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Potentiometric and Thermodynamic Studies of Vanillin and Its Metal Complexes

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The proton−ligand dissociation constant of vanillin (4-hydroxy-3-methoxy benzaldehyde) and metal−ligand stability constants of its complexes with metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) have been determined potentiometrically in 0.1 $mol \cdot dm^{-3}$ KCl and 10 % (by volume) ethanol−water mixture and at (298, 308, and 318) K. The stability constants of the formed complexes increase in the order Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}. The effect of temperature was studied, and the corresponding thermodynamic parameters (ΔG, ΔH, and ΔS) were derived and discussed. The dissociation process is nonspontaneous, endothermic, and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, endothermic, and entropically favorable.

Introduction

Vanillin (4-hydroxy-3-methoxy benzaldehyde) is the major component of natural vanilla which is one of the most widely used and important flavoring materials worldwide.[1−4] Vanillin occurs in nature as a glucoside, which hydrolyzes to vanillin and sugar. It has been identified in many oils, balsams, resins, and woods. The best known natural source of vanillin is the vanillin plant, *Vanilla planifolia*, a member of the orchid family. Besides being a very popular flavor, vanillin is also used in the synthesis of drugs, e.g., Aldomet and L-dopa. The chemistry of vanillin and its derivatives are important products of the chemical industry. Vanillin is used as an intermediate in pharmceuticals and is the most important flavoring agent in confectionery, beverage foods, and perfumery.[5−7] In continuation of earlier work,[8−11] we report here the dissociation constant of vanillin and the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} at different temperatures. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

Experimental Section

Vanillin (4-hydroxy-3-methoxybenzaldehyde) was used as received, from Aldrich (Figure 1).

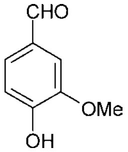

Figure 1

A vanillin solution (0.001 $mol \cdot dm^{-3}$) was prepared by dissolving an accurately weighed amount of the solid in ethanol (Analar). Metal ion solutions (0.0001 $mol \cdot dm^{-3}$) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA.[12] Solutions of 0.001 $mol \cdot dm^{-3}$ HCl and 1 $mol \cdot dm^{-3}$ KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 10 % (by volume) ethanol−water mixture was used as titrant and standardized against oxalic acid (Analar).

The apparatus, general conditions, and methods of calculation were the same as in previous work.[8−11] The following mixtures (i)−(iii) were prepared and titrated potentiometrically at 298 K against standard 0.002 $mol \cdot dm^{-3}$ NaOH in a 10 % (by volume) ethanol−water mixture:

(i) 5 cm^3 0.001 $mol \cdot dm^{-3}$ HCl + 5 cm^3 1 $mol \cdot dm^{-3}$ KCl + 5 cm^3 ethanol.

(ii) 5 cm^3 0.001 $mol \cdot dm^{-3}$ HCl + 5 cm^3 1 $mol \cdot dm^{-3}$ KCl + 5 cm^3 0.001 $mol \cdot dm^{-3}$ vanillin.

(iii) 5 cm^3 0.001 $mol \cdot dm^{-3}$ HCl + 5 cm^3 l $mol \cdot dm^{-3}$ KCl + 5 cm^3 0.001 $mol \cdot dm^{-3}$ vanillin + 10 cm^3 0.0001 $mol \cdot dm^{-3}$ metal chloride.

For each mixture, the volume was made up to 50 cm^3 with bidistilled water before the titration. These titrations were repeated for temperatures of (308 and 318) K. The temperature was controlled to within ± 0.05 K by circulating thermostatted water (Neslab 2 RTE 220) through the outer jacket of the vessel. The pH measurements were performed with a Metrohm 836 Titrando (KF & Potentiometric Titrator) equipped with a combined porolyte electrode. The pH-meter readings in the nonaqueous medium were corrected.[13] The electrode system was calibrated according to the method of Irving et al.[14] All titrations have been carried out between pH 3.0 and 11.0 and under a nitrogen atmosphere.

Results and Discussion

The average number of protons associated with the ligand (vanillin) at different pH values, $\bar{n}_A$, was calculated from the titration curves of the acid in the absence and presence of vanillin. Applying eq 1

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)TC^\circ_L} \qquad (1)$$

where Y is the number of available protons in vanillin ($Y = 1$); V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent,

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Table 1. Thermodynamic Functions for the Dissociation of Vanillin in 10 % (By Volume) Ethanol−Water Mixture and 0.1 mol·dm^{-3} KCl at Different Temperatures[a]

	dissociation constant	Gibbs energy kJ·mol^{-1}	enthalpy kJ·mol^{-1}	entropy J·mol^{-1}·K^{-1}
T/K	pK^{H}	ΔG_1	ΔH_1	$-\Delta S_1$
298	8.75 (0.10)	49.93	29.95	268.05
308	8.59 (0.09)	50.66		261.72
318	8.42 (0.09)	51.27		255.41

[a] Standard deviations are given in parentheses.

respectively; $V°$ is the initial volume (50 cm^3) of the mixture; $\mathrm{TC°_L}$ is the total concentration of the reagent; $N°$ is the normality of sodium hydroxide solution; and $E°$ is the initial concentration of the free acid. Thus, the formation curves ($\bar{n}_\mathrm{A}$ vs pH) for the proton−ligand systems were constructed and found to extend between 0 and 1 in the $\bar{n}_\mathrm{A}$ scale. This means that vanillin has one ionizable proton (the enolized hydrogen ion of the −OH group, pK^{H}). Different computational methods[15] were applied to evaluate the dissociation constant. Three replicate titrations were performed: the average values obtained are listed in Table 1. The completely protonated form of vanillin has one dissociable proton that dissociates in the measurable pH range. The deprotonation of the phenolic hydroxy group most probably results in the formation of stable intramolecular H-bonding with the oxygen of the $-\mathrm{OCH_3}$ group. Such an interaction decreases the dissociation process of vanillin, i.e., increases the pK^{H} value.[16,17]

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) vs the free ligand exponent (pL), according to Irving and Rossotti.[18] The average number of the reagent molecules attached per metal ion, $\bar{n}$, and free ligand exponent, pL, can be calculated using eqs 2 and 3

$$\bar{n} = \frac{(V_3 - V_2)(N° + E°)}{(V° + V_2)\bar{n}_\mathrm{A}\mathrm{TC}^{\circ}_\mathrm{M}} \qquad (2)$$

and

$$\mathrm{pL} = \log_{10}\frac{\sum_{n=\mathrm{O}}^{n=\mathrm{J}}\beta_n^\mathrm{H}\left(\frac{1}{[\mathrm{H}^+]}\right)^n}{\mathrm{TC}^{\circ}_\mathrm{L} - \bar{n}\mathrm{TC}^{\circ}_\mathrm{M}}\cdot\frac{V° + V_3}{V°} \qquad (3)$$

where $\mathrm{TC°_M}$ is the total concentration of the metal ion present in the solution and β_n^H is the overall proton-reagent stability constant. V_1, V_2, and V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand, and complex, respectively. These curves were analyzed, and the successive metal−ligand stability constants were determined using different computational methods.[19,20] The values of the stability constants (log K_1 and log K_2) are given in Table 2. The following general remarks can be pointed out:

(i) The maximum value of $\bar{n}$ was ∼2, indicating the formation of 1:1 and 1:2 (metal:ligand) complexes only.[21]

(ii) The metal ion solution used in the present study was very dilute ($2\cdot10^{-5}$ mol·dm^{-3}), hence there was no possibility of formation of polynuclear complexes.[22,23]

(iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves points to the formation of strong metal complexes.[24,25]

(iv) For the same ligand at constant temperature, the stability of the chelates increases in the order $\mathrm{Mn^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Zn^{2+}}$, and $\mathrm{Cu^{2+}}$.[26,27] This order largely reflects that the

Table 2. Stepwise Stability Constants for ML and $\mathrm{ML_2}$ Complexes of Vanillin in 10 % (by Volume) Ethanol−Water Mixtures and 0.1 mol·dm^{-3} KCl at Different Temperatures[a]

	298 K		308 K		318 K	
M^{n+}	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
$\mathrm{Mn^{2+}}$	5.75 (0.08)	4.45 (0.13)	5.90 (0.10)	4.61 (0.09)	6.04 (0.10)	4.77 (0.13)
$\mathrm{Co^{2+}}$	5.90 (0.10)	4.60 (0.11)	6.06 (0.10)	4.76 (0.10)	6.22 (0.08)	4.91 (0.08)
$\mathrm{Ni^{2+}}$	5.96 (0.11)	4.65 (0.11)	6.12 (0.12)	4.81 (0.10)	6.28 (0.12)	4.96 (0.09)
$\mathrm{Cu^{2+}}$	6.30 (0.10)	4.90 (0.10)	6.46 (0.09)	5.06 (0.09)	6.63 (0.10)	5.21 (0.09)
$\mathrm{Zn^{2+}}$	6.26 (0.10)	4.84 (0.10)	6.43 (0.11)	5.01 (0.11)	6.59 (0.10)	5.18 (0.10)

[a] Standard deviations are given in parentheses.

Table 3. Thermodynamic Functions for ML and $\mathrm{ML_2}$ Complexes of Vanillin in 10 % (By Volume) Ethanol−Water Mixture and 0.1 mol·dm^{-3} KCl

		Gibbs energy/kJ·mol^{-1}		enthalpy/kJ·mol^{-1}		entropy/J·mol^{-1}·K^{-1}	
M^{n+}	T/K	$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
$\mathrm{Mn^{2+}}$	298	32.81	25.39	26.32	29.04	198.42	182.65
	308	34.79	27.19			198.41	182.56
	318	36.78	29.04			198.42	182.64
$\mathrm{Co^{2+}}$	298	33.66	26.25	29.04	28.13	210.40	182.48
	308	35.74	28.07			210.32	182.47
	318	37.87	29.90			210.41	182.48
$\mathrm{Ni^{2+}}$	298	34.01	26.53	29.04	28.13	211.58	183.42
	308	36.09	28.37			211.46	183.44
	318	38.24	30.20			211.57	183.43
$\mathrm{Cu^{2+}}$	298	35.95	27.96	29.95	28.13	221.14	188.22
	308	38.10	29.84			220.94	188.21
	318	40.37	31.72			221.13	188.21
$\mathrm{Zn^{2+}}$	298	35.72	27.62	29.95	30.85	220.37	196.21
	308	37.92	29.55			220.36	196.10
	318	40.12	31.54			220.35	196.19

stability of Cu^{2+} complexes is considerably larger than those of other metals of the 3d series. Under the influence of both the polarizing ability of the metal ion[28] and the ligand field,[29] Cu^{2+} will receive some extra stabilization due to tetragonal distortion of octahedral symmetry in its complexes. The greater stability of Cu^{2+} complexes is produced by the well-known Jahn−Teller effect.[29]

The dissociation constant (pK^H) for vanillin, as well as the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, have been evaluated at (298, 308, and 318) K and are given in Tables 1 and 3, respectively. The enthalpy (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK^H or $\log K$ vs $1/T$ using the graphical reperesentation of van't Hoff eqs 4 and 5

$$\Delta G = -2.303RT \log K = \Delta H - T\Delta S \tag{4}$$

or

$$\log K = (-\Delta H/2.303R)(1/T) + (\Delta S/2.303R) \tag{5}$$

From the ΔG and ΔH values, one can deduce the entropy ΔS using the well-known relationships 4 and 6

$$\Delta S = (\Delta H - \Delta G)/T \tag{6}$$

All thermodynamic parameters of the dissociation process of vanillin are recorded in Table 1. From these results, the following conclusions can be made:

(i) The pK^H values decrease with increasing temperature; i.e., the acidity of the ligand increases.[11]

(ii) A positive value of ΔH indicates that the process is endothermic.

(iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous.[30]

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

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species,[20] 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. Examination of these values shows that:

(i) The stability constants ($\log K_1$ and $\log K_2$) for vanillin complexes increase with increasing temperature; i.e., its stability constants increase with increasing temperature.[31]

(ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such processes.[32]

(iii) The ΔH values are positive, meaning that these processes are endothermic and favorable at higher temperature.

(iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favorable.[8]

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