ACTA TECHNICA CORVINIENSIS – Bulletin of Engineering
Tome VI (Year 2013) – FASCICULE 2 [April–June]
ISSN 2067–3809

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ELECTROCHEMICAL DETECTION OF ASCORBIC ACID USING A POLYMER MODIFIED CARBON PASTE ELECTRODE

[1-5.] EQUIPE D'ELECTROCHIMIE MOLECULAIRE ET MATERIAUX INORGANIQUES, FACULTE DES SCIENCES ET TECHNIQUES DE BENI MELLAL, UNIVERSITE SULTAN MOLUAY SLIMANE, BP : 523, BENI MELLAL, MAROCCO

ABSTRACT: Ascorbic acid (Vitamin C) is a water soluble organic compound that participates in many biological processes. This paper reports the synthesis of polymer modified carbon paste electrode and its application for the electrochemical detection of ascorbic acid (AA). The cyclic voltammetry results obtained corrobate with square wave voltammetry. The influence of variables such the concentration of ascorbic acid adsorbed onto polymer, and the pH of solution were tested. The capacity of prepared electrode (P-CPE) for selective detection of AA was confirmed in a sufficient amount of ascorbic acid. The observed linear range for the determination of AA concentration was from 0.2 mM to 9 mM. The detection limit was estimated to be 5. 48 mM.
KEYWORDS: Ascorbic acid; Carbon paste electrode; Cyclic voltammetry; Electrochemical detection

INTRODUCTION

Ascorbic acid AA (vitamin C) is a water soluble organic compound involved in many biological processes. AA is used in large scale as an antioxidant in food, animal feed, beverages, pharmaceutical formulations and cosmetic applications. It is also important in helping to produce collagen, a protein needed in the development and maintenance of bones, cartilage, joint limings, skin, teeth, gums and blood vessels [1 - 3]. Due to the above importance of AA, its determination in their solution is more important.

Many analytical techniques including sensors and biosensors [4 - 6] have been suggested for a detection of ascorbic acid in very varied types of samples. Other methods, based on the most commonly employed physico-chemical methods for identification of AA such high performance liquid chromatography [7-9] or capillary electrophoresis [10-13]. Investigations aimed at the development of modern analytical techniques for AA determination are directed towards increasing their sensitivity, specificity, simplicity and rapidity [14-15].

Electrochemical detection is an attractive alternative method for detection of electroactive species, because of its inherent advantages of simplicity, ease of miniaturization, high sensitivity and relatively low cost.

In this paper, we describe the electrochemical analysis of ascorbic acid on a polymer modified carbon paste electrode. The electrochemical characterization of adsorbed electroactive AA was evaluated using cyclic voltammetric and square wave voltammetric (SWV) analysis.

EXPERIMENTAL. Reagents and instrumentation

All chemicals were of analytical grade and used without further purification. Na_2SO_4, KOH, eugenol and ascorbic acid were purcharged form Fluka. Carbon powder (Carbone, Lorraine, ref. 9900, French) was used for the preparation of electrode. All solutions were prepared with doubly distilled water.

Preparation of CPE

Substrates of commercial stainless steel metal 1 x 1 x 0.1 cm^3 in size were grinded, and cleaned in pure acetone and distilled water. An anodic oxidation system was composed of anode and cathode plates of steel, electrolyte of carbon solution contained in glass chamber and an extended range direct current (DC) power supply system. Substrates of stainless steel metal were fixed on the anode using steel wire and immersed in H_2SO_4 solution for 5 min to dissolve the air-formed oxide film on the surface. Then, they were immersed in electrolyte of carbon gel contained glass chamber, and subjected to anodic oxidation by applying DC for 72h at room temperature. The anodic oxidation was processed at 25 V.

Apparatus

Voltammetric experiments were investigated with a potentiostat (model PGSTAT 100,Eco Chemie B.V., The Netherlands), equipped with a three electrode system mounted on cell. Working electrode was polymer modified carbon paste electrode, the counter electrode was a platinum plate and SCE served as reference. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

RESULTS AND DISCUSSION. Electrochemical polymerization of eugenol

Figure 1 shows the consecutive cyclic voltammograms (CVs) of graphite carbon electrode in 0.1 M KOH solution containing 4 mM eugenol.

On the first anodic scan an oxidation peak was observed at -0.2 V which corresponds to the oxidation of primary hydroxyldthe group of monomers [16]. This peak disappears from the second cycle, this behavior indicates the rapid deposition of a non-conductive polymer to the electrode surface. However, when the potential scan is extended towards positive values is observed a second peak at about 0.5 V. Authors [17], in a study of the same molecule on a glass electrode, attributed the first peak in the deposition of a polymer on the electrode surface, the second peak is probably due to the phenomenon degradation / restriction of this polymer.

Figure 3 shows the SEM images of eugenol polymer coated electrode which indicated that thin film layer was covered the surface.

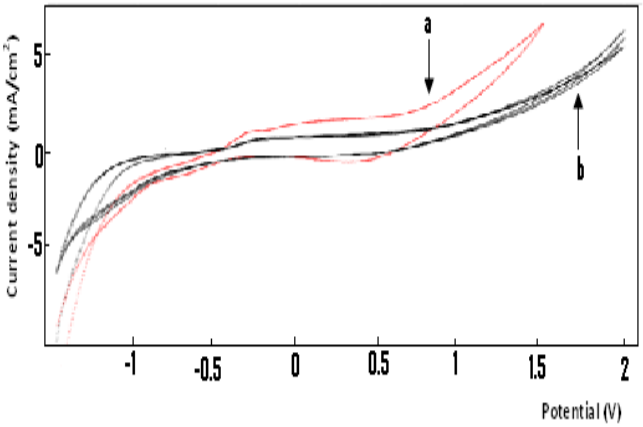


Figure 1. Cyclic voltammograms of the eugenol film on GC electrode from the electrolyte 0.1 M KOH solution containing 4 mM eugenol monomers. Scan rate = 0.1 V/s. a- 1 st cycle, b- 20 th cycle

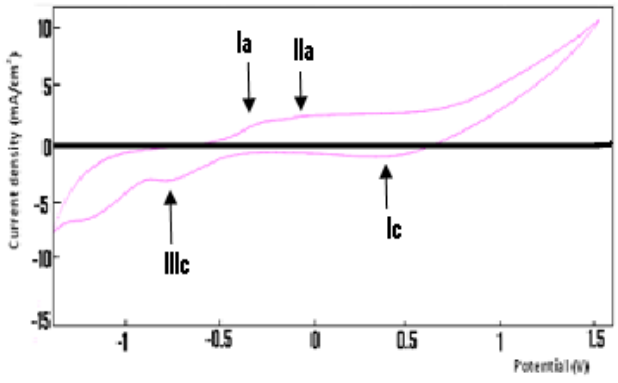
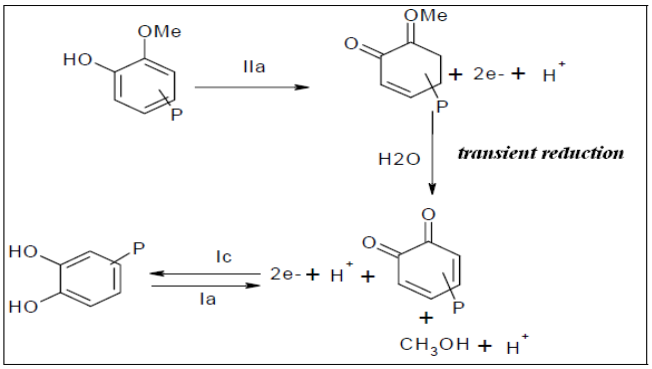
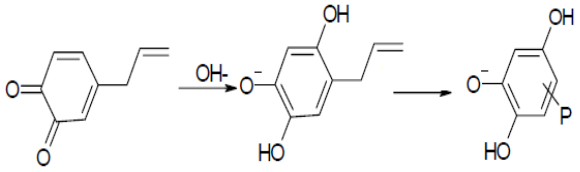


Figure 2. Cyclic voltammograms of the eugenol film on GC electrode from the electrolyte 0.1 M KOH solution containing 4 mM eugenol monomers. Scan rate = 0.1 V/s, first cycle

Upon scan reversal a cathodic wave there are two reduction peaks, at - 0.4 v and 0.5 V, based on the results of El Qouatli and al [16], the major reversible couple (Ia / Ic) Fig. 2, followed by a irreversible peak IIa can be attributed to the following steps:



where P indicates the polymeric structure in which a groups 2-methoxy-phenol are stationary, the second peak IIIc is probably associated to the transition of trihydroxybenzene derivative formed during the polymerization from 4-allyl-1 ,2-quinone according to the reaction:



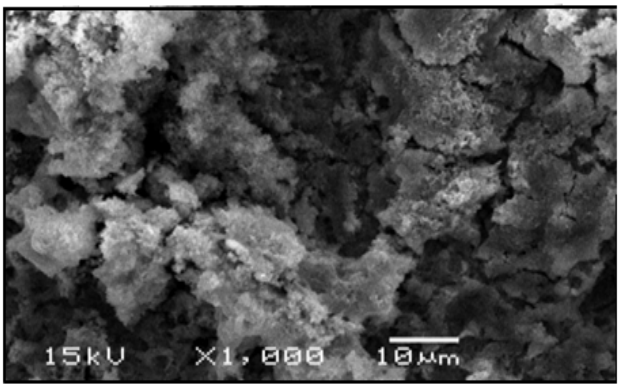


Figure 3. SEM image of eugenol polymer film modified electrode

Electrochemical detection of ascorbic acid

The determination of AA concentration using eugenol polymer modified electrode was performed with cyclic and square wave voltammetry. Figure 4 shows the cyclic voltammogram of ascorbic acid in 0.1M Na_2SO_4 solution. One peak was observed during the negative scan, attributed to reduction of eugenol polymer. According to the literature [18], the absence of defined peak of ascorbic acid can be explained by the interaction between eugenol polymer film and AA. The formation of a complex of ascorbate concentration with the oxidized active site of polymer is expected followed by spontaneous of the resulting complex. [19-20].

The square wave voltammetric determination of a series of standards solutions of ascorbic acid was performed under the optimized working conditions. The results show that reduction peak current have a linear relationship with a concentration of AA in the range from 3 mM to 9 mM (Figures 5 and 6). The linear correlation coefficient is 0.9917. According to Miller and Miller [21] the standard deviation of the mean current (S.D.) measured for seven voltammograms of the blank solution in pure electrolytes was calculated from:

$$SD = \frac{1}{(n-2)} \sum_{j=0}^{n} (i_j - I_j)^2$$

where i_j is the experimental value of the experiment number j and I_j is the corresponding recalculated value, at the same concentration using the regression line equation.

The calculated S.D. was used in the determination of the detection limit (DL, 3 x S.D./slope) and the quantification limit (QL, 10 x S.D./slope). From these values, the detection and quantification limits were 12.4 x 10^{-8}M and 9.6 x 10^{-6} M.

The linear regression analysis gave

Y = 0.2 X - 0.437.

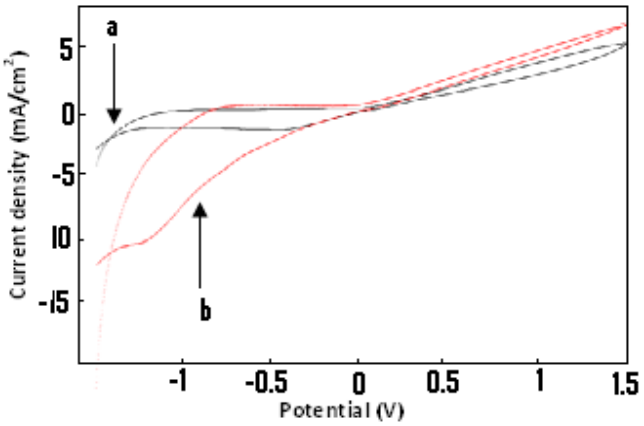


Figure 4. CVs of eugenol polymer/GC modified electrode in pH 6.0, O.1M Na_2SO_4, [AA] = (a) 0 M, (b) 3mM, scan rate 100 mV/s

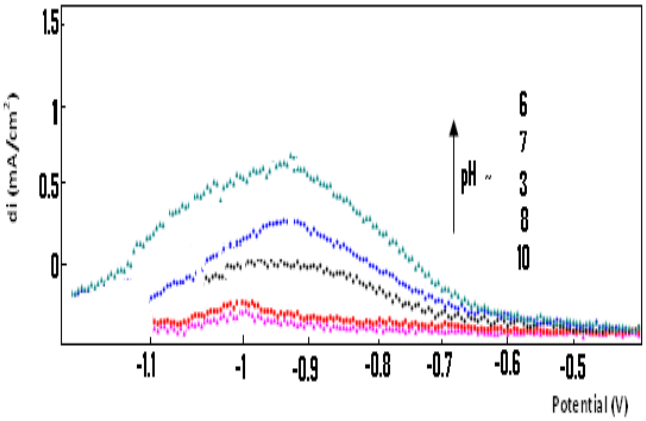


Figure 5. Square voltammograms at eugenol polymer/GC modified electrode for different concentrations of ascorbic acid

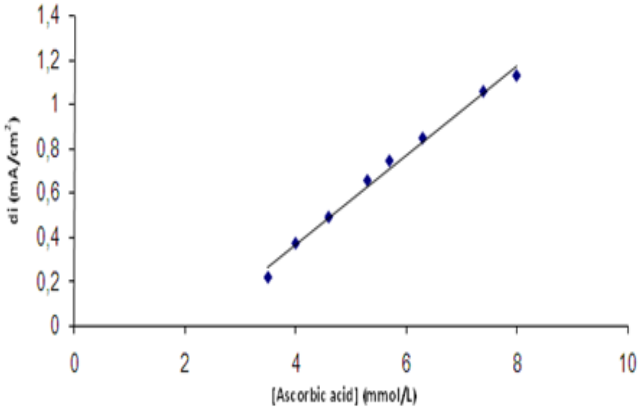


Figure 6. Calibration curve for AA in Na_2SO_4

Effect of pH

The effect of varying pH on the current response of eugenol polymer/GC modified electrode at constant ascorbic acid concentration (3 mM) is shown in Figures 7 and 8.

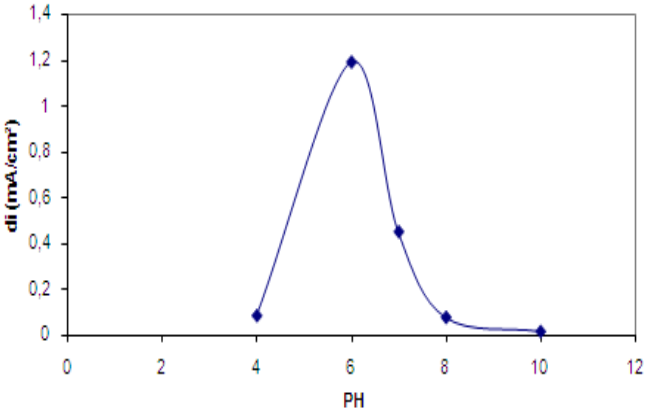


Figure 7. Effect of pH on SWV peak of 3 mM AA in Na_2SO_4 0.1M

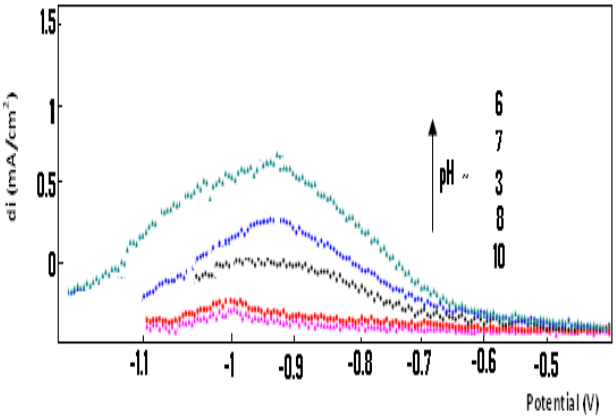


Figure 8. Square wave voltammograms of 3 mM AA in 0.1 M Na_2SO_4 at different pH values

As can be seen, the peak current gradually increases with the increase of pH and reach a maximum value when the pH is 6.0. Further increase in the solution pH yields a gradual decrease in the AA peak current. As a result, a solution with pH 6.0 was used in the subsequent experiments.

The peak current seem to be affected by the concentration of H^+, suggesting that the oxidation of the AA includes some proton transfer processes. The current decreases significantly in higher pH value.

CONCLUSIONS

It was demonstrated here that eugenol polymer/GC modified electrode exhibits higher electrocatalytic activity towards ascorbic acid oxidation. The anodic peak of AA is not well defined but the cyclic voltammograms in negative wave gave significantly increased peak currents and a fast electron transfer process to AA.

The obtained results revealed that determination of AA can be easily performed using the eugenol polymer film. The proposed methodology was successfully applied in quantifying ascorbic acid in electrolyte solution with very satisfactory recovery percentages values for the application of the analytic methods proposed. The sensitivity signal is proportional to the concentration value of AA.

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ACTA TECHNICA CORVINIENSIS – BULLETIN of ENGINEERING

ISSN: 2067-3809 [CD-Rom, online]