April 2007 Volume 2 Issue 1

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 2(1), 2007 [6-10]

Removal Of Some Heavy Metals From Aqueous Solutions:Potentiometric And Thermodynamic Studies Of Vanillin And Its Metal Complexes

Corresponding Author

A.S.Al-Shihri
Chemistry Department, Faculty of Science,
King Khalid University, P.O. Box 9004,
Abha 61413, (SAUDI ARABIA)
E-mail: alshihri@hotmail.com

Co-Authors

A.A.El-Bindary, A.M.AL-Sharhani
Chemistry Department, Faculty of Science, King Khalid University,
P.O. Box 9004, Abha 61413, (SAUDI ARABIA)

Received: 6th November, 2006
Accepted: 11st November, 2006

Web Publication Date : 7th February, 2007

ABSTRACT

Proton-ligand dissociation constant of 3-methoxy-4-hydroxybenzaldehyde (Vanillin) and metal-ligand stability constants of its complexes with (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) metal ions have been determined potentiometrically in 0.1 M–KCl and 10 vol.% ethanol–water mixture. The stability constants of the formed complexes increases 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 unfavourable. The fotmation of the metal complexes has been found to be spontaneous, endothermic and entropically favourable.

KEYWORDS

Ferrocene derivatives;
Bond length;
Bond angle;
Computational study;
Transition metal derivatives.

INTRODUCTION

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. Beside being a very popular flavor vanillin is also used in the synthesis of drugs, e.g. Aldomet and L-dopa.

Chemistry of vanillin and its derivatives are important product of fine chemical industry. Vanillin is used as intermediate in pharmaceuticals and it is the most important flavoring agents in confectionery, beverage food and in perfumery[1–3]. In continuation of the earlier work[4–7], we report here the dissociation constant of vanillin and its stability constants of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes at different temperatures. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

RESULTS AND DISCUSSION

The average number of the 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 the following equation 1:

$$\bar{n}A = Y + \frac{(v_1 - v_2)(N^o + E^o)}{(v^o + v_1)TC^o_L} \tag{1}$$

where Y is the number of available protons in vanillin(Y=1) and 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, respectively, V° is the initial volume(50cm^3) of the mixture, $TC°_L$ 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($\bar{n}_A$ vs. pH) for the proton-ligand systems were constructed and found to extend between 0 and 1 in the $\bar{n}_A$ scale. This means that vanillin has one ionizable proton(the enolized hydrogen ion of -OH group, pK^H). Different compuional methods[8] 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, dissociate in the measurable pH range. The deprotonation of the phenolic hydroxy group most probably result in the formation of stable intramolecular H-bonding with the oxygen of the -OMe group. Such an interaction decreases the dissociation process of vanillin, i.e. increases the pK^H value[9,10].

TABLE 1: Thermodynamic functions for the dissociation of vanillin in 10 % vol. ethanol-water mixture and 0.1 M–KCl at different temperatures

T/K	Dissociation constant pK^H	Gibbs energy change kJ mol^{-1} ΔG_1	Enthalpy change kJ mol^{-1} ΔH_1	Entropy change J mol^{-1} K^{-1} $-\Delta S_1$
298	8.75	49.93	31.59	61.54
308	8.59	50.66		61.92
318	8.42	51.27		61.89

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions($\bar{n}$) vs. the free ligand exponent(pL), according to Irving and Rossotti[11]. The average number of the reagent molecules attached per metal ion, $\bar{n}$, and free ligand exponent, pL, can be calculated using the equations 2 and 3:

$$\bar{n} = \frac{(v_3 - v_2)(N^o + E^o)}{(v^o + v_2)\bar{n}_A\, TC^o{}_M} \tag{2}$$

$$pL = \log_{10} \frac{\sum_{n=O}^{n=J} \beta^H_n \left(\frac{1}{\text{anti}\log pH}\right)^n}{TC^\circ_L - \bar{n}\,TC^\circ_M} \cdot \frac{V^\circ + V_3}{V^\circ} \tag{3}$$

where $TC°_M$ is the total concentration of the metal ions present in the solution, β^H_n 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 computional methods[12,13]. 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:

(1) The maximum value of $\bar{n}$ was ≈2 indicating the formation of 1:1 and 1:2(metal:ligand) complexes only.

(2) The metal ion solution used in the present study was very dilute (2×10^{-5} mol dm^{-3}), hence there was no possibility of formation of polynuclear complexes[14].

TABLE 2: Stepwise stability constants for ML and ML_2 complexes of vanillin in 10% vol. ethanol-water mixtures and 0.1M–KCl at different temperatures

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

TABLE 3: Thermodynamic functions for ML and ML_2 complexes of vanillin in 10% vol. ethanol-water mixture and 0.1 M-KCl

M^{n+}	T/K	Gibbs energy change kJ mol^{-1}		Enthalpy change kJ mol^{-1}		Entropy change J mol^{-1} K^{-1}	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	32.81	25.39	27.76	30.64	203.26	188.02
	308	34.79	27.19			203.08	187.96
	318	36.78	29.04			202.96	187.67
Co^{2+}	298	33.66	26.25	30.64	29.68	215.77	187.68
	308	35.74	28.07			215.52	187.50
	318	37.87	29.90			215.44	187.36
Ni^{2+}	298	34.01	26.53	30.64	29.68	216.95	188.62
	308	36.09	28.37			216.66	188.47
	318	38.24	30.20			216.60	188.30
Cu^{2+}	298	35.95	27.96	31.59	29.68	226.64	193.42
	308	38.10	29.84			226.27	193.25
	318	40.37	31.72			226.29	193.08
Zn^{2+}	298	35.72	27.62	31.59	32.55	225.87	201.91
	308	37.92	29.55			225.68	201.62
	318	40.12	31.54			225.50	201.54

(3) 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 point to the formation of strong metal complexes[15].

(4) For the same ligand at constant temperature, the stability of the chelates increases in the order Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+}[16,17]. This order largely reflects that the stability of Cu^{2+} complexes are considerably larger as compared to other metals of the 3d series. Under the influence of both the polarizing ability of the metal ion[18] and the ligand field[19] Cu^{2+} will receive some extra stabilization due to tetragonal distortion of octahedral symmetry in their complexes. The greater stability of Cu^{2+} complexes are produced by the well known Jahn-Teller effect[19].

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 K, 308 K, and 318 K, and are given in TABLES 1 and 3. The enthalpy change(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 representation of Van't Hoff equation (4) and (5):

$$-2.303\,RT\log K = \Delta H - T\Delta S \qquad (4)$$

$$\log K = (\Delta H/2.303R)(1/T) + (\Delta S/2.303R) \qquad (5)$$

From the Gibbs energy change ΔG and ΔH values one can deduce the entropy changes ΔS using the well known relationships (6) and (7):

$$\Delta G = -2.303RT\log K \qquad (6)$$

$$\Delta G = -2.303RT\log K \qquad (7)$$

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

(1) The pK^H values decrease with increasing temperature, i.e. the acidity of the ligand increases[7].

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

(3) A large positive value of ΔG indicates that the dissociation process is not spontaneous[20].

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

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[13] 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:

(1) The stability constants (log K_1 and log K_2) for vanillin complexes increases with increasing temperature, i.e. its stability constants increase with increasing the temperature[21].

(2) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process[22].

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

(4) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favourable[4].

EXPERIMENTAL

3-methoxy-4-hydroxybenzaldehyde(vanillin) was used as recived, from Aldrich Co.

Vanillin solution(0.001mol dm^{-3}) was prepared by dissolving the accurate weight of the solid in ethanol (Analar). Metal ion solutions(0.0001mol dm^{-3}) were prepared from Analar metal chloride in bidistilled water and standardized with EDTA[23].

Solutions of 0.001 M-HCl and 1 M-KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 10% vol. 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 the previous work[4-7]. The following mixtures (1) - (3) were prepared and titrated potentiometrically at 298 K against standard 0.002 M-NaOH in 10% vol. ethanol-water mixture:

(1) 5cm^3 0.001 M-HCl + 5cm^3 1 M-KCl + 5cm^3 ethanol.

(2) 5cm^3 0.001 M-HCl + 5cm^3 1 M-KCl + 5cm^3 0.00l M-vanillin.

(3) 5cm^3 0.001 M-HCl + 5cm^3 l M-KCl + 5cm^3 0.001 M-vanillin + 5cm^3 0.0002 M- metal chloride.

For each mixture, the volume was made up to 50cm^3 with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K.

A constant temperature was maintained at ±0.05K by circulating thermostated 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 non–aqueous medium were corrected[24]. The electrode system was calibrated according to the method of Irving et al.[25]. All titrations have been carried out between 3.0-11.0 and under nitrogen atmosphere.

ACKNOWLEDGMENTS

This work was supported by Grand of SABIC No. 44/229 from the Research Center of the College of Science at King Khalid University, Saudi Arabia.

REFERENCES

[1] V.Dalpiaz, M.P.Giovannoni, C.Castellana, J. M.Palacios, J.Beleta, T.Domenech, V.Segarra; J.Med.Chem., **40**, 1417 **(1997)**.

[2] T.J.Torphy, M.S.Barnette, D.C.Underwood, D.E. Griswold, S.B.Christensen, R.D.Murdoch, R.B. Nieman, C.H.Compton; Pulm.Pharmacol.Ther., **12**, 131 **(1999)**.

[3] M.Braun, K.Opdenbusch, C.Unger; Synlett., 1174 **(1995)**.

[4] A.M.Khedr, A.A.El-Bindary, A.M.Abd El-Gawad; Chem.Pap., **59**, **(2005)**.

[5] A.S.Al-Shihri, A.M.Abdel-Hady, A.A.El-Bindary; Chem.Pap., **58**, 155 **(2004)**.

[6] A.S.Al-Shihri; King Khalid Univ. J. (Saudia), **1**, 21 **(2004)**.

[7] A.S.Delta; J.Sci. (Egypt), **26**, 15 **(2002)**.

[8] H.Irving, H.S.Rossotti; J.Chem.Soc., 2904 **(1954)**.

[9] E.Farkas, H.Csoka; J.Inorg.Biochem., **89**, 219 **(2002)**.

[10] M.M.Omar, G.G.Mohamed; Spectrochim.Acta Part, A, **61**, 929 **(2005)**.

[11] H.Irving, H.S.Rossotti; J.Chem.Soc., 3397 **(1953)**.

[12] F.J.C.Rossotti, H.S.Rossotti; Acta Chem.Scand., **9**, 1166 **(1955)**.

[13] M.T.Beck, I.Nagybal; 'Chemistry of Complex Equilibrium', Wiley, New York, **(1990)**.

[14] P.Sanyal, G.P.Sengupta; J.Ind.Chem.Soc., **67**, 342 **(1990)**.

[15] V.D.Athawale, V.Lele; J.Chem.Eng.Data, **41**, 1015 **(1996)**.

[16] G.A.Ibanez, G.M.Escandar; Polyhedron, **17**, 4433 **(1998)**.

[17] W.U.Malik, G.D.Tuli, R.D.Madan; 'Selected Topics in Inorganic Chemistry', 3rd Ed., Chand, S. & Company LTD, New Delhi, **(1984)**.

[18] F.R.Harlly, R.M.Burgess, R.M.Alcock; 'Solution Equilibria', 257. Ellis Harwood, Chichester, **(1980)**.

[19] L.E.Orgel; 'An Introduction to Transition Metal Chemistry Ligand Field Theory', 55, Methuen, London, **(1966)**.

[20] A.Bebot-Bringaud, C.Dange, N.Fauconnier, C.Gerard; J.Inorg.Biochem., **75**, 71 **(1999)**.

[21] A.A.Al-Sarawy, A.A.El-Bindary, A.Z.El-Sonbati, T.Y.Omar; Chem.Pap., **59**, **(2005)**.

[22] A.T.Mubarak, A.Z.El-Sonbati, A.A.El-Bindary; Chem.Pap., **58**, 320 **(2004)**.

[23] G.H.Jeffery, J.Bassett, J.Mendham, R.C.Deney; 'Vogel's Textbook of Quantitative Chemical Analysis', 5th Ed. Longman, London, **(1989)**.

[24] R.G.Bates, M.Paabo, R.A.Robinson; J.Phys.Chem., **34**, 581 **(1972)**.

[25] H.M.Irving, M.G.Miles, L.D.Pettit; Anal.Chim.Acta **38**, 475 **(1967)**.