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Cyclic voltammograms obtained from the optical signals: Study of the successive electro-oxidations of rutin

Jian-Bo He [a,b,*], Yan Wang [a], Ning Deng [a], Zheng-Gen Zha [b], Xiang-Qin Lin [b]

[a] *Engineering Research Centre for Bio-process of Ministry of Education of China, School of Chemical Engineering, Hefei University of Technology, Hefei 230009, PR China*
[b] *Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China*

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Abstract

This paper describes a novel method of obtaining cyclic voltammograms (CVs) from optical signals. The obtained CVs correspond to the various specific species involved in the electrode process, which give more detailed information on the system under investigation than the common CV. For this purpose cyclic voltabsorptometry was used to investigate the successive oxidation processes of rutin on a graphite-wax electrode by using a long optical-path thin-layer electrochemical cell. The dynamic UV spectra of rutin showed the information on the structures of the oxidation products at different potentials. Cyclic voltabsorptiograms (CVAs) were measured in three potential ranges at the characteristic absorption wavelengths of rutin, 346, 254 and 296 nm, respectively. The CVs of three species in solution (rutin and its two products) were obtained from the derivative cyclic voltabsorptiograms (DCVAs). Based on this the redox mechanisms of rutin in different CV peaks were discussed.

Keywords: Cyclic voltammetry; Cyclic voltabsorptometry; Spectroelectrochemistry; Rutin; Redox mechanism

1. Introduction

The combination of cyclic voltammetry and spectrophotometry offers the possibility of recording simultaneously the cyclic voltammogram (CV) and cyclic voltabsorptomogram (CVA) [1,2]. The optical signal is another potential-dependent coordinate that gives additional information on the system under investigation. The derivative cyclic voltabsorptomogram (DCVA) with a shape resembling that of the common CV allows more direct comparison between the both. Recent years more attentions have been paid to cyclic voltabsorptometry, which was used to investigate the redox processes of protein films [2,3] and conducting polymer films on indium-tin oxide transparent electrodes, especially the latter films, such as polyaniline [4,5], aniline-*o*-aminophenol copolymer [6], poly(3,4-ethylenedioxythiophene) [7], hybrid organic/inorganic films [8], poly(3,4-dimethoxy-thiophene) [9] and poly-(Azure A) [10], etc.

The oxidation of flavonoids is of great interest because of their action as antioxidants with the ability to scavenge superfluous superoxide free radicals in human body [11] by electron transfer. They are a group of polyphenolic compounds widely distributed in vegetables, fruits and other plants. Owing to the antioxidant ability, they can prevent DNA and cells from oxidative damage [12], and then possess a wide range of pharmacological activities such as antitumor, anti-inflammatory and antiaging, etc. Rutin is one of the most abundant flavonoids in the human diet, and has been used clinically as the therapeutical medicine [13,14]. Recent years Brett and her co-workers studied the electro-oxidation of rutin [15], quercetin [16] and catechin [17], etc. using various voltammetries, and revealed that the various hydroxyl groups of these compounds can be oxidized in different CV peaks via adsorption-involved and pH-dependent transitions. The oxidation mechanisms are very complicated due to the formation of multi-products.

The CVA should be very applicable for studying a complicated electrochemical system involving multi-species with optical absorption, since it has the advantage of separately mon-

* Corresponding author at: Engineering Research Centre for Bio-process of Ministry of Education of China, School of Chemical Engineering, Hefei University of Technology, Hefei 230009, PR China. Tel.: +86 551 2901450; fax: +86 551 2901450.
E-mail address: jbhe@hfut.edu.cn (J.-B. He).

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itoring the specific species participating in specific transitions (not limited to electron transfer) by selecting the corresponding adsorption wavelengths. In this work cyclic voltabsorptometry was used to investigate the oxidation mechanism of rutin in different potential ranges, using a long path-length thin-layer electrochemical cell (LTE-cell). This cell allows the species in solution to be monitored and an opaque working electrode to be used. Considering the superposition of the absorption bands of different species, the DCVA data were resolved by the help of a self-prepared computer program. A novel method of obtaining the CVs of various species in thin-layer solution from the optical signals was proposed for the first time, for the purpose of getting more effective information from the DCVA data.

2. Experimental

2.1. Chemicals and solutions

Rutin is reagent-grade materials from Shanghai Chemical Works (Shanghai, China). Spectrograde graphite powder (320 meshes, Shanghai Chemical Works) was used for construction of GWE. Doubly-distilled water from an all-glass distillatory apparatus was used. High pure N_2 was used for solution deaeration. All other chemicals were of analytical grade from Shanghai Chemical Works (Shanghai, China).

The 0.2 M Britton-Robinson buffered solutions (BRS) containing 0.5 M KCl with various pH values were prepared as the supporting electrolytes. With the aid of ultrasonication, 1.0 mM stock solution of rutin was prepared with ethanol and then stored at 4 °C in a refrigerator. Before used it was diluted to various convenient concentrations by mixing with buffer supporting electrolyte.

2.2. Apparatus

UV–vis absorption spectra and kinetic curves were measured using a model UV-2500 spectrophotometer with UV probe data software (Shimadzu, Japan). Electrochemical measurements were carried out on a model CHI 660 microcomputer-based electrochemical analyzer (CHENHUA, Shanghai, China).

Three-electrode system was used, which is consisted of a graphite-wax working electrode (GWE), a platinum grid counter electrode, and a $Ag/AgCl/KCl_{sat}$ reference electrode. The GWE was selected because of its advantages of low background currents, low noise and fast base line stabilization. A small disk GWE with a geometrical area of 12 mm^2 was used for the common CV, while another with a large area of 77 mm^2 was for the spectroelectrochemistry. The fabrication of GWE has been presented in ref. [18], along with the construction of LTE-cell. The cell was a commercial available quartz photometric cell with an optical path length of 10 mm, containing three-electrode system. The thickness and volume of the thin layer can be estimated as 0.2 mm and 16 μL, respectively. The time constant of the LTE-cell was less than 1 ms in 0.5 M KCl solution, which was characterized by chronoamperometric experiments.

2.3. Procedure

Before experiment, the electrochemical cell was washed with water and ethanol successively for 1 min under ultrasonication. All the experiments were carried out at room temperature (22 ± 1 °C). Rutin solutions were bubbled with N_2 for about 15 min to remove dissolved oxygen before put into the cell. The GWE was degreased before each run by repetitive cyclic scans between −1.2 and 1.5 V in 1.0 M KCl water–ethanol solution, until only the background current presented.

For spectroelectrochemical experiment, a 1.0-ml portion of rutin solution was injected into the LTE-cell through the thin-layer chamber and then infiltrated into the two side chambers, ensuring no gas bubble in the thin layer compartment. An *in-situ* UV–vis absorption spectrum was measured during the thin-layer solution was electrolyzed at a steady potential. On the other hand, kinetic absorbance monitoring coupled with CV scans was taken at certain wavelengths to follow the concentration changes of species in the thin layer solution. Considering the strong adsorption of rutin on GWE, a pre-accumulation step was always performed in open circuit. The accumulation time of 400 s was used in this work.

2.4. Principle of the DCVA data processing

In a multi-species system an absorption spectra band usually contains the contributions of different species. By resolution of the absorption signals, the dependences of the reaction rates of various species on potential (dc/dt versus E) can be derived from the superposed DCVA data (dA/dt versus E) at different absorption wavelengths during the cyclic potential scan. For a three-species system which has three characteristic bands, we have

$$\frac{dA_I}{dt} = \varepsilon_{I,1} l \frac{dc_1}{dt} + \varepsilon_{I,2} l \frac{dc_2}{dt} + \varepsilon_{I,3} l \frac{dc_3}{dt} \quad (1)$$

$$\frac{dA_{II}}{dt} = \varepsilon_{II,1} l \frac{dc_1}{dt} + \varepsilon_{II,2} l \frac{dc_2}{dt} + \varepsilon_{II,3} l \frac{dc_3}{dt} \quad (2)$$

$$\frac{dA_{III}}{dt} = \varepsilon_{III,1} l \frac{dc_1}{dt} + \varepsilon_{III,2} l \frac{dc_2}{dt} + \varepsilon_{III,3} l \frac{dc_3}{dt} \quad (3)$$

where ε is the molar extinction coefficient; l is the path length of the light through the solution; c is volume molar concentration; the subscripts I, II, and III indicate three absorption bands; 1, 2, and 3 denote three species in the thin-layer solution, which result in the optical absorption. By solving these simultaneous equations we get

$$\frac{dc_1}{dt} = \frac{1}{l\,\Delta\varepsilon^3}\left(a_{11}\frac{dA_I}{dt} + a_{21}\frac{dA_{II}}{dt} + a_{31}\frac{dA_{III}}{dt}\right) \quad (4)$$

$$\frac{dc_2}{dt} = \frac{1}{l\,\Delta\varepsilon^3}\left(a_{12}\frac{dA_I}{dt} + a_{22}\frac{dA_{II}}{dt} + a_{32}\frac{dA_{III}}{dt}\right) \quad (5)$$

$$\frac{dc_3}{dt} = \frac{1}{l\,\Delta\varepsilon^3}\left(a_{13}\frac{dA_I}{dt} + a_{23}\frac{dA_{II}}{dt} + a_{33}\frac{dA_{III}}{dt}\right) \quad (6)$$