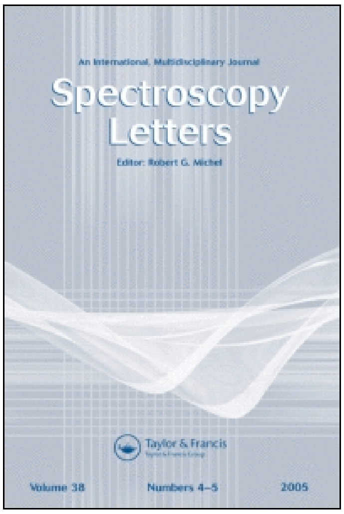

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Thermodynamics of substituted coumarin VII: Potentiometric and spectrophotometric studies of 1-acetyl-2-(coumarin-iminecarboxamide-3-yl) hydrazine transition metal complexes

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Thermodynamics of substituted coumarin VII:

Potentiometric and spectrophotometric studies of 1-acetyl-2-(coumarin-iminecarboxamide-3-yl) hydrazine transition metal complexes.

Keywords. 1-acetyl-2-(coumariniminecarboxamide-3-yl) hydrazine; dissociation and stability constants; thermodynamic functions.

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Abstract.

The dissociation constant of 1-acetyl-2-(coumariniminecarboxamide-3-yl) hydrazine (ACCH) has been determined potentiometrically in 0.1 M KCl and 40% (v/v) ethanol-water mixture. The stepwise stability constants of the formed complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} with ACCH have been determined. The stability constants were found to $UO_2^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$. The effect of temperature on the dissociation of ACCH and the stability of its formed complexes were studied. The corresponding thermodynamic functions were also determined and discussed. The spectral data of ACCH were investigated in pure organic solvents as well as in Britton Robinson buffer solutions of varying pH values. The dissociation constant pK_1^H of ACCH and the overall stability constants logβ of their complexes were determined in 20% (v/v) ethanol-water mixture at 298K.

1. Introduction

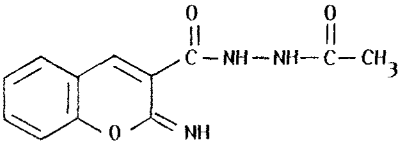
Coumarin compounds are of a large family of organic compounds having a lactone structure and extensively used in many fields. The parent coumarin is a naturally occuring constituent of many plants. It is mainly used as a substitute for vanillin in pharmaceutical preparations [1] and it has been used extensively as a flavoring material. Its metabolism in rats and rabbits has been investigated [2-4]. Moreover, Cu^{2+}, Co^{2+} and Ni^{2+} are present in all healthy tissue in man and their roles are of utmost importance.

Although an extensive work has been done on coumarin derivatives, no potentiometric or spectrophotometric work has apparently been carried out with an acetylhydrazide moiety. Furthermore, nothing about the thermodynamics of ACCH and its complexes with metal ions has been cited in the literature. In continuation of our earlier work [5-9] on the metal complexes in solution, we report herein the dissociation constant of ACCH, and the stability constants for its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} at different temperatures are determined potentiometrically and spectrophotometrically. The corresponding thermodynamic functions are derived and discussed. Moreover, the stoichiometries of these complexes are determined applying the continuous variation method.

2. Experimental

2.1. Preparation of the ligand

1-acetyl-2-(coumariniminecarboxamide-3-yl)hydrazine was prepared as mentioned previously [10]. The compound has the general structure:



2.2. Reagents and materials

Metal ion solutions (0.001 M) were prepared from AnalaR metal chloride in bi-distilled water and standardized with EDTA [11]. The ligand solution (0.01 M) was prepared by dissolving the accurate weight of the solid in ethanol (AnalaR). Solutions of 1 M KCl was also prepared in bi-distilled water. A carbonate-free sodium hydroxide solution in 40% (v/v) ethanol-water mixture was used as titrant and standardized against AnalaR oxalic acid.

2.3. Apparatus and procedures

The apparatus, general conditions and methods of calculation were the same as in the previous work [6-9]. The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.01 M NaOH in 40% (v/v) ethanol-water mixture:

1- 5 ml 0.001 M HCl + 5 ml 1 M KCl + 20 ml ethanol.

2- 5 ml 0.001 M HCl + 5 ml 1 M KCl + 15 ml ethanol + 5 ml 5 x 10^{-3} M ligand.

3- 5 ml 0.001 M HCl + 5 ml 1 M KCl + 15 ml ethanol + 5 ml 5 x 10^{-3} M ligand + 5 ml 5x10^{-4} M metal salt.

For each mixture the volume was made up to 50 ml with bi-distilled water before the titration. These titrations were repeated for temperatures of 308 and 318 K. A constant temperature was adjusted to ±0.05 K by using an ultrathermostate (Neslab 2 RTE 220). The pH-meter readings in 40% (v/v) ethanol-water mixture are corrected according to the Van Uitert and Hass relation [12].

3. Results and discussion

3.1. Potentiometric studies

Proton-ligand dissociation and metal-ligand stability constants of ACCH with Mn^{2-}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} were calculated potentiometrically in 40% (v/v) ethanol-water mixture and 0.1 M KCl. The proton-ligand formation number, $\bar{n}_A$, was calculated by the method of Irving and Rossotti [13] and used to draw the proton-ligand formation curve. Various computational methods [14, 15] were applied to determine the value of the proton-ligand stability constant. The average values obtained are listed in Table 1.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) versus the free ligand exponent (pL). Various computational methods [14, 15] were applied to determine the stepwise metal-ligand stability constants. The values of stability constants (log K_1, log K_2 and log K_β) as well as the ratio log K_1/log K_2 are given in Table 2.

Table (1) : Thermodynamic functions for the dissociation of ACCH in 40 % (v/v) ethanol-water mixture and 0.1 M KCl at different temperatures.

Temp. (K)	Dissociation constant pK_1^H	Free Energy Change (k J mol^{-1}) ΔG_1	Enthalpy Change (k J mol^{-1}) ΔH_1	Entropy Change (J mol^{-1} K^{-1}) ΔS_1
298	6.30	35.90		
308	6.17	36.40	20.00	53.4 ± 0.1
318	6.07	37.0		

Table (2) : Stepwise stability constants for ML and ML_2 complexes of ACCH in 40 % (v/v) ethanol-water mixture and 0.1 M KCl at different temperatures.

M^{n+}	298 K				308 K				318 K			
	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$
Mn^{2+}	4.05	3.90	7.90	1.05	4.18	4.00	8.18	1.05	4.31	4.13	8.44	1.04
Co^{2+}	4.25	4.20	8.40	1.02	4.37	4.30	8.67	1.02	4.50	4.45	9.10	1.02
Ni^{2+}	4.40	4.29	8.69	1.03	4.53	4.39	8.92	1.03	4.66	4.52	9.18	1.03
Cu^{2+}	4.50	4.55	9.15	1.01	4.75	4.65	9.40	1.02	4.90	4.80	9.70	1.02
Zn^{2+}	4.44	4.33	8.77	1.03	4.56	4.45	9.01	1.02	4.68	4.57	9.25	1.02
UO_2^{2+}	4.75	4.65	9.43	1.03	4.84	4.75	9.59	1.02	4.98	4.90	9.88	1.02

The following general remarks can be pointed out:

(1) The maximum value of $\bar{n}$ was ≅ 2 indicating the formation of both ML and ML_2 complexes.

(2) For all complexes formed $\log K_1 > \log K_2$ because the vacant sites of the metal ions are more freely available for the binding of a first ligand than for a second one.

(3) No precipitate was observed in the titration vessel, indicating that the possibility of formation of metal hydroxide is excluded.

(4) The order of the stability constants of the metal complexes of ACCH was found to be $UO_2^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$. This order is in a good agreement with the order observed by Mellor and Maley [16] and by Irving and Williams [17].

The sequence of stability ($Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$) of the complexes of ACCH are in agreement with that found by Irving and Williams [18, 19]. The order largely reflects the changes in the heat of complex formation across the series and arise from a combination of the influence of both polarizing ability of the metal ion [20] and crystal-field stabilization energies [21]. The greater stability of Cu^{2+} complexes is produced by the well known Jahn-Teller effect. The stability constant of the divalent oxygenated cation complex (UO_2^{2+}) has higher value than the other divalent cation complexes (Table 2). This may be attributed to the bonded oxygen atoms which may increase the electrostatic attraction between the metal ion and the coordinated ligands and overcome any steric hindrance offered by the oxygen of the oxygenated cation [22].

3.2. Effect of temperature

The dissociation constant (pK_1^H) for ACCH as well as the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} have been evaluated at 298, 308 and 318 K, and are given in Tables 1 and 2. The slope of the plot pK_1^H or $\log K$ vs. $^{1}/_{T}$ (Fig. 1) was utilized to evaluate

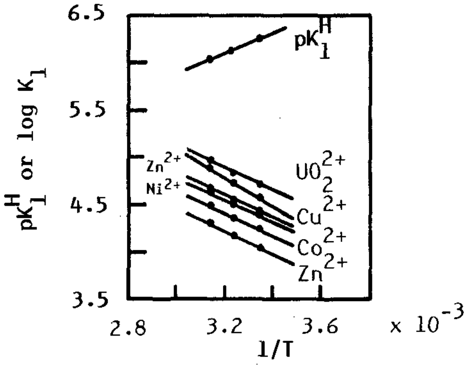


Fig. 1 : Arrhenius plots of pK_1^H of ACCH and log K_1 of M^{n+}-ACCH complexes vs. $^1/_T$.

the enthalpy change (ΔH) for the dissociation or complexation process, respectively.

From the free energy change (ΔG) and (ΔH) values one can deduce the entropy change (ΔS) using the well known relationships (1) and (2):

$$\Delta G = -2.303\, RT \log K = 2.303\, RT\, pK \quad \text{.............. (1)}$$

$$\Delta S = (\Delta G - \Delta H) / T \quad \text{.............................. (2)}$$

All thermodynamic parameters of the dissociation process of ACCH are recorded in Table 1. Inspection of these values reveals that:

(i) The pK_1^H value decreases with increasing temperature revealing that its acidity increases with increasing temperature.

(ii) A positive value of ΔH indicating that its dissociation is accompanied by adsorption of heat and the process is endothermic.

(iii) A large positive value of ΔG indicating that the dissociation process is not spontaneous.

(iv) A negative value of ΔS is obtained, due to increased order as a result of solvation processes.

All the thermodynamic parameters of the stepwise stability constants of ACCH complexes are recorded in Table 3.

It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions:

(a) release of H_2O molecules, and

(b) metal-ligand bond formation.

It was suggested [23] that the ions in aqueous solution, order the water molecules around them and during complex formation between oppositely charged ions (ligand L^- and M^{n+}) will lead to the breakdown of metal-water arrangement resulting in positive entropy and enthalpy changes. Examination of these values shows that:

(i) The stepwise stability constants ($\log K_1$ and $\log K_2$) for ACCH complexes increases with increasing temperature, revealing that the complexation process is favorable at a higher temperature.

(ii) The negative values of ΔG for the complexation process of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} with ACCH suggests a spontaneous nature for such a process.

(iii) The ΔH values are positive. This means that these processes are endothermic and favorable at higher temperatures.

(iv) The entropy values, ΔS, for all complexes are positive, indicating that the disorder of the system increases much more rapidly than the increase in the order taking place in the chelation. This stems from the

Table (3) : Thermodynamic functions ML and ML_2 complexes of ACCH in 40 % (v/v) ethanol-water mixture and 0.1 M KCl.

M^{n+}	Temp.	Free Energy Change (k J mol^{-1})			Enthalpy Change (k J mol^{-1})			Entropy change (J mol^{-1} K^{-1})		
	(K)	$-\Delta G_1$	$-\Delta G_2$	$-\Delta G_\beta$	ΔH_1	ΔH_2	ΔH_β	ΔS_1	ΔS_2	ΔS_β
Mn^{2+}	298 308 318	23.1 24.7 26.2	22.3 23.6 25.1	45.4 48.3 51.3	22.0	21.8	43.8	151.5 (±0.17)	147.6 (±0.2)	299.1 (±0.1)
Co^{2+}	298 308 318	23.7 25.8 27.4	24.0 25.4 27.5	47.7 51.2 54.9	20.5	21.0	41.5	149.8 (±1.96)	151.4 (±0.74)	301.1 (±2.0)
Ni^{2+}	298 308 318	25.1 26.7 28.4	24.5 25.9 27.5	49.6 52.6 55.9	22.6	20.0	42.6	160.2 (±0.1)	149.2 (±0.2)	309.4 (±0.3)
Cu^{2+}	298 308 318	25.7 28.0 29.8	26.0 27.4 29.2	51.7 55.4 59.0	26.1	25.2	51.3	175.1 (±1.3)	171.2 (±0.4)	346.3 (±0.7)
Zn^{2+}	298 308 318	25.3 26.9 28.5	24.7 26.2 27.8	50.0 53.1 56.3	20.9	21.2	42.1	155.2 (±0.1)	154.0 (±0.1)	309.2 (±0.2)
UO_2^{2+}	298 308 318	27.1 28.5 30.3	27.1 28.0 29.8	54.2 56.5 60.1	21.1	21.8	42.9	161.4 (±0.4)	162.7 (±1.0)	324.1 (±1.4)

Error is given between parantheses.

fact that the order of the arrangement of the solvent around the ligand and the metal is lost when the complex is formed.

3.3. Spectrophotometric studies:

The electronic absorption spectrum of ACCH was recorded in organic solvents of different polarities and composed of three sets of bands. The first one (A) near 230 nm is due to the medium energy ($\pi \rightarrow \pi^*$) transition corresponding to the ($^1L_a \rightarrow ^1A$) transition. This band is obscured in the spectra in DMF, $CHCl_3$ and CCl_4 due to the opacity of these solvents in the uv region. The second one (B) in

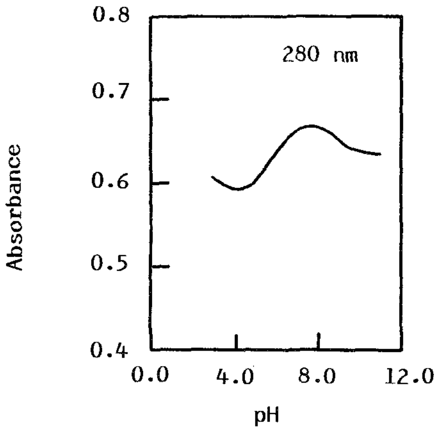


Fig. 2 : The electronic absorption spectra of 5 x 10^{-5} M of ACCH in Britton universal buffer solutions containing 20% (v/v) ethanol-water mixture at 298 K.

the (275-290 nm) region is due to the $\pi \rightarrow \pi^*$ transition corresponding to ($^1L_b \rightarrow {}^1A$) within the aromatic system and its conjugation with the =NH group. The third broad and less intense band (C) around 300 nm can be assigned to the $\pi \rightarrow \pi^*$ transition of the CO group [7].

The spectra of 5x10^{-4} M of ACCH were studied in 20% (v/v) ethanol-water mixture of varying pH values at 298 K. The absorption spectra exhibit a clear isobestic point at 290 nm, suggesting the existence of acid-base equilibrium between the two forms existing in solution.

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

The absorbance-pH curve at 280 nm (Fig. 2) is a typical dissociation curve supporting the hypothesis of an acid-base equilibrium.

Table (4) : Overall stability constants of ACCH complexes in 20% (v/v) ethanol-water mixture by continuous variation method at 298 K..

M^{n+}	UO_2^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
λ_{max}, nm	350	370	360	365	350	350
log β	9.54	9.45	9.24	9.20	9.18	4.05

Therefore, the variation of absorbance with pH is utilized to determine the mean value of pK_1^H using the different spectrophotometric methods [7]. The evaluated pK_1^H value was found to be 5.9 and in fair agreement with the value obtained potentiometrically.

The optimum pH value at which ACCH forms a highly colored complex was found to be 9 for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} stoichiometries. Stability constants of the formed complexes result from measurements in the range 300-400 nm for the complex solutions,with ACCH at the optimum pH values with characteristic absorption maxima. These studies were carried out to investigate the stoichiometries of the formed complexes from continuous variation [24] method. This method indicated the formation of 1:2 (metal:legand) complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+}, whereas 1:1 (metal:legand) complex was obtained with Mn^{2+}. The overall stability constants (log β) were determined applying the continuous variation [24] method at 298 K (Table 4).

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