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THERMODYNAMIC PARAMETERS OF IONIZATION OF KOJIC ACID AND ITS COORDINATING BEHAVIOUR TOWARDS TRANSITION METALS

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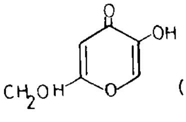
ABSTRACT

The thermodynamic parameters of ionization (pK, ΔG, ΔH and ΔS) of Kojic acid have been evaluated potentiometrically. The pK value decreases with increase in temperature and has a linear relationship with the concentration of dioxane. The process of solvation and aquation is discussed. The mechanism of complexation between Kojic acid and some transition metals is discussed and the log β value is calculated.

INTRODUCTION

Kojic acid (5-hydroxy-(2-hydroxy methyl)-4H-pyron-4-one), **I**, has analytical applications in the determination of many metals [1–12]. Iron–Kojic acid [1–3] has a 1 : 3 stoichiometry at different pH values with pK_1, pK_2 and pK_3 values of −10.16, −8.29 and −6.90. UO_2(II)– and Th(IV)–Kojic acid are pH dependent; the pK_1, pK_2 and pK_3 values for the UO_2–**I** reaction [4] are 0.5, 2.1 and 4.3 respectively. The Mg–Kojic acid reaction has an SN^1 mechanism at 25 °C in the presence of 0.5 M KCl [9]. The Ce^{4+}–Kojic acid reaction has been found to be an oxidation–reduction type [10]. The thermodynamic stabilities of some transition metal Kojate complexes have been reported [11]. The stopped-flow method [12] was applied to the analysis of Kojic acid. The main aims of the present study are to evaluate the thermodynamic parameters of ionization of Kojic acid, the formation constants of some Kojic acid complexes, and to study the phenomena of aquation and solvation [13].



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EXPERIMENTAL

Preparation of solutions

A 10^{-3} M stock solution of Kojic acid was prepared. 10^{-2} M transition metal salts (Fe, Co, Ni and Cu) were prepared and analysed complexometrically in the normal way [14]. The dioxane solvent used was of spectroquality grade.

The potentiometric titration measurements were done using a Beckman model 4500 digital pH-meter (reading to ± 0.002 pH units). The electrode system was calibrated before and after each series of pH measurements by means of standard buffer solutions of pH 4 and 7. The titration runs were carried out in a thermostatted cell under purified nitrogen atmosphere to exclude CO_2 [15]. An Ultrathermostate-U-10, G.D.R. ($\pm 0.1°$C) was used for controlling the temperature. Purified nitrogen gas was slowly bubbled through the solution. An appropriate volume of the organic compound was introduced in the titration cell followed by 3 ml of 0.5 M KCl solution, and the volume was made up to 50 ml with doubly distilled water. The prepared solution was pH-metrically titrated against standard KOH solution. For the complex titration studies, 0.1 ml of 0.01 M metal chloride + 5 ml of 10^{-3} M ligand + 3 ml of 0.5 M KCl + 20 ml dioxane were made up to 50 ml in a measuring flask. The reaction mixture was pH-metrically titrated against standard KOH, at the same temperature as for the free ligand.

The pH-meter readings (B) recorded in 50% v/v dioxane–water solutions were converted to $[H^+]$ by the method of Van Uitert and Haas [16]

$$-\log[H^+] = B + \log U_H \qquad (1)$$

where U_H is the correction factor for the solvent composition and ionic strength for which B is read.

RESULTS AND DISCUSSION

The potentiometric titration curves of Kojic acid (5-hydroxy-(2-hydroxy methyl)-4H-pyron-4-one) and its complexes versus standard KOH are represented in Fig. 1. A proton–ligand formation curve was constructed by plotting $\bar{n}_A$ (the average number of protons attached to the ligand) against the pH of the solution corresponding to each addition of the alkali [17]. $\bar{n}_A$ Values were calculated from the titration data based on the simplified equation [18]

$$\bar{n}_A = Y - \frac{V_1 N^{\ominus}}{V_L^{\ominus} C_L^{\ominus}} \qquad (2)$$

where V_1 is the volume of the alkali required to reach a given pH on the titration curve, $V_L^{\ominus}$ is the initial volume of the ligand, $N^{\ominus}$ denotes the

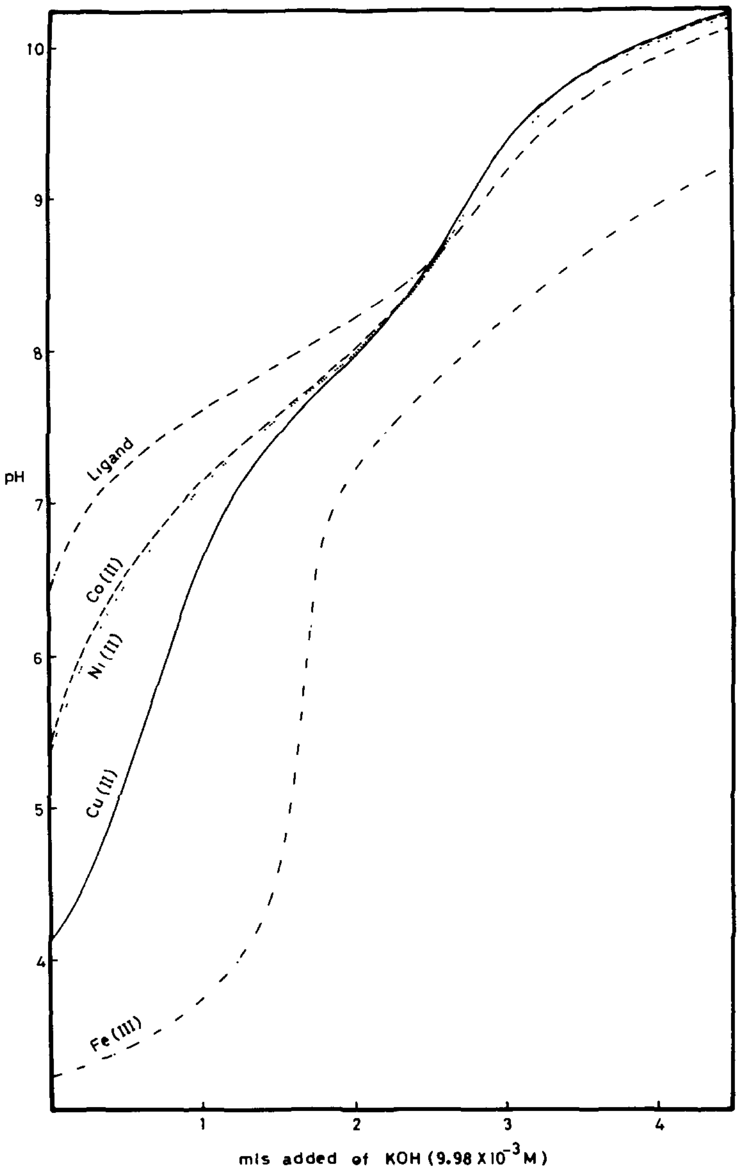

Fig. 1. pH-metric titration curves of Kojic acid and its complexes against standard KOH solution: the Kojic acid was 5 ml of 10^{-3} M solution, 3 ml of 0.5 M KCl + 20 ml 50% dioxane–water media made up to 50 ml, titrated against 9.98×10^{-3} M KOH solution; the complex solution was 0.1 ml of 1×10^{-2} M metal chloride + 5 ml of 10^{-3} M Kojic acid + 3 ml of 0.5 M KCl + 20 ml 50% dioxane–water media, made up to 50 ml, titrated against 9.98×10^{-3} M KOH solution.

alkali concentration, $C_L^{\ominus}$ is the total concentration of the ligand and Y is the number of displaceable hydrogen ions in the ligand. Only one pK is deduced from the proton–Kojic acid formation curves at $\bar{n}_A = 0.5$ in pure

TABLE 1

Formation constants of Kojic acid complexes

Metal ion	Stoichiometry	log K	log β
Co(II)	1:1	4.51	
	1:2	3.51	8.02
Ni(II)	1:1	4.62	
	1:2	3.55	8.17
Cu(II)	1:1	5.42	
	1:2	4.75	10.17

aqueous and mixed media, see Table 1, indicating that only one proton is liberated. The obtained value of the acidity constant (7.68) for the protolytic equilibria involving the neutral and the anionic species is in agreement with the reported literature values of 7.75, 7.83, 7.61 and 7.80, respectively. Furthermore, the pK value increases linearly as the mole fraction of the dioxane cosolvent increases, see Fig. 2. In other words, the pK values of Kojic acid in dioxane–water mixed solvent are higher than those obtained in pure aqueous media. This could be due to the decrease in the dielectric constant of the bulk solvent [19]. As the transfer of the cosolvent plays a part in controlling the dissociation of the ligand, therefore, if J represents a solvent transfer number characteristic of the compound, the following equation [13] can be written

$$J \log[\mathrm{S}] + \log K = \frac{-\Delta G}{2.3RT} - W \log\frac{[\mathrm{H_2O}]}{[\mathrm{S}]} \tag{3}$$

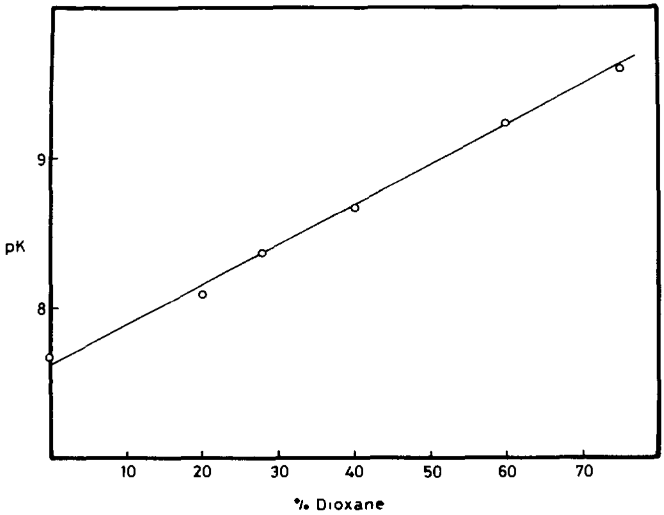

Fig. 2. pK versus %dioxane–water media (v/v) relation for Kojic acid.

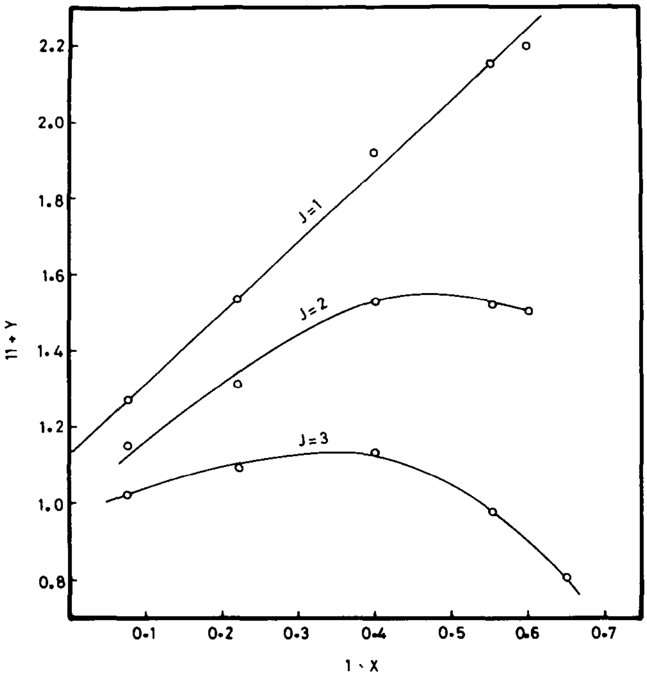

Fig. 3. X–Y relation for Kojic acid.

or, for simplicity [21]

$$J \log[\mathrm{S}] + \log K = Y \quad \text{and} \log[\mathrm{H_2O}]/[\mathrm{S}] = X \tag{4}$$

where J and W are unknown parameters and [S] is the concentration of the cosolvent used. The other terms have their usual meanings. Trial values of $J = 1$, 2 and 3 were used to find values of W (the number of water molecules). The most probable value of J is that which gives a minimum variance in the value of W. It was found that when $J = 1.0$, $W = 2.0$, indicating that the compound contains more water (Fig. 3).

The pK values of the Kojic acid were determined pH-metrically in aqueous media at different temperatures in the range 25–40 °C to evaluate its thermodynamic parameters (ΔH, ΔG and ΔS). It was found that as the temperature increases (25, 30, 35 and 40 °C), the pK values decrease (7.75, 7.68, 7.62 and 7.55), respectively, indicating that more ionization takes place (Fig. 4). The value of the enthalpy, ΔH, for the ionization of Kojic acid was determined by plotting pK against $1/T$: a straight line was obtained of slope $\Delta H/2.3RT$, from which $\Delta H^{\ominus} = 23.57$ kJ mol^{-1} can be computed. The free energy value, $\Delta G^{\ominus} = 42.51$ kJ mol^{-1}, was calculated based on the equation $\Delta G = 2.3RT$ pK and from the relation $\Delta G = \Delta H - T\Delta S$. The entropy, $\Delta S^{\ominus}$ was evaluated as -69.10 J mol^{-1} K^{-1}. The negative ΔS may be taken as a criterion for the presence of intermolecular hydrogen bonds [13].

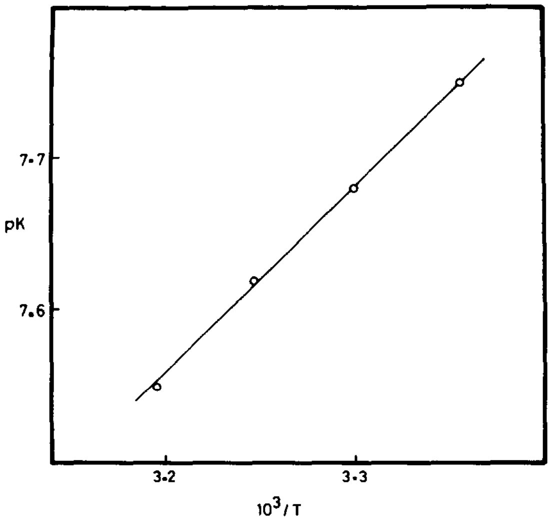

Fig. 4. pK–$1/T \times 10^3$ relation for Kojic acid.

Complex formation studies

In the course of investigating the coordination behaviour of Kojic acid towards the transition metals Co(II), Ni(II) and Cu(II), titration of mixtures of 1×10^{-3} M solutions of the compound and 2.0×10^{-4} M solution of metal ion against 1×10^{-2} M KOH solution in the presence of 0.083 M KCl were carried out, Fig. 1. Comparing the pH titrations of the free ligand with those of the complex solutions, a drop in pH is apparent assuming that the mechanism of complexation is based on H^+ liberation.

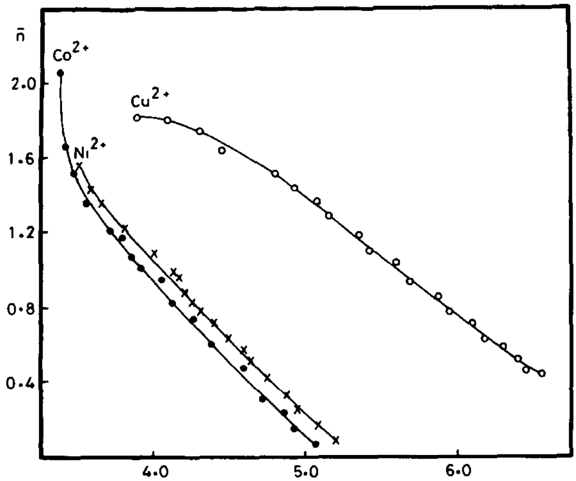

Fig. 5. Formation curves ($\bar{n}$–pL relation) for Kojic acid complexes.

The pH titration curves for free and complexed ligand gave only one proton dissociation between $a = 0$ and 1 (a = moles of base added per mole of ligand). This suggests that under these conditions, the ligand behaves as a monoprotic species with the dissociation of enolic OH-group proton.

The $\bar{n}$–pL relation [20] is applied for two purposes (Fig. 5): the detection of the possible species present; and the evaluation of the formation constants of the complexes. The $\bar{n}$ parameter indicates the average number of ligands bound to the metal. The pL value indicates the free ligand exponent.

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