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Electrochemistry of chlorogenic acid: experimental and theoretical studies

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Abstract

Cyclic voltammetry, chronoamperometry and rotating disk electrode voltammetry as well as quantum chemical methods, are used for electrochemical study of chlorogenic acid, as an important biological molecule. The standard formal potential, diffusion coefficient, and heterogeneous electron transfer rate constant of chlorogenic acid in aqueous solution are investigated. Acidic dissociation constant of chlorogenic acid is also obtained. Quantum mechanical calculations on oxidation of chlorogenic acid in aqueous solution, using density functional theory are presented. The change of Gibbs free energy and entropy of oxidation of chlorogenic acid are calculated using thermochemistry calculations. The calculations in aqueous solution are carried out with the use of polarizable continuum solvation method. Theoretical standard electrode potential of chlorogenic acid is achieved to be 0.580 V versus standard calomel electrode (SCE) which is in agreement with the experimental value of 0.617 V obtained experimentally in this work. The difference is consistent with the values we previously reported for other quinone derivatives.

Keywords: Chlorogenic acid; Standard formal potential; Cyclic voltammetry; Electrochemical oxidation; DFT calculations

1. Introduction

Chlorogenic acid (CGA) is the major phenolic compound found in many fruits such as apple, pear, peach, plum, cherry and apricot [1]. This compound is well-known substrate of polyphenol oxides (PPOs). Phenolic compounds give bitterness and astringency to the juices and contribute to the flavor of processed apple product like cider, although they are in lower proportion [2]. Moreover, browning of apples is due to enzymatic oxidation of phenolic compounds to quinone, which subsequently polymerize to brown product. Among the hydroxycinnamic acids presents in apple juice, chlorogenic acid is the most abundant. This acid is considered as the preferential natural substrate for polyphenol oxidase and therefore it may have an effect on the oxidation process and color development during cider making [3]. Therefore, redox potential of CGA is an important factor which affects on its biological behavior.

We previously reported the use of CGA for the electrocatalytic oxidation-reduction of nicotinamide adenine dinucleotide (NADH) [4] and hydrazine [5] and found the role of CGA very important in the redox reactions of the studied molecules [4,5]. In the present work, we report the electrochemical study of CGA in aqueous solution. We have investigated the standard formal potential, dissociation constant and transfer coefficient of CGA as well as charge transfer rate constant between glassy carbon electrode and CGA. We have recently showed that standard electrode potentials can be calculated using quantum mechanical calculations [6–8], in which we theoretically studied the standard electrode potentials of quinone derivatives in aqueous solution [7,8] and non-aqueous solution of DMSO [6]. The employed theories were able to predict the electrode potential of studied molecules in non-aqueous solvent of DMSO and aqueous solution. In this study, we also present the result of quantum mechanical calculations for the oxidation of CGA in aqueous solution using

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density functional theory (DFT) [9] at the level of B3-LYP [10]. Agreement between experimental and theoretical values for standard redox potential verifies mutually the accuracy of experimental methods and the validity of mathematical models.

2. Experimental

2.1. Reagents and apparatus

Chlorogenic acid [1,3,4,5-tetrahydroxy cyclohexane carboxylic acid 3(3,4-dihydroxy cinnamate)] (CGA) and the chemicals used for buffer solutions were reagent grade from Merck and used as received. All solutions were prepared with doubly distilled water. The potentiostat (Autolab-PGSTAT 30, Eco Chemie, Utrecht, The Netherlands) which was connected to a personal computer for data acquisition and potential control was used for electrochemical measurements. All electrochemical experiments were carried out with a glassy carbon disk (2 mm diameter) as working electrode, a graphite electrode as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. All potentials in the text are quoted versus this reference electrode. A Metrohm model 691 pH/mV meter was used for measuring the pH. The experiments were carried out inside a faraday cage at room temperature (ca. 25 °C) under a N_2 atmosphere and after deaerating solution with high purity nitrogen (99.999%). Prior to experiment, the glassy carbon electrode was hand-polished to a mirror-like finish with 0.05 μm alumina in slurry using a polishing cloth and rinsed with doubly distilled water.

2.2. Theoretical consideration

The oxidised form of chlorogenic acid (CGA_{ox}) can be converted to its reduced form (CGA) using *o*-dihydroxybenzene (Q) as a reference molecule according to the following isodesmic reaction [6]:

$$Q_{(sol)} + CGA_{ox(sol)} \rightarrow Q_{ox(sol)} + CGA_{(sol)} \qquad (1)$$

The difference between the electrode potential of two species can be obtained from the change in Gibbs free energy of reaction (1):

$$\Delta G^{\circ} = -nF(E^{\circ}_{CGA} - E^{\circ}_{Q}) \qquad (2)$$

where *n* is number of electrons transferred (*n* = 2 in this case) and *F* is the Faraday constant [6,8]. In order to obtain standard electrode potential of chlorogenic acid, the change of Gibbs free energy of reaction (1), ΔG°, is required along with the experimental value of electrode potential of the reference molecule, *o*-benzoquinone.

In order to calculate the standard Gibbs energy of reaction (1), ΔG°, one should calculate the standard Gibbs energy of each component, ΔG°_{i}, in reaction (1):

$$\Delta G^{\circ} = \sum v_i \Delta G^{\circ}_{i} \qquad (3)$$

The standard Gibbs energy of each component, $\Delta G^{\circ}_{\mathrm{i}}$, is obtained using the following expression [8,9]:

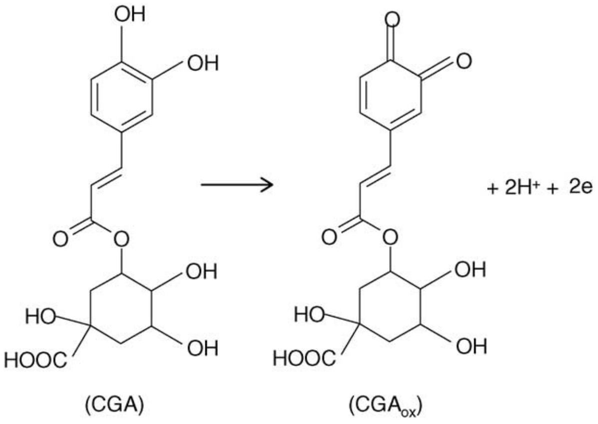
$$\Delta G^{\circ}_{i} = \Delta G^{\circ}_{i,\mathrm{gas}} + \Delta G^{\circ}_{i,\mathrm{solv}} \qquad (4)$$

where $\Delta G^{\circ}_{i,\mathrm{gas}}$ is the gas-phase energy of each component and $\Delta G^{\circ}_{i,\mathrm{solv}}$ is the solvation energy of the component. In the present work, the gas phase contribution to the Gibbs energy, $\Delta G^{\circ}_{i,\mathrm{gas}}$, was determined from density functional theory calculations. These calculations have been performed at the DFT-B3LYP level using 6-31G(d,p) basis set [11]. The zero-point energies and thermal corrections together with entropies have been used to convert the internal energies to the Gibbs energies at 298.15 K. Solvation energies, $\Delta G^{\circ}_{i,\mathrm{solv}}$, have been calculated using Polarisable Continuum Model (PCM) [12]. Gaussian98 [13] have been employed for all DFT calculations.

3. Results and discussion

3.1. Voltammetric investigations of chlorogenic acid

Since the chlorogenic acid (CGA) has an *o*-hydroquinone moiety (Scheme 1), we anticipated that the redox response of the CGA solution would be pH dependent. Therefore, the voltammetric responses of a 0.3 mM aqueous solution of CGA at a glassy carbon electrode was obtained in solution with various buffered pHs from 1.0 to 12.0 (Fig. 1). As can be seen in Fig. 1B (curve a) the formal potential of the redox couple was pH dependent, with a slope of −57.1 mV/pH unit in a wide range, which is close to the anticipated Nernstian value of 59 mV for a two-electron, two-proton process. The process could be expressed as Scheme 1. The formal potentials are obtained from the equation of $E^{0'} = E_{\mathrm{p,a}} - \alpha(E_{\mathrm{p,a}} - E_{\mathrm{p,c}})$ [14] and considering $\alpha = 0.26$ (see below). There is also a change in the slope for pH values higher than 7.8, which



Scheme 1.