

Potentiometric Determination of Stability Constants and Thermodynamic Parameters of Complexation Reactions of Some Transition Metal Ions with 6,7-Dihydroxy-4-Methylcoumarin Azo Compounds

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Summary: The acid dissociation constants of some azo compounds based on 6,7-dihydroxy-4-methylcoumarin [namely; 8-arylazo-6,7-dihydroxy-4-methylcoumarin, and the stepwise formation constants of their complexes with Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} have been determined potentiometrically at different temperature, ethanol-water ratio and ionic strengths. The thermodynamic parameters of complexation (ΔG , ΔH and ΔS) have been calculated. The acid dissociation constants (pK) of the ligands were found to decrease with increase of both temperature and ionic strength, whereas they increase with the increase in ethanol content. The overall stability constants of the metal complexes followed Irving-Williams order. Thermodynamic parameters ΔG , ΔH and the majority of ΔS values are negative, indicating the formation of strong complexes with higher order in the molecules.

Keywords: 6,7-Dihydroxy-4-methylcoumarin, thermodynamic functions, potentiometry.

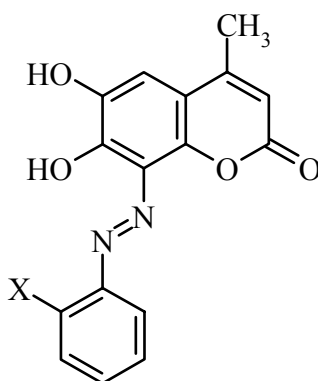
Introduction

6,7-Dihydroxy-4-methylcoumarin (CAS 529-84-0) is used as a good organic chelating agent and a metal indicator for the analytical determination of minute amounts of transition metal ions⁽¹⁾. Also, azo compounds, particularly substituted with hydroxyl groups gained much attention because of their use in analytical and biological systems⁽²⁻⁴⁾. In a previous work⁽⁵⁾, we have prepared some azo compounds based on 6,7-dihydroxy-4-methylcoumarin and their structure was studied spectrophotometrically in addition to their antibacterial activity. Complexes of some transition metal ions with these azo compounds both in solution and solid state were also studied⁽⁶⁾.

In the present study, the results of potentiometric studies on complex formation of 8-arylaazo-6,7-dihydroxy-4-methylcoumarin with some transition metal ions have been reported in different ethanol-water mixtures, at different ionic strength and temperature then the thermodynamic parameters are evaluated.

Experimental

All chemicals used were of the highest purity available. Bidistilled water from all glass equipment was used in all experiments. The azo compounds (I-V) were synthesized as described previously⁽⁵⁾. They have the following general structural formula:



X = H(I), OH(II), COOH(III), NO₂ (IV) and OCH₃(V).

10⁻³ M solutions of the dyes were prepared by dissolving the accurate weights of the recrystallized products in the appropriate volume of pure ethanol. Samples for potentiometric measurements were obtained by accurate dilution. Stock solution of the metal ions (0.01 M) were prepared from their chlorides and standardized by conventional method⁽⁷⁾. Sodium hydroxide (Merck) was dissolved in carbon dioxide-free bidistilled water in a Pyrex beaker. The solution was kept over night in a desiccator over lime then a portion was diluted and its concentration was determined by titration against a standard oxalic acid solution. The required standard solution (0.02 M) was prepared by diluting the stock one. Solutions of 0.1 M perchloric acid and

sodium perchlorate (1.0 M) were also prepared in bidistilled water from their BDH Analar products.

For potentiometric titrations, the following three mixtures were prepared.

- A) 5 mL of 0.5, 0.7 and 1.0 M NaClO_4 + 3 mL of 0.1 M HClO_4 .
- B) Mixture (A) + 20 mL of 10^{-3} M ethanolic ligand solution.
- C) Mixture (B) + 2 mL of 10^{-3} M metal ion solution.

Each mixture was completed to 50 mL with bidistilled water and ethanol so as to obtain the desired ethanol-water ratio (40, 60 and 75% v/v) and then titrated potentiometrically as previously described⁽⁸⁻¹⁰⁾ with 0.02 M NaOH freed from carbonate and containing the same content of ethanol-water ratio to keep the ratio of ethanol in the titration vessel constant. The temperature was maintained constant with the help of a Hooke A 79 thermostat accurate to ± 0.1 °C. The titration double jacket vessel, covered with a card board with two holes, was kept at constant temperature with the aid of water stream circulation having the desired temperature. The electrode was introduced through one hole and the tip of the burette provided with a jet, closed the second hole. The solution was then magnetically stirred and the change in the pH corresponding to the addition of small increments of alkali was measured using Orion pH-meter model 601/A Digital Ionalyzer. The appropriate correction for converting pH-meter reading in mixed solvent medium was made as described by Bates⁽¹¹⁾ using the relation:

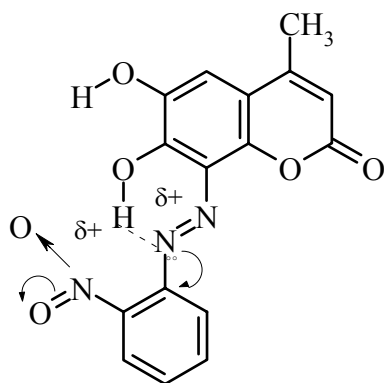
$$\text{pH}(X) = \text{pH}(S) + 0.484$$

Where pH(X) is the operational pH value of a solution (X) and pH(S) is the measured one.

Results and Discussion

Acid dissociation constant in ethanol-water system

Due to the presence of phenolic and substituent groups in their structure, 8-aryl-azo-6,7-dihydroxy-4-methylcoumarin compounds (I-V) behave as weak acids. The protons associated with the ligands naturally dissociate in steps in solution which correspond to two or three dissociation constants. In the present work, the values of pK have been evaluated by calculating n_A at various pH values from the acid and ligand titration curves. The n_A values were then plotted against the corresponding pH and the formation curves so obtained are analyzed to calculate the proton-ligand stability constants. The formation curves of ligands I, IV and V extended from 0 to \cong 2.0 on the n_A scale, indicating their dibasic character, so two proton-ligand stability constants K_1 and K_2 are obtained. The values of both are found to be affected by the nature of substituent (X) where they lie in the order $IV > V > I$ ($X = NO_2 > OCH_3 > H$) which is probably due to the withdrawing effect of NO_2 group which help the breakdown of the hydrogen bonded structure.



On the other hand, proton-ligand formation curves for ligands II and III extended from 0 to \cong 3.0 on the n_A scale indicating the presence of three dissociable hydrogen ions. The values of the third dissociation constant (K_3) follow the order $II > III$ ($X = OH > COOH$). The distribution diagram of the relative population of

protonated species of the acid-base equilibrium versus pH demonstrate the conditions under which only monomers exist (Fig.1).

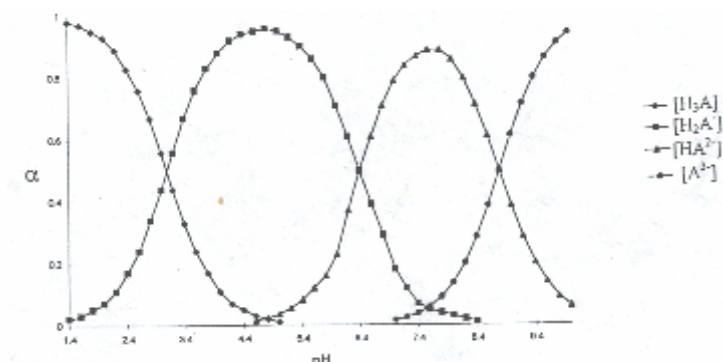


Fig.1: The distribution diagram of the relative population of the different protonated species of ligand III as a function of pH.

Effect of solvent composition on the acid-dissociation constant

At constant temperature (298 K) and constant ionic strength (0.1 M NaClO₄), the acid dissociation constants were determined at three different ethanol-water ratio (40, 60, and 75% v/v). It was found that an increase in the ethanol content causes an increase in the (pK) values which is consistent with the conclusion of Coetzee and Ritchie⁽¹²⁾, who related the acidity constant in pure aqueous media (K) with that in water-organic solvent mixture (K') by the equation:

$$K = K' (\gamma_{H^+} + \gamma_{A^-} / \gamma_{HA})$$

Where γ is the activity coefficient of the subscripted species in a partially aqueous medium to that in a pure aqueous one. It has been also reported that electrostatic effect of solvents operate only on the activity coefficient of charged species[12], so it can be expected that an increase in the amount of ethanol will increase the activity coefficient of both H⁺ and A⁻ ions leading to a decrease in the acid dissociation constant. It is also important to mention that, in addition to the role of electrostatic effect, there must be the effect of hydrogen-bonding interaction between the conjugate base (A⁻) and the solvent molecule. So, the increase in the pK values with increase in ethanol content is expected due to the destabilization of the conjugate base (A⁻) because water molecules

have a higher tendency to form hydrogen bond. This is shown from the plot of pK versus mole-fraction of ethanol, (Fig. 2), where a linear relation is obtained from which the values of the acid dissociation constants are determined at 100 and 0% ethanol by extrapolation, hence the corresponding thermodynamic parameter (ΔG) values are calculated (Table 1).

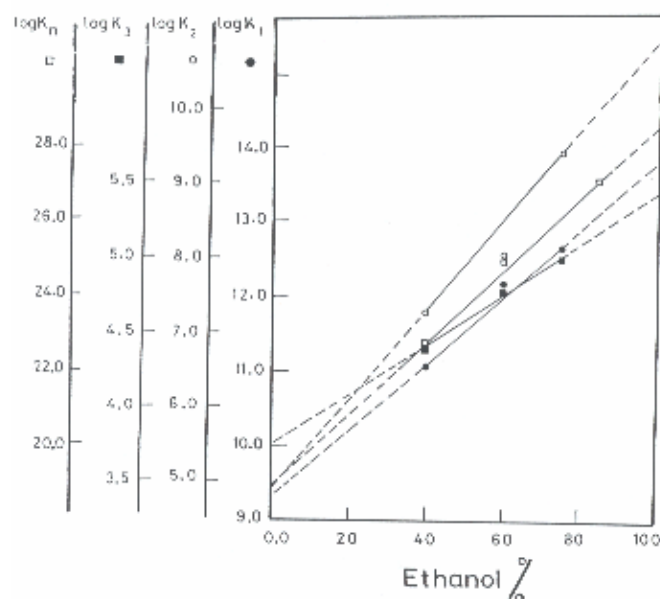


Fig.2: Effect of ethanol ratio on the acid dissociation constant of ligand (III) (0.1 M NaClO_4 , 298 K).

Effect of ionic strength on the acid-dissociation constant

The proton-ligand stability constants of the azo compounds under study were determined at 298 K, 40% v/v ethanol-water ratio and three different ionic strength (0.05, 0.07 and 0.1 M NaClO_4). It is found that an increase in the ionic strength of the medium results in a decrease in the proton-ligand stability constants. The values of the latter at infinitely diluted solution ($\sqrt{\mu} = 0$) and the corresponding free energy change (ΔG) are calculated by extrapolation and are given in (Table 1).

Effect of temperature on the proton-ligand stability constant

In 0.1 M NaClO_4 and 40% v/v ethanol, the acid dissociation constants were determined at four different temperatures (288, 298, 308 and 318 K). The thermodynamic parameters (ΔG , ΔH and ΔS) of the processes are then calculated, the

data are cited in (Table 2). The free energy change (ΔG) and the entropy change (ΔS) are calculated using the relations:

Table (1): Overall acid dissociation constants for ligands I – V at different ethanol ratio and ionic strength.

Ligand	-log K_n^* and ($-\Delta G$)kJ/mole				
	%Ethanol				
	0**	40	60	75	100**
I	14.60 (83.31)	17.15 (97.86)	18.40 (104.99)	19.35 (110.41)	20.90 (119.26)
II	13.60 (77.60)	16.40 (93.58)	17.70 (101.00)	18.73 (106.88)	20.35 (116.12)
III	18.90 (107.85)	22.80 (130.10)	24.80 (141.51)	26.25 (149.79)	28.70 (163.77)
IV	10.25 (58.49)	11.75 (67.05)	12.50 (71.33)	13.08 (74.64)	14.05 (80.17)
V	10.40 (59.34)	12.00 (68.47)	12.80 (73.04)	13.40 (76.46)	14.40 (82.17)
Ligand	M of NaClO ₄				
	0**	0.05	0.07	0.10	
	I	17.95 (102.42)	16.45 (93.87)	15.90 (90.73)	15.00 (85.59)
II	32.50 (185.45)	29.00 (165.48)	27.50 (156.92)	25.40 (144.94)	
III	25.50 (145.51)	23.00 (131.24)	22.00 (125.53)	20.40 (116.40)	
IV	13.58 (77.49)	12.58 (71.87)	12.28 (70.07)	11.60 (66.19)	
V	14.80 (85.45)	13.65 (77.89)	13.20 (75.32)	12.50 (71.33)	

* $K_n = K_1 \cdot K_2 \cdot K_3$

** Values obtained by extrapolation and least square method

$$\Delta G = -2.303 RT \log K$$

$$\Delta S = (\Delta H - \Delta G) / T$$

The enthalpy change (ΔH) was determined from the Arrhenius plot of $\text{p}K$ versus $1/T$.

Table (2): Thermodynamic parameters and overall stability constants of metal complexes with ligands I - V at different temperatures (0.1 M NaClO_4 and 40% v/v ethanol).

Ligand	Cation	-log K_n				Thermodynamic parameters		
		288 K	298 K	308 K	318 K	$-\Delta G^*$	$-\Delta H^*$	ΔS^{**}
I	H^+	17.75	17.15	17.70	16.45	97.86	74.38	78.79
	Mn^{2+}	13.15	12.75	12.45	11.90	72.75	77.33	-15.37
	Fe^{3+}	21.70	20.90	20.20	19.10	119.26	162.20	-43.50
	Co^{2+}	12.10	12.25	11.30	11.60	69.90	147.29	-59.71
	Ni^{2+}	19.20	17.60	17.80	16.30	100.43	169.39	-231.41
	Cu^{2+}	18.15	16.70	16.55	15.10	95.29	184.12	-298.07
II	H^+	19.50	18.30	16.40	15.40	104.42	257.76	-514.57
	Mn^{2+}	22.70	21.20	20.60	19.90	120.97	173.07	-174.83
	Fe^{3+}	33.50	30.70	27.05	25.00	175.18	301.95	-425.40
	Co^{2+}	27.50	26.10	24.30	24.10	148.93	209.89	-204.57
	Ni^{2+}	24.20	23.10	21.80	21.50	131.81	165.71	-113.74
	Cu^{2+}	31.40	29.10	26.90	235.30	166.05	375.60	-703.18
III	H^+	25.75	25.45	23.80	25.00	145.22	47.87	326.68
	Mn^{2+}	22.90	22.20	21.90	21.90	126.68	114.15	42.03
	Fe^{3+}	29.45	25.10	25.40	24.30	143.22	309.32	-557.35
	Co^{2+}	24.90	24.10	22.50	21.70	133.52	154.66	-70.92
	Ni^{2+}	24.90	24.10	22.10	21.90	137.52	276.18	-465.29
	Cu^{2+}	25.50	24.00	22.30	21.00	136.95	272.99	-454.85
IV	H^+	12.30	12.40	11.10	9.90	70.76	224.62	-516.32
	Mn^{2+}	11.10	10.50	10.20	9.80	59.91	115.99	-188.18
	Fe^{3+}	15.20	13.60	13.20	12.40	77.60	173.07	-320.36
	Co^{2+}	13.40	12.70	11.80	10.90	72.47	162.02	-300.52
	Ni^{2+}	13.90	12.80	13.00	11.80	73.04	128.88	-187.39
	Cu^{2+}	17.30	16.00	14.90	17.70	91.30	117.83	-89.05
V	H^+	13.80	13.10	12.10	11.00	74.75	191.48	-391.72
	Mn^{2+}	15.20	15.00	14.40	14.35	85.59	52.29	111.76
	Fe^{3+}	19.60	19.50	19.40	18.05	111.27	18.41	311.60
	Co^{2+}	16.55	16.50	16.20	15.25	94.15	30.93	212.14
	Ni^{2+}	16.20	15.85	14.95	14.05	90.44	112.31	73.39
	Cu^{2+}	18.90	17.40	16.30	15.35	99.29	202.53	-346.45

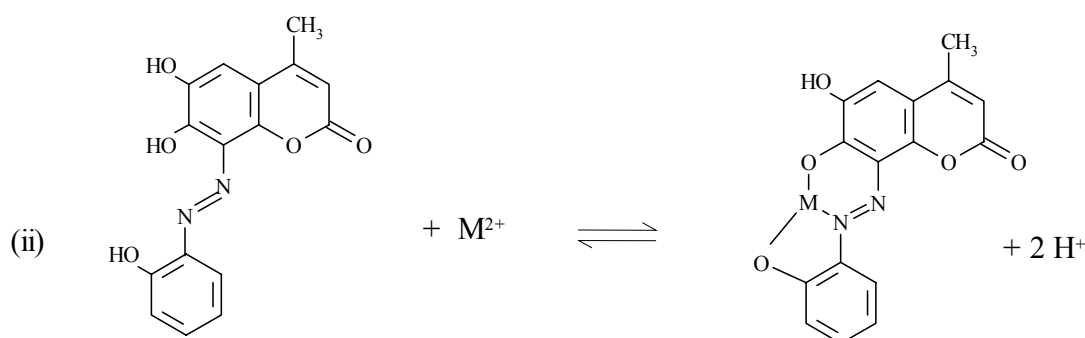
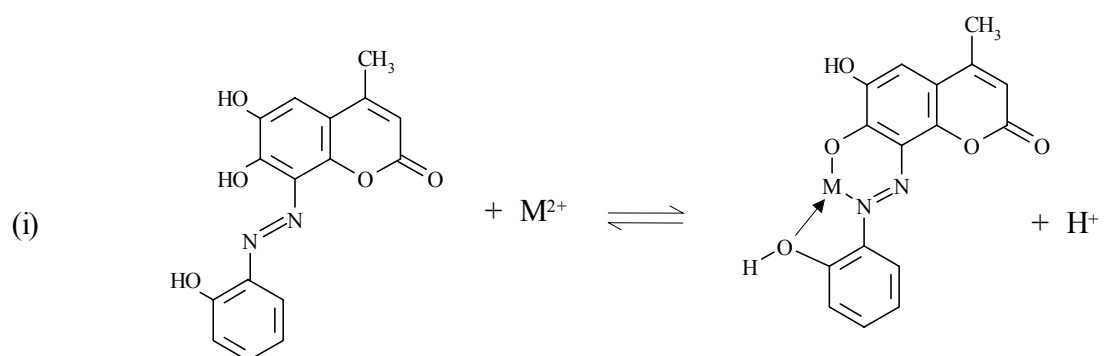
* kJ mol^{-1} at 298 K.

** $\text{J mol}^{-1} \text{ deg}^{-1}$ at 298 K.

Study of the temperature effect on the acid-dissociation constants shows that as the temperature increases, pK_a values decrease. The negative values of both ΔG and ΔH indicate the spontaneous and exothermic nature of the process. It was reported that⁽¹³⁾ intramolecular hydrogen bonding gives rise to a positive entropy change whereas intermolecular hydrogen bonding to solvent leads to higher degree of solvent ordering with a negative entropy change, so the $-\Delta S$ values obtained in the majority of cases can be attributed to the predominance of intermolecular hydrogen bonding. On the other hand, the positive entropy values obtained in some cases indicated that both inter-and intramolecular hydrogen bonding coexist⁽¹⁴⁾.

Metal-ligand stability constants

Examination of the titration curves, (Fig.3), shows that the metal titration curves are well separated from those of the media and the ligands; thus the liberation of protons is due to complexation process which can be represented, for ligand II as an example, as:



Reaction (i) can take place at lower pH values ($\text{pH} < 6$) where only one H^+ is liberated from the ligand, but with increasing pH, complexation process takes place via reaction (ii). It is worthy to mention that, the tendency of complex formation is high enough as it prevents the metal from precipitation as hydroxide (especially for Fe^{3+}) even when the pH of the solution surpasses the pH of hydrolysis.

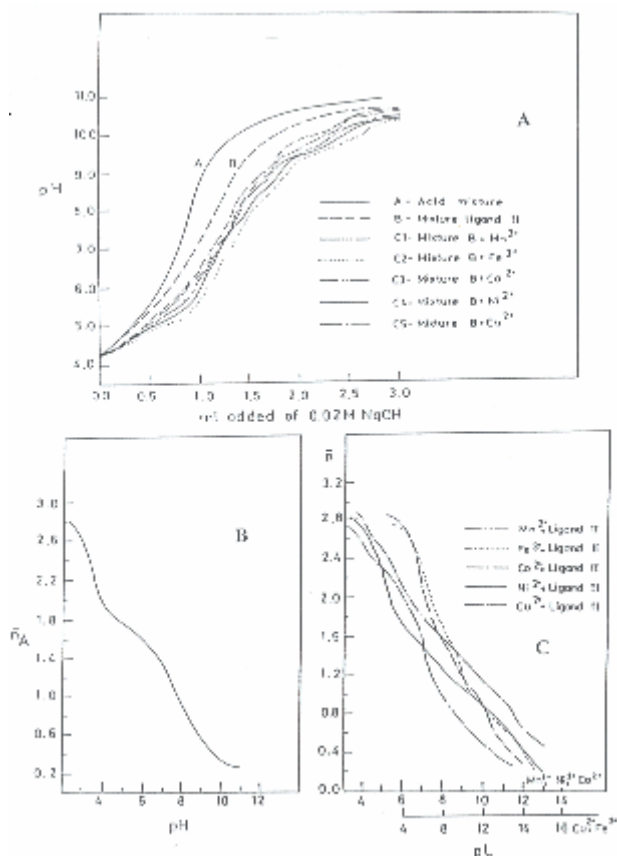


Fig.3 A: potentiometric titration of ligand (II) in presence of Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} at 298 K (40% ethanol, 0.1 M NaClO_4).
 B: Formation curve of proton ligand (II).
 C: Formation curve of: Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} with ligand (II) at 298 K (40% ethanol, 0.1 M NaClO_4)

It was reported that⁽¹⁵⁾, the general trend of the stability constants follow the order; $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. In the present work, for one and the same ligand, the stability trend lies in the order; $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$, thus it is obvious that Irving-Williams rule⁽¹⁶⁾ for the stability of metal complexes is

obeyed from Cu^{2+} to Mn^{2+} . On the other hand, when keeping metal ion constant, the stability is affected by the nature of substituent attached to the phenyl moiety of the ligand molecule, where it follows the order: $\text{II} > \text{III} > \text{IV} > \text{V} > \text{I}$ ($\text{X} = \text{OH} > \text{COOH} > \text{NO}_2 > \text{OCH}_3 > \text{H}$), indicating that the withdrawing nature of the substituent group helps the ionization of the OH in position 7 of the coumarin moiety and hence facilitates the complexation process via reactions (i) and (ii).

Effect of temperature on the metal-ligand stability constant

The metal-ligand stability constants were evaluated at four different temperatures; (288, 298, 308 and 318 K) at 0.1 M NaClO_4 and 40% v/v ethanol. The thermodynamic parameters ΔG , ΔH and ΔS have been also determined, the values are cited in (Table 2). By inspection of the data obtained, it is found that the stability constants decrease with the increase in temperature suggesting the exothermic nature of the complexation process. The negative values of the free energy change (ΔG) indicate the spontaneous nature of the interaction and that metal complexes are thermodynamically stable. Enthalpy changes (ΔH) show also negative values which indicate that metal-ligand bonds are fairly strong and the complexation reaction is exothermic in nature. The majority of entropy changes (ΔS) show also negative values proving the formation of strong complexes with greater order in their molecules.

Effect of ionic strength and solvent ratio on the metal-ligand stability constant

The values of stepwise and overall stability constants of metal-ligand complexes are determined at three different concentration of NaClO_4 (0.05, 0.07 and 0.1 M). The respective values at infinite dilution are obtained by applying the least squares method and by extarapolation, where it is found that an increase in the ionic strength of the medium causes a decrease in the values of metal-ligand formation constant.

On the other hand, the values of the stepwise and overall stability constants show an increase with the increase in ethanol content and linear relationship was obtained when plotting logK values against mole-fraction of ethanol.

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