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Electrochemical behavior of antioxidants: I. Mechanistic study on electrochemical oxidation of gallic acid in aqueous solutions at glassy-carbon electrode

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Mechanism of electrochemical oxidation of gallic acid in aqueous phosphate buffer solutions of different pH's was studied at glassy-carbon electrode. The study was performed using cyclic, convolution–deconvolution sweep voltammetry, chronoamperometry and chronocoulometry. It gives two irreversible diffusion-controlled cyclic voltammetric waves at the entire range of pH. The electrochemical oxidation mechanism was proposed to be an ECEC-first order mechanism in which the two electron transfer steps and the two chemical follow-up deprotonation reactions are irreversible. The proposed mechanism was confirmed by digital simulation and the electrode kinetic parameters are estimated on comparing the simulated response with the experimental ones.

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1. Introduction

Gallic acid, GA, and its derivatives are a group of naturally occurring polyphenol antioxidants which have recently been shown to have potential health effects [1]. GA is a strong natural antioxidant [2,3]. The acid and its derivatives have a wide range of biological activities, including anti-oxidant, anti-inflammatory, anti-microbial, and anti-cancer activities [4–7]. Electrochemical oxidation of gallic acid has been studied at glassy-carbon electrode [8,9]. It was found that the oxidation process is quasireversible over the studied pH range. An electroanalytical procedure was proposed and applied for determination of gallate content in green tea [8]. The electrochemical oxidation of gallic acid on polyaniline (PAn) and polyaniline-ferrocene phosphonic acid (PAnFc) electrodes was studied by cyclic voltammetry at pH range of 5.0–6.6 [9]. It was found that, the modified electrodes catalyze the oxidation process and are dependent on pH. Furthermore, the PAnFc modified electrode catalyzes better than that of the PAn one.

Antioxidant properties are related with the redox characteristics and consequently, knowledge of the redox behavior is very crucial the antioxidant properties. Antioxidant activity of gallates was studied electrochemically in aqueous media [10].

The electro-oxidation mechanism of gallic acid has been poorly explored in literature. Accordingly, it seems very important to clarify the electrochemical oxidation mechanisms. The objective of the present work is, therefore, to intensively study the electrochemical oxidation of gallic acid in aqueous solutions of different pH's at glassy-carbon electrode. The mechanism is investigated using cyclic, convolution–deconvolution sweep voltammetry, double step chronoamperometry and chronocoulometry and digital simulation under different experimental conditions.

2. Experimental

Gallic acid, GA (99%) was purchased from Sigma–Aldrich. 0.4 M phosphate buffer supporting electrolyte was prepared with various pH values from monosodium phosphate and disodium phosphate in deionized water. Fresh stock standard solution (10 mM) was prepared from the dry pure substances in the phosphate buffer. These solutions were diluted to the convenient concentration just prior to use. All other used solutions were prepared from BHD analytical grade chemicals. A conventional three-electrode electrolytic cell was employed, in which saturated calomel electrode, SCE, a platinum electrode were used as reference and counter electrodes, respectively. Glassy-carbon electrode, GC (surface area = 0.0106 cm^2) was employed as a working electrode. For each voltammetric measurement, the GC working electrode was freshly polished to a smooth surface finish, using successively fine (0.5 µm) grades of

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SiC paper and washed with deionized water. Test solutions were degassed with pure nitrogen prior to the voltammetric measurements. A nitrogen blanket was maintained thereafter. All experiments were performed at room 25 °C temperature. The electrochemical experiments were preformed with an EG & G Princeton Applied Research Model 273A potentiostat controlled by a computer. The electrochemical experiments were controlled by PC and the electrochemical set-up was controlled with an EG & G Princeton Applied Research Model M 270 software. Background data were stored and subtracted from the experimental data set, minimizing side effects such as double layer charging current.

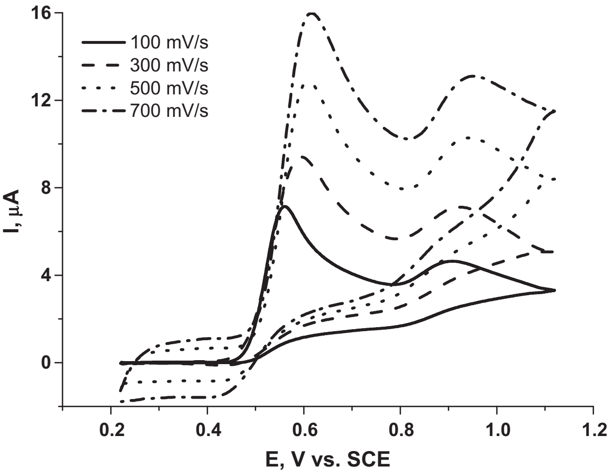

Fig. 1. Cyclic voltammograms of 0.95 mM gallic acid in 0.4 M (pH 1.55) phosphate buffer at different scan rates.

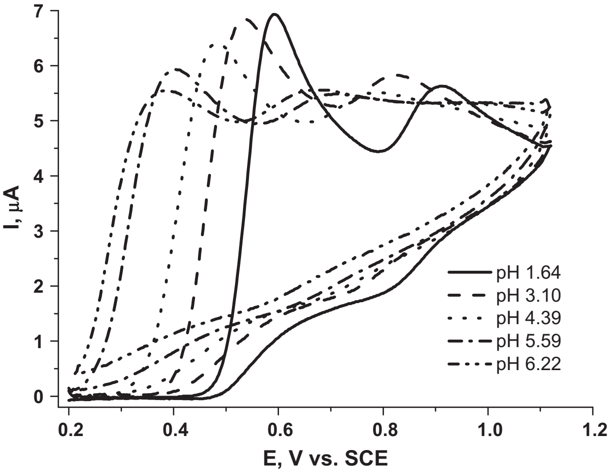

Fig. 2. Cyclic voltammograms of 0.26 mM gallic acid in 0.4 M phosphate buffer with different pH's at scan rate of 100 mV s^{-1}.

For determination of uncompensated resistance, the electrochemical cell is considered electronically equivalent to a RC circuit with the uncompensated resistance, R_u, in series with the double-layer capacitance, C_{dl}. Since faradaic impedance is not considered part of the model, the test potential must be a value at which no faradaic process occurs. A potential step between 25 and −25 mV relative to a test potential is applied and the current is sampled at 50 ms and 100 ms after the step [11]. Assuming the expected exponential decay of the current, characteristic of double layer charging, the initial current, i_o, is determined by extrapolation to zero time. Using Ohm's law, R, is calculated from this measurement as:

$$R_u = \Delta E/i_0 = 50\ \mathrm{mV}/i_0$$

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammograms, cv, of 0.95 mM gallic acid, GA, on glassy-carbon electrode in 0.40 M phosphate buffer at pH 1.55 at different scan rates, v, are shown in Fig. 1. Two irreversible anodic cv waves are seen, their reduction counter-parts are lacking. A linear log–log variation, log peak current, log i_p, versus log scan rate, log v, for both waves is obtained with slope of 0.48 and 0.55 for first and second waves, respectively. Furthermore, the peak current of both waves shows a linear dependence on GA concentration. These results indicate that the two waves are purely diffusion-controlled in nature.

A linear positive shift is observed in the oxidation peak potential, E_p (for the two waves) on increasing scan rate (100–1000 mV s^{-1}). Furthermore, the peak current function, $i_p/v^{1/2}$, diminishes slightly with increasing scan rate. Such behavior is adopted as indicative of an ECEC mechanism [12–14]. On repeated cycling of GA, a decrease of the peak current and a shit of the peak potential towards more positive potentials for the two cv waves are seen with increasing the number of potential cycles during electrolysis (data not shown). This is presumably due to generation of electro-inactive oxidation species on increasing the scanning time. These products block the electrode surface.

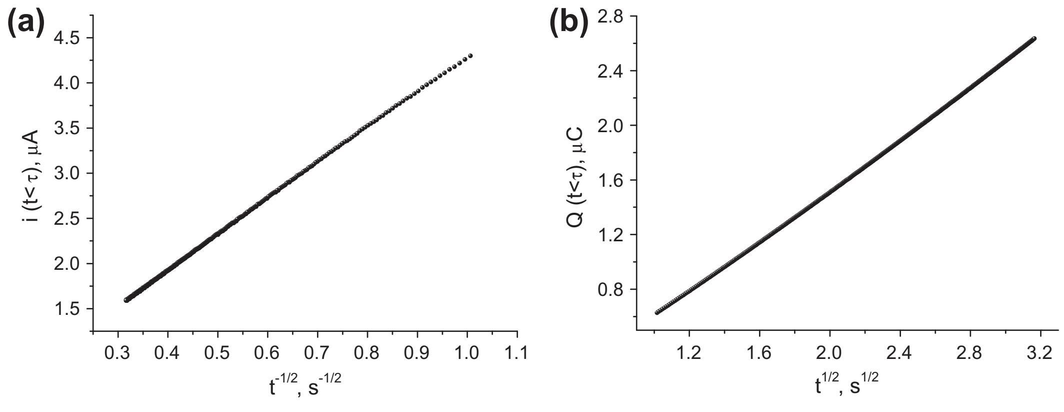

Fig. 3. Chronoamperometry of 0.20 mM gallic acid at pH 1.64, $i(t < \tau)$ versus $(t^{1/2})$ (a) and chronocoulometry, $Q(t < \tau)$ versus $t^{1/2}$ (b).

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