



Acid–base and UV behavior of 3-(3,4-dihydroxyphenyl)-propenoic acid (caffeic acid) and complexing ability towards different divalent metal cations in aqueous solution



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ARTICLE INFO

Article history:

Received 8 October 2013

Received in revised form 20 January 2014

Accepted 22 January 2014

Available online 03 February 2014

Keywords:

Caffeic acid

Zn^{2+} , Cu^{2+} , Cd^{2+} , $(CH_3)_2Sn^{2+}$ complexes

Spectrophotometry

Potentiometry

Acid–base properties

UV properties

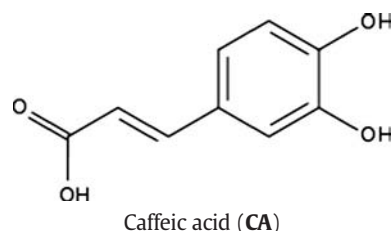
ABSTRACT

The acid–base and the UV behavior of 3-(3,4-dihydroxyphenyl)-propenoic acid (caffeic acid) was studied by potentiometry and UV spectrophotometry at $T = 298.15$ K and $0.1 \leq I/\text{mol L}^{-1} \leq 1$ in NaCl aqueous solution. The complex formation with Zn^{2+} , Cu^{2+} , Cd^{2+} , $(CH_3)_2Sn^{2+}$ at $I = 0.1 \text{ mol L}^{-1}$ in NaCl has been also determined by using potentiometric and spectrophotometric titration techniques. The results obtained by the spectrophotometric measurements fully confirm those obtained by potentiometry, with a particularly good agreement for the system containing Cu^{2+} . The results showed that, for the ML species, at $I = 0.1 \text{ mol L}^{-1}$ in NaCl and $T = 298.15$ K, the stability of the caffeate- $(CH_3)_2Sn^{2+}$, and $-Cu^{2+}$ species is high, with $\log\beta_{ML} = 16.577$ and 13.05 , respectively, while that of the caffeate- Zn^{2+} and $-Cd^{2+}$ species is considerably lower, with $\log\beta_{ML} = 8.526$ and 7.272 , respectively. Speciation profiles for all the systems under study were also calculated and sequestering ability of the caffeate towards the different metal cations considered in this investigation was also evaluated. For example, at physiological pH, $I = 0.1 \text{ mol L}^{-1}$ in NaCl and $T = 298.15$ K, the order of sequestering ability is $Cu^{2+} > (CH_3)_2Sn^{2+} > Zn^{2+} > Cd^{2+}$.

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1. Introduction

3-(3,4-dihydroxyphenyl)-propenoic acid or caffeic acid is a derivative of hydroxycinnamic acid. The structure of caffeic acid is as follows:



Hydroxycinnamic acid derivatives are widely present in plants and vegetable foods and also exert some biological activities, such as antioxidative and free-radical scavenging properties [1]. Their presence in food affects quality as color, flavor, stability and nutritional value [2]. Caffeic acid is present in many fruits, vegetables, seasonings, beverages (coffee, wine) and olive oil. In sunflower seeds, it is the main phenolic acid having the characteristic of affecting the solubility of plant proteins [2,3]. Coffee, in particular,

represents a source of polyphenolic compounds having antioxidant activity. Among them, there are chlorogenic acids, esters formed between quinic acid and different cinnamic acids, such as caffeic, ferulic, and p- and o-coumaric acids, mainly responsible of the bitter taste of coffee [4]. Phenolic compounds have potential chemical and biological activities, such as natural antioxidant, free-radical scavenging, anti-inflammatory, anticarcinogenic, chemoprevention, and UV filtering properties. Phenolic compounds may act as free-radical scavengers, with the formation of alkyl, peroxy, and aryloxy radicals. Other functional groups may contribute to the stabilization of these radicals enhancing the antioxidant activity [3,5]. Other mechanisms of action may also occur through the complexation of metals, such as copper, well-known catalyst of oxidative stress. The formation of CA-metal species inhibits free radical formation and also propagation reactions and may also have indirect effects, such as inactivating metabolic reactions and simplifying cell penetration [5]. For this reason, the study of CA metal complexation is of therapeutic interest, for the evaluation of antioxidant mechanisms and of biological interest for the determination of the bioavailability of metal ions.

The first step of this study was the determination of reliable formation constants of CA at different ionic strengths. In literature, data reported on CA protonation constants are few, they refer only at low ionic strengths ($\leq 0.15 \text{ mol L}^{-1}$), and are not in agreement with each other, especially as regards the first protonation constant [5–14]. The second step was the determination of metal-CA species. Among the metals, for this study Zn^{2+} and $-Cu^{2+}$ were chosen for

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the biological relevance, Cd^{2+} and $(\text{CH}_3)_2\text{Sn}^{2+}$ for their well-known toxicity. Despite the importance of the knowledge of stability data, few thermodynamic studies have been performed on this topic. Data reported in the literature on formation constants of **CA** with Zn^{2+} , $-\text{Cd}^{2+}$ and $-\text{Cu}^{2+}$ are extremely few and there are no data on the formation of **CA**- $(\text{CH}_3)_2\text{Sn}^{2+}$ species [5–9,15]. In this paper the protonation constants of **CA** at different ionic strengths and at $T = 298.15$ K and the complex formation with Zn^{2+} , Cu^{2+} , Cd^{2+} , $(\text{CH}_3)_2\text{Sn}^{2+}$ at $I = 0.1$ mol L^{-1} in NaCl and at $T = 298.15$ K have been investigated by using potentiometric and spectrophotometric titration techniques.

2. Experimental

2.1. Chemicals

The **CA** ligand was supplied by Alfa Aesar and was used without further purification. Its purity (always > 99.5%) was checked by potentiometric titrations. Solutions of zinc(II) chloride, cadmium(II) chloride and copper(II) chloride were prepared from corresponding Riedel de Haen and Fluka products and standardized with standard EDTA. Dimethyltin(IV) chloride solutions were prepared from corresponding Alfa Aesar product. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated Fluka ampoules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. NaCl (Fluka, puriss.) was used after stove drying at 110 °C. All solutions were prepared using analytical grade water ($\rho \geq 18$ M Ω cm) and grade A glassware.

2.2. Potentiometric equipment and procedure

Potentiometric titrations were carried out at 298.15 ± 0.1 K using an 809 Metrohm Titrando apparatus equipped with a combined Orion glass electrode Ross type 8102. The estimated accuracy was ± 0.20 mV and ± 0.02 mL for e.m.f. and titrant volume readings, respectively. The apparatus was connected to a PC, and automatic titrations were performed using the Metrohm TiAMO 1.0 software to control titrant delivery, data acquisition and to check for e.m.f. stability.

To determine the ligand protonation constants, 25 mL of solution containing **CA** ($C_L = 0.75$ mmol L^{-1}) and the background salt (NaCl), in order to reach the prefixed ionic strength values ($0 < I/\text{mol L}^{-1} \leq 1$), was titrated with standard NaOH. To evaluate the metal–ligand interactions, solutions were prepared by dissolving different amounts of ligand ($0.75 \leq C_L \leq 0.9$ mmol L^{-1}) and divalent cation ($0.5 \leq C_M \leq 1.6$ mmol L^{-1}) to obtain a concentration C_M/C_L ratios ranging from 0.55 to 2. Ionic strength was fixed to a predetermined $I = 0.1$ mol L^{-1} value in NaCl. A volume of 25 mL of each solution was titrated with standard sodium hydroxide in the pH range 2.5 to 11. For each experiment, independent titrations of hydrochloric acid with NaOH standard solutions were performed in the same experimental conditions of temperature and ionic strength as the systems under study in order to determine the formal electrode potential. The free hydrogen ion concentration scale was used ($\text{pH} = -\log[\text{H}^+]$). Pure N_2 was bubbled through the solutions in the titration cells in order to avoid O_2 and CO_2 inside and the solutions were magnetically stirred.

2.3. Spectrophotometric equipment and procedure

The UV spectra, at 298.15 ± 0.1 K, were recorded using a Varian Cary 50 UV–VIS spectrophotometer with an optic fiber probe having a fixed 1 cm path length, from 220 to 440 nm. The spectrophotometer was connected to a PC for the acquisition of the spectra. The measurement cell and potentiometric apparatus are the same of those described in the previous potentiometric equipment and procedure paragraph.

For the investigation of ligand protonation constants, 25 mL of solution containing the ligand under study, at $0.03 \leq C_L \leq 0.07$ mmol L^{-1} , was analyzed in a wide pH range. The measurements were carried out in the range $0 < I/\text{mol L}^{-1} \leq 1$, in NaCl as supporting electrolyte and at $T = 298.15$ K. For the investigation of formation constants of metal cation–ligand species, 25 mL of solution containing metal cation (at $0.05 \leq C_M \leq 0.1$ mmol L^{-1}) and **CA** (at $0.04 \leq C_L \leq 0.07$ mmol L^{-1}), at different metal ligand ratios from $C_M/C_L = 0.7$ to $C_M/C_L = 2$, was analyzed in a wide pH range. Small increments of standard NaOH solution were added to each solution in order to obtain the maximum absorbance of each predominant species, according to the preliminarily determined speciation diagrams of the system.

2.4. Calculations

The computer programs STACO and BSTAC were used to refine conditional protonation constants of the ligand from potentiometric titrations at the specific ionic strength of the measurement and all the parameters relative to the electrode system, such as formal potential E^0 and coefficient of the liquid junction potential j ($E_j = j_a [\text{H}^+]$), and to determine the alkalimetric purity [16,17]. From the conditional values at different ionic strengths, the nonlinear fitting program LIANA refines, using different equations, the thermodynamic protonation values of the ligands at $I = 0$ mol L^{-1} [18]. For the dependence of **CA** protonation constants on ionic strength, the Debye–Hückel type equation is used [19]:

$$\log \beta = \log {}^T\beta - z^* \frac{0.51I^{1/2}}{1 + 1.5I^{1/2}} + C_I \quad (1)$$

where, β = stoichiometric formation constant, ${}^T\beta$ = formation constant at infinite dilution, $z^* = \Sigma(\text{charge})^2_{\text{reactants}} - \Sigma(\text{charge})^2_{\text{products}}$, C_I is an empirical parameters that depends on stoichiometric coefficients and charges. From potentiometric data, formation constants of metal cation–**CA** species were refined using the nonlinear least squares computer programs STACO and BSTAC. Speciation profiles were obtained using the computer program ES4EC. Details of calculation methods and computer programs have already been reported [18]. UV spectra were analyzed by the Hyperquad 2006 and HypSpec programs [20,21], which allow to calculate the protonation or formation constants and the molar absorption coefficient spectrum of each absorbing species, using experimental absorbances, analytical concentrations of reagents and the proposed chemical model as input. Hydrolysis of Zn^{2+} , Cu^{2+} , Cd^{2+} , $(\text{CH}_3)_2\text{Sn}^{2+}$ and species formation with chloride were taken into account. Formation constant values of metal cations under study with OH^- and Cl^- at $I = 0.1$ mol L^{-1} and $T = 298.15$ K were reported in Supplementary Information [22–24].

3. Results and discussion

3.1. Protonation constants of CA

The strong basicity of the first protonation constant of **CA**, can be attributed mainly to electrostatic attraction of the adjacent negative charge and, to a lesser extent to the formation of the hydrogen bond involving the phenoxide and hydroxyl groups [8,9]. The few literature data on the protonation constants of **CA** are collected in Table 1. The $\log K_1^H$ value, in several investigations was not determined or in the cases where it has been obtained, the comparison among the values at the same ionic strength, shows very large differences. For example, $\log K_1^H$ values at 298.15 K, and $I = 0.1$ mol L^{-1} in KNO_3 and KCl , are 11.50 and 12.6, respectively [5,12]. The **CA** protonation value reported by Lamy et al. [25] ($\log K_1^H = 11.5$ at $I = 0.1$ mol L^{-1} in NaClO_4 and $T = 298.15$ K), obtained by potentiometric titrations, has been considered inaccurate by Adams et al. [12], as outside the range for reliable pH

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