9.774	0.951	9.545
8.5	0.9775	10.137	0.971	10.024	0.947	9.753
8.75			0.961	10.141	0.942	9.964
9			0.952	10.297	0.937	10.178
	Average $logk_1$=9.65		Average $logk_1$=9.69		Average $logk_1$=9.502	

Table 3. The stability constants of Ni^{+2}- ligand in 30% ethanol-water mixture at different temperatures

pH	298(K)			308(K)			318(K)		
	n	$logk_1$	$logk_2$	n	$logk_1$	$logk_2$	n	$logk_1$	$logk_2$
5.25	0.441	7.804	2.353	0.073	7.932	3.353	0.1	7.925	3.205
5.5	0.56	7.985	2.396	0.121	8.17	3.362	0.245	8.133	2.989
5.75	0.625	8.185	2.529	0.199	8.398	3.355	0.247	8.383	3.235
6	0.625	8.435	2.779	0.198	8.649	3.608	0.248	8.632	3.482
6.25	0.657	8.657	2.968	0.25	8.882	3.728	0.2	8.897	3.853
6.5	0.633	8.928	3.264	0.2496	9.133	3.98	0.199	9.146	4.103
6.75	0.515	9.264	3.724	0.2491	9.382	4.23	0.199	9.397	4.354
7	0.47	9.539	4.053	0.247	9.633	4.485	0.198	9.648	4.608
7.25	0.284	9.87	4.652	0.269	9.877	4.685	0.223	9.89	4.793
7.5	0.283	10.12	4.904	0.271	10.126	4.93	0.224	10.14	5.04
7.75	0.258	10.379	5.209	0.2972	10.365	5.124	0.224	10.39	5.29
8	0.327	10.604	5.314	0.2979	10.615	5.373	0.225	10.522	5.478
8.25	0.601	10.705	5.073	0.296	10.865	5.625	0.226	10.889	5.785
8.5	0.986	10.527	3.653	0.295	11.116	5.878	0.201	11.147	6.1
	Average $logk_1$=9.357			Average $logk_1$=9.51			Average $logk_1$=9.51		
	Average $logk_2$=3.776			Average $logk_2$=4.408			Average $logk_2$=4.451		

Thus, the formation curve (n_A versus pH) (Figure 2) for the proton ligand system was constructed and found to extend between 0 and 1 in the n_A scale, this means that ligand have one ionizable proton (El-Bindary *et al*., 2013). The curves in (Figures 3 and 4) were analyzed and the successive metal – ligand stability constants (log k_1 and log k_2) were determined using different computational methods.

The dissociation constant (log k^H) for ligand as well as the stability constants of its complexes with (Ni^{+2} and Cu^{+2}) has been evaluated at 298, 308 and 318K, are given in (Tables 1, 2, 3 and 4). The average number of the reagent molecules attached per metal ion (n), can be calculated using equation 2:

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2)\, n_A\, T^0_{CM}} \quad \ldots 2$$

Where T^0_{CM} is the total concentration of the metal ion present in the solution, V_2 and V_3 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid, organic ligand and complex, respectively (Askar *et al*., 2010).

Table 4. The stability constants of Cu^{+2}- ligand in 30% ethanol-water mixture at different temperatures

pH	298(K)			308(K)			318(K)		
	n	$logk_1$	$logk_2$	n	$logk_1$	$logk_2$	n	$logk_1$	$logk_2$
5.25	0.294	7.866	2.631	0.024	7.943	3.852	0.087	7.928	3.271
5.5	0.389	8.079	2.697	0.097	8.187	3.479	0.172	8.156	3.183
5.75	0.408	8.32	2.912	0.1244	8.419	3.598	0.173	8.405	3.43
6	0.409	8.569	3.16	0.124	8.669	3.85	0.174	8.655	3.677
6.25	0.258	8.879	3.709	0.15	8.912	4.003	0.15	8.912	4.004
6.5	0.258	9.129	3.959	0.1497	9.162	4.255	0.149	9.162	4.257
6.75	0.234	9.387	4.266	0.1494	9.412	4.506	0.124	9.419	4.6
7	0.186	9.65	4.642	0.148	9.662	4.76	0.124	9.669	4.85
7.25	0.449	9.8	4.339	0.147	9.913	5.013	0.148	9.912	5.011
7.5	0.33	10.103	4.808	0.148	10.162	5.26	0.149	10.162	5.257
7.75	0.117	10.421	5.628	0.1734	10.405	5.429	0.149	10.412	5.507
8	0.163	10.658	5.711	0.1738	10.655	5.678	0.150	10.662	5.754
8.25	0.323	10.856	5.572	0.1731	10.905	5.93	0.151	10.912	6
8.5	0.573	10.986	5.373	0.1971	11.148	6.11	0.151	11.162	6.25
	Average logk1=9.43			Average logk1=9.53			Average logk1=9.54		
	Average logk2=4.27			Average logk2=4.694			Average logk2=4.646		

Table 5. Thermodynamic functions for ligand and its complexes

Compound	T(K)	Gibbs energy change (kJ . mol^{-1})		Enthalpy change (kJ . mol^{-1})		Entropy change (kJ . mol^{-1} . K^{-1})	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Ligand	298	55.061	24.449			251.59	117.379
	308	57.145	25.352	19.913	10.53	250.188	116.5
	318	57.478	26.181			243.367	115.443
Ni^{+2}	298	53.389	21.545			246.620	297.177
	308	51.713	25.995	20.104	67.014	233.172	301.977
	318	57.898	27.101			245.289	295.959
Cu^{+2}	298	58.262	29.151			240.483	218.614
	308	56.254	27.682	13.402	35.996	226.155	206.746
	318	58.068	28.288			224.748	202.150

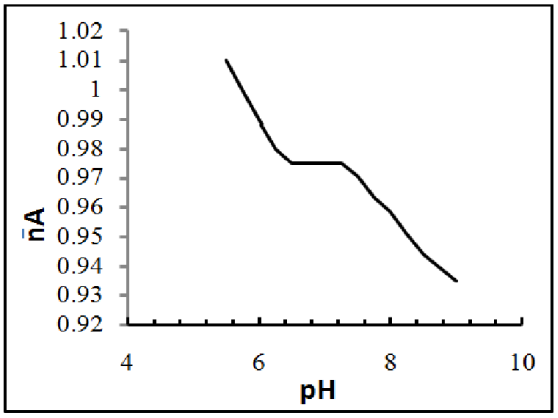

Figure 2. The relationship between $\bar{n}_A$ and pH

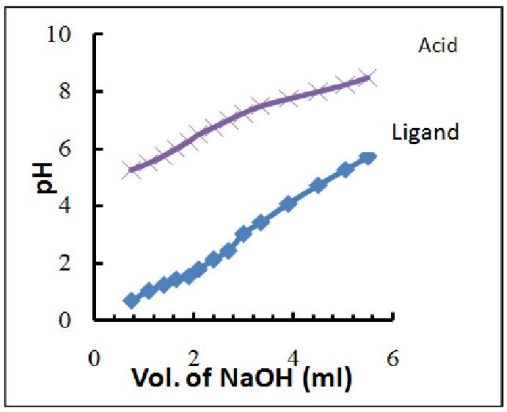

Figure 3. Potentiometric titration curve for acid and ligand in 30% ethanol-water mixture 298K

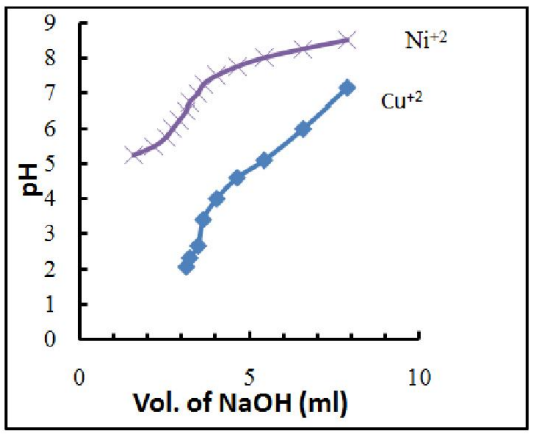

Figure 4. Potentiometric titration curve for Ni^{+2} and Cu^{+2} in 30% ethanol-water mixture at 298K

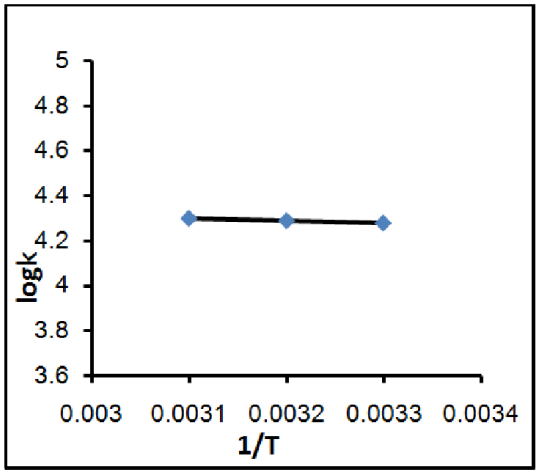

Figure 5. Van't Hoff plot logk of ligand against 1/T

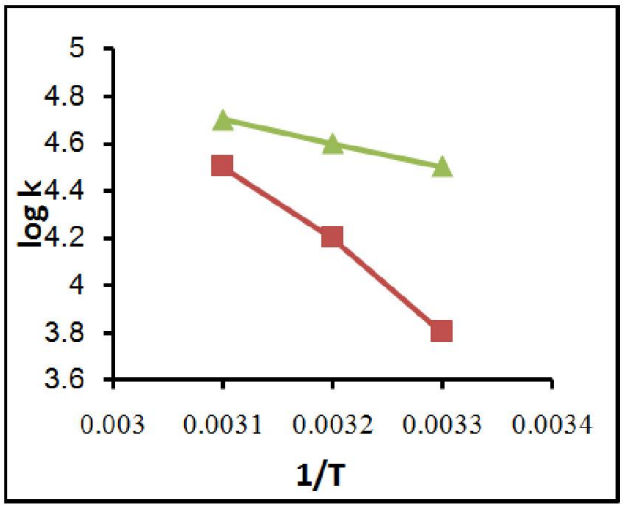

Figure 6. Van't Hoff plot logk of complexes against 1/T

The stepwise stability constants (log k_1 and log k_2) for the complexes increase with increasing temperature in the order:

Ni^{+2} The enthalpy (ΔH) for the dissociation and complexation process was calculated from the slope of the plot log k versus 1/T using the graphical representation of Van't Hoff equation (3)

$$\log k = \frac{\Delta H}{2.303\ R\ T} \quad ....3$$

The change in free energy (ΔG) can be calculated from the equation (4):

$$\Delta G = - 2.303\ R\ T \log k \quad ....4$$

And it can calculate the change in entropy (ΔS) from the relationship between (ΔH and ΔG) which represented by the Following equation (5) (Al-Shihri *et al*., 2004):

$$\Delta G = \Delta H - T\ \Delta S \quad ....5$$

Table (5) showed the thermodynamic functions for the ligand and its complexes: From the values of thermodynamic functions showed that the dissociation process of ligand is endothermic and spontaneous and the formation of the metal complexes has been found to be spontaneous and endothermic.

Conclusion

The interaction process between the ligand [2-oxo-2H-chromene-3-carbo hydrazide] and metal ions (Ni^{+2} and Cu^{+2}) is spontaneous and endothermic. Potentiometrically the stability constants of metal complexes were increased with increasing the temperature

Acknowledgments

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