ORIGINAL PAPER

# Electrocatalytic oxidation of ascorbic acid at a 2,2'-(1,8octanediylbisnitriloethylidine)-bis-hydroquinone modified carbon paste electrode

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Abstract Cyclic voltammetry and chronoamperometry were used to investigate the electrochemical behavior of ascorbic acid at a carbon paste electrode modified with 2,2'-(1,8-octanediylbisnitriloethylidine)-bis-hydroquinone (1,8-OBNEBHQ). The modified carbon paste electrode showed high electrocatalytic activity toward ascorbic acid; the current was enhanced significantly relative to the situation prevailing when an unmodified carbon paste electrode was used. The electrocatalytic process was highly dependent on the pH of the supporting electrolyte. The apparent charge transfer rate constant,  $k_s$ , and transfer coefficient,  $\alpha$ , for electron transfer between 1,8-OBNEBHO and carbon paste electrode were calculated as  $20.2 \pm 0.5 \text{ s}^{-1}$  and 0.47, respectively. Using differential pulse voltammetry, the calibration curves for AA were obtained over the range of 5-30 and 40-1,500 µM, respectively. The detection limit (k $\sigma$ , k = 2) was 0.6  $\mu$ M. With good selectivity and sensitivity, the present method provides a simple method for selective detection of ascorbic acid in biological samples.

**Keywords** Electrocatalytic oxidation · 2,2'-(1,8-Octanediylbisnitriloethylidine)bis-hydroquinone · Carbon paste electrode · Ascorbic acid

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#### 1 Introduction

Ascorbic acid (AA) or vitamin C is an essential nutrient for higher primates and a small number of other species. The presence of ascorbic is required for a range of essential metabolic reactions in all animals and in plants and is made internally by almost all organisms, humans being one notable exception. Vitamin C is also present in many other biological systems and multivitamin preparation, which are commonly used to supplement inadequate dietary intake. Nevertheless, it is widely used in foods as an antioxidant for the stabilization of color and aroma with subsequent extension of the storage time of the products [1-3]. Therefore it is essential to develop simple and rapid methods for its determination in routine analysis. Among the methods available for the measurement of ascorbic acid we can highlight highperformance liquid chromatography (HPLC) [4-6], gas chromatography (GC) [7], flow injection spectrophotometry [8], sequential injection analysis [9], calorimetry [10], flame atomic absorption spectrometry [11], enzymatic spectrophotometry [12], polarography [13] and titration [14], etc. Nevertheless some of the above techniques suffer from diverse disadvantages with regard to the expensive equipment, insufficient selectivity, complicated derivatization for sensitive detection, and time-consuming process of sample clear-up to prevent deteriorating chromatographic columns [15]. In this sense, the development of sensors for AA determination is of considerable interest because its use involves several advantages such as rapid response, high specificity, low cost and no need of sample preparation. Carbon-based electrodes, mainly modified carbon paste electrode (CPE), are the best suited for the determination of compounds present in biological fluids [16, 17].

Carbon paste electrodes constitute a convenient conductive matrix for the preparation of chemically modified

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electrodes by simple mixing of graphite/binder paste and modifier [18]. These kinds of electrode are inexpensive and possess many advantages such as low background current, wide range of potential, easy fabrication, and rapid renewal [19]. Carbon paste electrodes modified with tetrabromo*p*-benzoquinone [20], cobalt salophen/cationic surfactant [21], ruthenium (III) diphenyl dithiocarbamate [22] and 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone [23] have been reported for voltammetric determination of ascorbic acid.

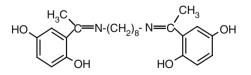
In the present work, we describe the catalytic behavior of a 2,2'-(1,8-octanediylbisnitriloethylidine)-bis-hydroquinone (1,8-OBNEBHQ) modified carbon paste electrode for the oxidation of AA. The electrochemical properties and electrocatalytic activity of the modified electrodes toward the oxidation of AA were studied using various electrochemical procedures. In order to demonstrate the catalytic ability of the 2,2'-(1,8-octanediylbisnitriloethylidine)-bishydroquinone modified carbon paste electrode in the oxidation of AA in real samples, AA in some pharmaceutical samples was determined by differential pulse voltammetry.

## 2 Experimental

#### 2.1 Apparatus and reagents

All electrochemical experiments were carried out using a microAutolab Type III (Eco Chemie B. V.) equipped with GPES 4.9 software. The cell used was equipped with a modified carbon paste electrode as the working electrode, a saturated Ag/AgCl reference electrode and a platinum wire counter electrode. All potentials were measured and reported versus the Ag/AgCl reference electrode.

2,2'-[1, 8-Octanediylbis (nitriloethylidine)]-bis-hydroquinone (Scheme 1) was synthesized from 2,5-dihydroxyacetophenone and 1,8-diaminooctane in our laboratory and characterized by physical and spectroscopic data. Ascorbic acid, graphite fine powder and viscous paraffin were obtained from Merck and used as received. All solutions were prepared with twice distilled water. Buffer solutions were prepared from orthophosphoric acid and its salts. All solvents were of the highest purity available from Merck and were used without further purification.



Scheme 1 Structure of 2,2'-[1, 8-octanediylbis (nitriloethylidine)]-bishydroquinone

2.2 Procedure for preparation of 2,2'-[1,8-octanediylbis(nitriloethylidyne)]-bis-hydroquinone

To a mixture of 2,5-dihydroxyacetophenone (0.3 g, 2 mmol) in methanol was added 1,8-diaminooctane (0.144 g, 1 mmol) by stirring in one portion. Stirring was continued for 65 min. The progress of the reaction was monitored by TLC. After completion of the reaction, a yellow substance was precipitated. The solid product was filtered off and washed with cold methanol. The obtained crude product was recrystallized in methanol and the 2,2'-[1,8-octanediylbis(nitriloethylidyne)]-bis-hydroquinone as yellow crystalline with m.p. 224–226 °C in 94% yield was obtained. The structure of the Schiff base product was identified by physical and spectroscopic data as follows.

2,2'-[1, 8-octanediylbis (nitriloethylidine)]-bis-hydroquinone; yellow solid m.p: 224–226; IR (KBr)/ $\nu$  (cm<sup>-1</sup>) 3,320–3,340 (br, OH), 3,032, 2,929 (s), 2,852 (s), 2,700, 1,608 (s, C=N), 1,552, 1,390 (s, Ar C=C), 1,526, 1,413, 1,470, 1,311, 1,225 (s, C–O), 850 (s), 800 (s), 500 (m); <sup>1</sup>H NMR (400 MHz/DMSO)/ $\delta$  ppm: 1.1 (br, 8H, 4CH<sub>2</sub>), 1.4 (m, 4H, 2CH<sub>2</sub>), 2.1 (s, 6H, 2CH<sub>3</sub>), 3.4 (t, 4H, 2CH<sub>2</sub>), 6.4 (d, 2H, Ar), 6.5 (d, 2H, Ar), 6.7 (d, 2H, Ar), 8.6 (br, 2H, 2OH), 15.3 (s, 2H, 2OH); <sup>13</sup>C NMR (100 MHz/DMSO)/ $\delta$  ppm: 15.9, 28.4, 30.4, 31.6, 50.4, 115.16, 119.6, 120.6, 121.6, 149.5, 157.15, 173.0.

### 2.3 Working electrode

A 1% (w/w) 2,2'-[1, 8-octanediylbis (nitriloethylidine)]-bishydroquinone spiked carbon powder was made by dissolving a given quantity of 2,2'-[1, 8-octanediylbis (nitriloethylidine)]-bis-hydroquinone in diethyl ether and hand mixing with 99-times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring a 1:1 (w/w) mixture of 1% 2,2'-[1,8-octanediylbis(nitriloethylidyne)]-bis-hydroquinone spiked carbon powder and paraffin oil was blended by hand mixing and the resulting paste was then inserted in the bottom of a glass tube. Electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without 2,2'-[1, 8-octanediylbis (nitriloethylidine)]-bis-hydroquinone was used as a blank to determine background current.

#### 2.4 Procedures for pharmaceutical preparations

Pharmaceutical preparation: The following commercial ascorbic acid formulations available from local sources were subjected to the described analytical procedure: (1) Tablets containing sodium saccharin combined with ascorbic acid (effervescent tablets); (2) Ampoules containing ascorbic acid as the single component; and

(3) Multivitamin syrup containing vitamins A,  $B_1$ ,  $B_2$ ,  $B_6$ ,  $B_{12}$ ,  $D_3$ , E and C and nicotinamide.

Injection: A 1 mL ampoule volume was transferred to a 100 mL flask and diluted to volume with twice distilled water. A 1 mL portion of the solution was diluted in a voltammetric cell to 10 mL of 0.1 M phosphate buffer (pH 7.0), and the differential pulse voltammogram was recorded.

Effervescent vitamin C tablets: A 100 mg portion of a finely powdered sample was dissolved in a 50 mL flask with twice distilled water. A 1 mL portion of the solution was diluted in a voltammetric cell to 10 mL of 0.1 M phosphate buffer (pH 7.0), and the differential pulse voltammogram was recorded.

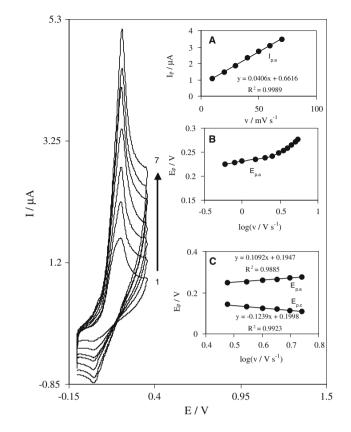
Multivitamin syrup: A 5 mL multivitamin syrup volume was transferred to a 50 mL flask and diluted to 10 mL of 0.1 M phosphate buffer (pH 7.0), and the differential pulse voltammogram was recorded.

Iodine titration method: A 0.05 M iodine solution was standardized in the usual way with a standard of thiosulfate solution. For pharmaceutical analysis, an iodimetric procedure described in the US pharmacopoeia (USP), was used [24].

#### **3** Results and discussion

# 3.1 Electrochemistry of 1,8-OBNEBHQ modified carbon paste electrode

To our knowledge there has been no study of the electrochemical properties, and especially the electrocatalytic activity, of 1,8-OBNEBHQ in aqueous media. Because this compound is insoluble in aqueous media we prepared 1,8-OBNEBHQ modified carbon paste electrode (1,8-OBNEBHQMCPE). Therefore, we studied the electrochemical behavior of 1,8-OBNEBHQMCPE in a pure buffered aqueous solution by cyclic voltammetry. Figure 1 shows the cyclic voltammograms of the 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer solution (pH 7.0) at various scan rates. For low scan rates no cathodic peak was observed in the reverse scan. For sweep rates between 10 and  $600 \text{ mV s}^{-1}$  the anodic peak potential is constant. For sweep rates above 600 mV  $s^{-1}$  the anodic peak potential changes positively, indicating the limitation arising from charge transfer kinetics (Fig. 1, inset B). Also, the electrochemical responses of the 1,8-OBNEBHQMCPE were those anticipated for a surface-confined redox couple, because the peak currents were directly proportional to scan rate (Fig. 1, inset A), as predicted for a diffusionless system. An approximate estimate of the surface coverage of the electrode was made by adopting the method used by Sharp et al. [25]. According to this method, the peak



**Fig. 1** Cyclic voltammograms of 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer (pH 7.0) at various scan rates: The numbers 1–7 correspond to 10, 20, 30, 40, 50, 60 and 70 mV s<sup>-1</sup> scan rates, respectively. Insets: (A) Variations of  $I_{p,a}$  versus scan rate. (B) Variation of  $E_{p,a}$  versus the logarithm of the scan rate. (C) Magnification of the same plot for high scan rates

current is related to the surface concentration of electroactive species  $\Gamma$  by the following equation:

$$Ip = n^2 F^2 A \Gamma v / 4RT \tag{1}$$

where n represents the number of electrons involved in the reaction, A is the surface area  $(0.09 \text{ cm}^2)$  of the modified carbon paste electrode (MCPE),  $\Gamma$  (mol cm<sup>-2</sup>) is the surface coverage and other symbols have their usual meanings. From the slope of the anodic peak currents of 1,8-OBNEBHQ is  $1.2 \times 10^{-10}$  mol cm<sup>-2</sup> for n = 2 the apparent charge transfer rate constant, k<sub>s</sub>, and the charge transfer coefficient,  $\alpha$ , of a surface-confined redox couple can be evaluated from cyclic voltammetric experiments and using the variation of anodic and cathodic peak potential with scan rate, according to the procedure of Laviron [26]. Inset B of Fig. 1 shows the variations of anodic peak potential (E<sub>p.a</sub>) with scan rate. E<sub>p</sub> values are proportional to the logarithm of scan rate, for scan rates higher than 3,000 mV s<sup>-1</sup> (Fig. 1, inset C). Under these conditions the following equation can be used to determine the electron transfer rate constant between 1,8-OBNEBHQ and the carbon paste electrode (CPE) [26]:

$$\log k_{s} = \alpha \log(1 - \alpha) + (1 - \alpha) \log\alpha - \log[RT/nF\nu] - \alpha(1 - \alpha)n_{\alpha}F\Delta E_{p}/2.3RT$$
 (2)

where  $(1 - \alpha)n_{\alpha} = 0.54$ , n = 2,  $\Delta E_p = E_{p.a} - E_{p.c}$ , v is the sweep rate and all other symbols have their conventional meanings. From the values of  $\Delta E_p$  corresponding to different sweep rates, an average value of  $k_s$  was found to be  $20.2 \pm 0.5 \text{ s}^{-1}$ . The value obtained for the charge transfer coefficient from the slopes of the inset C plots was found to be 0.47.

#### 3.2 Effect of pH on peak potential

The voltammetric behavior of the 1,8-OBNEBHQMCPE was characterized at various pHs by CV. Figure 2 shows peak currents of solution buffers at various pH values ranging from 2.0 to 10.0. The anodic peak potential was pH dependent. The inset of Fig. 2 shows  $E_{p.a}$  as a function of pH. The results showed that the slope ( $E_{p.a}$ /pH) is -49.7 mV/pH unit over a pH range from 2.0 to 10.0. This slope was close to the Nernstian value of -59.2 mV for a two-electron, two-proton process [27]. So two protons are transferred in the redox reaction in the pH range 2.0–10.0

#### 3.3 Electrochemistry of AA at 1,8-OBNEBHQMCPE

In order to test the potential electrocatalytic activity of the 1,8-OBNEBHQMCPE, its cyclic voltammetric responses at 50 mV s<sup>-1</sup> were obtained in pH 7.0, phosphate buffer in the absence and presence of 1 mM AA, and the data are presented in Fig. 3. In the absence of AA an anodic peak of 1,8-OBNEBHQMCPE can be observed (Fig. 3, curve a). Upon addition of 1.0 mM AA there was a drastic enhancement of the anodic peak current (Fig. 3, curve b). This behavior is consistent with a very strong electrocatalytic effect. Under the same experimental conditions the direct oxidation of AA at an unmodified carbon paste

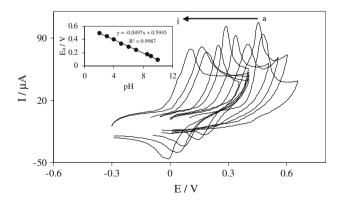


Fig. 2 Cyclic voltammograms of 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer solution of pH 2–10 (respectively a–i). Inset: Plot of  $E_a$  vs. pH

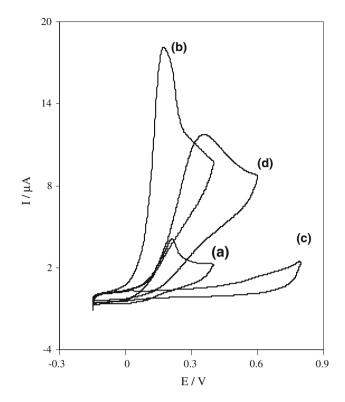
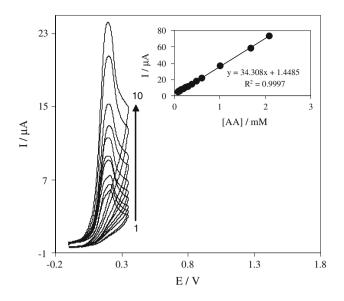


Fig. 3 Cyclic voltammograms of: (a) 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer (pH 7.0) solution and (b) the same electrode in 1.0 mM AA, pH 7.0 solution. (c) as (a) and (d) as (b) for an unmodified CPE. In all cases the scan rate was 50 mV s<sup>-1</sup>

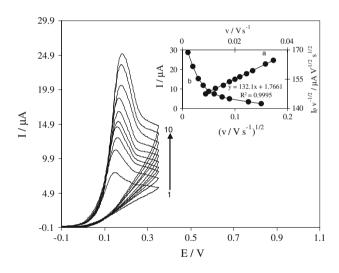
electrode shows an irreversible wave at more positive potentials (Fig. 3, curve d). The catalytic peak potential is found to be about 169 mV, whereas that of the uncatalyzed peak is about 375 mV. Thus, a decrease in the overvoltage of approximately 206 mV and enhancement of the peak current is also achieved with the modified electrode.

Figure 4 shows the dependence of the voltammetric response of 1,8-OBNEBHQMCPE on the AA concentration. With the addition of AA, there was an increase in the anodic current. The plot of electrocatalytic current versus AA concentration is shown in the inset of Fig. 4. The calibration plot was linear for a wide concentration range, 0.08–2.1 mM ascorbic acid (inset of Fig. 4).

The cyclic voltammogram of 1,8-OBNEBHQMCPE at various scan rates (2–30 mV s<sup>-1</sup>) in the presence of 1 mM AA was studied (Fig. 5). The oxidation current for AA increased linearly with the square root of scan rate (inset, curve a), suggesting that at sufficient overpotential the reaction is diffusion limited. A plot of the sweep rate-normalized current ( $\text{Ip}/v^{1/2}$ ) versus scan rate (inset, curve b) exhibits the characteristic shape typical of an EC catalytic process. Andrieux and Saveant [28] developed a theoretical model for such a mechanism and derived a relation between the peak current and concentration of the substrate



**Fig. 4** Dependence of cyclic voltammetry response at a 1,8-OBNEBHQMCPE on AA concentration in 0.1 M buffer phosphate solution (pH 7.0) at 50 mV s<sup>-1</sup>. The numbers of 1–10 correspond to 0.08, 0.1, 0.12, 0.16, 0.20, 0.24, 0.30, 0.38, 0.48 and 0.6 mM AA. Inset: Variations of electrocatalytic current versus AA concentration in the range of 0.08–2.1 mM



**Fig. 5** Cyclic voltammograms of 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer (pH 7.0) containing 1 mM AA at different scan rates. The numbers 1–10 correspond to 2, 4, 6, 8, 10, 12, 15, 18, 25 and 30 mV s<sup>-1</sup> scan rates, respectively. Inset: Curve a, variation of the electrocatalytic currents versus the square root of scan rate and curve b, variation of the scan rate normalized current ( $I_p/v^{1/2}$ ) with scan rate

for the case of a slow rate, v, and a large catalytic rate constant,  $k'_{h}$ :

$$I_{cat} = 0.496 n FAC_s D^{1/2} v^{1/2} [n F/RT]^{1/2}$$
(3)

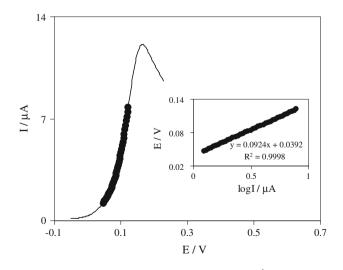
where D and C<sub>s</sub> are the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>) and the bulk concentration (mol cm<sup>-3</sup>) of the substrate (AA in this case), respectively. Low values of  $k'_h$  result in values lower than 0.496 for the constant. Based on extensive computations, a working curve showing the relationship between the numerical values of the constant,  $I_{cat/}$  nFAC<sub>s</sub>(DnFv/RT)<sup>1/2</sup>, log [k $\Gamma/(DnFv/RT)^{1/2}$ ] (Fig. 1 of reference [28]) is given. The value of k'<sub>h</sub> can thus be calculated from such a working curve. For low scan rates (2–30 mV s<sup>-1</sup>), we find the value of this constant to be 0.30 for a 1,8-OBNEBHQMCPE, with a coverage of  $\Gamma = 1.2 \times 10^{-10}$  mol cm<sup>-2</sup>, a geometric area (A) of 0.09 cm<sup>2</sup> and considering D = 8.08 × 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> (this is obtained by chronoamperometry as below), in the presence of 1 mM AA. Using this value and Fig. 1 from the theoretical paper by Andrieux and Saveant [28], the value of k'<sub>h</sub> was found to be 3.22 × 10<sup>-3</sup> cm s<sup>-1</sup> for low scan rates (2–30 mV s<sup>-1</sup>).

The number of electrons in the overall reaction can also be obtained from the slope of the  $I_p$  vs.  $v^{1/2}$  plot (Fig. 5, inset, curve a). Using the slope of this plot and according to the following equation for a totally irreversible diffusioncontrolled process [29]:

$$n = I_p / \nu^{1/2} / \left\{ 3.01 \times 10^5 [(1 - \alpha)n]^{1/2} A D^{1/2} C_s \right\}$$
(4)

and considering  $(1 - \alpha)n_{\alpha} = 0.64$  (see below), it is estimated that the total number of electrons involved in the anodic oxidation of AA is n = 2.

Figure 6 shows the linear sweep voltammogram, at 7 mV s<sup>-1</sup>, of a 1,8-OBNEBHQ-MCPE in 0.1 M phosphate buffer solution (pH 7.0) containing 1 mM AA. The points show the rising part of volammogram which is the Tafel region and is affected by electron transfer kinetics between AA and 1,8-OBNEBHQMCPE, assuming the deprotonation of AA as a sufficiently fast step. In this condition, the number of electrons involved in the rate determining step

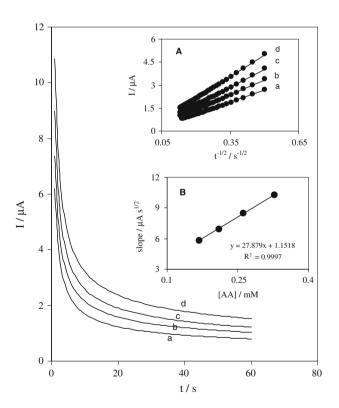


**Fig. 6** Linear sweep voltammogram (at  $7 \text{ mV s}^{-1}$ ) of an 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer (pH 7.0) containing 1 mM AA. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the linear sweep voltammogram

can be estimated from the slope of Tafel plot. The inset of Fig. 6 shows a Tafel plot drawn from points of the Tafel region of the linear sweep voltammogram. A Tafel slope of 0.0924 V decade<sup>-1</sup>, obtained in this case, agrees well with the involvement of one electron in the rate determining step of the electrode process, assuming a charge transfer coefficient of  $\alpha = 0.36$  [27]. In addition, the exchange current density, j<sub>o</sub>, is obviously readily accessible from the intercept of the Tafel plot [27]. The value obtained for the exchange current density for AA at the 1,8-OBNEBHQMCPE was found to be 4.19  $\mu$ A cm<sup>-2</sup>.

#### 3.4 Chronoamperometric studies

The catalytic oxidation of AA, by a 1,8-OBNEBHQMCPE was also studied by chronoamperometry. Chronoamprograms obtained at a potential step 200 mV are depicted in Fig. 7. In chronoamperometric studies, we have determined the diffusion coefficient of AA for a 1,8-OBNEBHQMCPE. Figure 7, inset A, shows the experimental plots of I vs.  $t^{-1/2}$  with the best fits for different concentrations of AA employed. The slopes of the resulting straight lines were



**Fig. 7** Chronoamperometric response at 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer (pH 7.0) at a potential step of 200 mV for different concentration of AA: (a) 0.17, (b) 0.21, (c) 0.26 and (d) 0.33 mM. Insets: (A) Plots of I vs.  $t^{-1/2}$  obtained from chronoamperograms. (B) Plot of the slope of straight lines against the AA concentration

then plotted versus the AA concentration (Fig. 7, inset B), from whose slope and using the Cottrell equation [27]

$$\mathbf{I} = \mathbf{n} \mathbf{F} \mathbf{A} \mathbf{D}^{1/2} \mathbf{C}_{\mathbf{b}} \pi^{-1/2} \mathbf{t}^{-1/2}$$
(5)

we calculated a diffusion coefficient of  $8.08 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for AA.

#### 3.5 Differential pulse voltammetry

Sensitivities in differential pulse voltammetry (DPV) are better than other techniques of voltammetry. Since, the improvement comes from a reduced contribution from background currents. Figure 8 shows the DPVs obtained for the oxidation of different concentrations of AA at the 1,8-OBNEBHQMCPE. The dependence of the peak current on the AA concentration is shown in the inset A of Fig. 8. Inset B and C of this figure clearly show that the plot of peak current versus AA concentration is constituted of two linear segments with different slopes, corresponding to two different ranges of substrate concentration. The decrease in sensitivity (slope) in the second linear range (Fig. 8, inset C) is likely to be due to kinetic limitation. Using differential pulse voltammetry, the calibration curves for AA were obtained over the range 5–30  $\mu$ M and 40–1,500  $\mu$ M, respectively. The detection limit (k $\sigma$ , k = 2) was 0.6 µM. This value is comparable with other reports (Table 1).

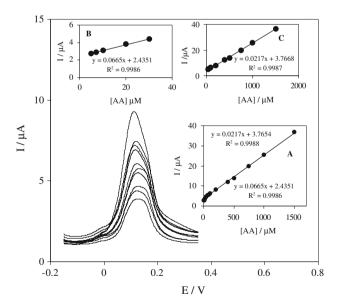


Fig. 8 Differential pulse voltammetry of 1,8-OBNEBHQMCPE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of AA (from inner to outer): 5.0, 7.0, 10.0, 20.0, 30.0, 40.0, 60.0, 80.0, 100.0 and 200  $\mu$ M. Insets shows the plots of the electrocatalytic peak current as a function of AA concentration in the range of: (A) 5–1,500  $\mu$ M, (B) 5–30  $\mu$ M, (C) 40–1,500  $\mu$ M

Table 1 Comparison of the efficiency of some modified electrodes used in the electrocatalysis of AA

Substrate	Modifier	pН	Peak potential Shift (mV)	Scan rate (mV s <sup>-1</sup> )	Limit of detection (M)	Dynamic range (M)	References
Carbon paste electrode	Tetrabromo- <i>p</i> -benzoquinone	7.0	430	20	$0.62 \times 10^{-6}$	$\begin{array}{c} (4-10) \times 10^{-6} - \\ (20-1,000) \times 10^{-6} \end{array}$	[20]
Carbon paste electrode	Cobalt-5-nitrosalophen	5.0	190	100	$7.0 \times 10^{-7}$	$1 \times 10^{-6} - 1 \times 10^{-4}$	[21]
Carbon paste electrode	Ruthenium(III) diphenyldithiocarbamate	3.0	-	100	$2.8 \times 10^{-5}$	$1.4 \times 10^{-4} - 7.1 \times 10^{-4}$	[22]
Carbon paste electrode	1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone	7.0	260	10	$6.3 \times 10^{-5}$	$6 \times 10^{-5} - 7 \times 10^{-3}$	[23]
Carbon paste electrode	1,8-OBNEBHQMCPE	7.0	206	50	$6 \times 10^{-7}$	$\begin{array}{c} (5-30) \times 10^{-6} - \\ (40-1,500) \times 10^{-6} \end{array}$	Present work

Table 2Determination ofascorbic acid in pharmaceuticalsamples

Pharmaceutical	Claimed (mg)	Proposed method (mg; %RSD)	Iodine method (mg; %RSD)
Effervescent table	1,000 per tablet	997.0 (±2.7)	964.0 (±0.3)
Ampoule	500 per 5 mL	495.0 (±2.2)	501.0 (±0.6)
Multivitamin syrup	Syrup 60 per 60 mL	58.6 (±2.5)	60.8 (±2.8)

#### 3.6 Interference study

The effect of a number of organic compounds such as uric acid, dopamine and some ions such as chloride, calcium, potassium and sodium on the determination of ascorbic acid was investigated. The tolerance limit was taken as the maximum concentration of the foreign substances, which caused an approximately  $\pm 5\%$  relative error in the determination. We found that dopamine interferes with the ascorbic acid electrode signal. Also, uric acid and other ions did not interfere.

#### 3.7 Determination of AA in real samples

In order to demonstrate the catalytic oxidation of AA in the real samples, we examined this ability in the voltammetric determination of AA in some pharmaceutical samples, such as effervescent tablets, vitamin C, ampoules and multivitamin syrup purchased from local sources. Therefore, we studied the electrochemical behavior of the 1,8-OBNEBH QMCPE in 0.1 M phosphate buffer (pH 7.00) containing each pharmaceutical sample by differential pulse voltammetry. The determination of AA in pharmaceutical samples was carried out by the standard addition method in order to prevent any matrix effect. The results for the analysis of these pharmaceutical samples with the voltammetric method compared favorably with those obtained the USP standard method (Table 2).

#### 4 Conclusions

This work demonstrates the construction of a chemically modified carbon paste electrode by the incorporation of 2,2'-(1,8-octanediylbisnitriloethylidine)-bis-hydroquinone as modifying species. The carbon paste electrode modified with 2,2'-(1,8-octanediylbisnitriloethylidine)-bis-hydroquinone was considerably stable. This electrode is simple, easy to prepare and its surface is renewable. The electrochemical behavior of 2,2'-(1,8-octanediylbisnitriloethylidine)-bishydroquinone was studied by cyclic voltammetry and chronoamperometry in both the absence and presence of AA. The results show that the oxidation of AA is catalyzed at pH 7.0, whereas the peak potential of AA is shifted by 206 mV to a less positive potential at the surface of the 1,8-OBNEBHQMCPE.

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#### References

- 1. Faulkner LR (1984) Chem Eng News 62:27
- Martin DW Jr (1983) In: Martin DW Jr, Mayes PA, Rodwell VW (eds) Harper's review of biochemistry, 19th edn. Lang, Los Altos, CA, p 112
- 3. Dryhurst G, Kadish KM, Renneberg R (1982) Biological electrochemistry, vol 1. Academic press, New York

- 4. Pérez-Ruiz T, Martinez-Lozano C, Sanz A, Guillen A (2004) J Pharm Biomed Anal 34:551
- 5. Wolucka BA, Davey MW, Boerjan W (2001) Anal Biochem 294:161
- 6. Lykkesfeldt J (2000) Anal Biochem 282:89
- 7. Silva FO (2005) Food Control 16:55
- 8. Jain A, Chaurasia A, Verma KK (1995) Talanta 42:779
- 9. Anastos N, Barnett NW, Hindson BJ, Lenehan CE, Lewis SW (2004) Talanta 64:130
- Antonelli ML, Ascenzo GD, Lagana A, Pusceddu P (2002) Talanta 58:961
- Yebra MC, Cespon RM, Moreno-Cid A (2001) Anal Chim Acta 448:157
- 12. Esteban MR, Ho CN (1997) Microchem J 56:122
- 13. Sahbaz F, Somer G (1992) Food Chem 44:141
- Washko PW, Welch RW, Dhariwal KR, Wang Y, Levine M (1992) Anal Biochem 204:1
- 15. Casella JG, Gatta M (2001) J Chromatogr A 912:223
- 16. Wring SA, Hart JP (1992) Analyst 117:1215
- 17. Kalcher K (1990) Electroanalysis 2:419

- Zen JM, Kumar AS, Tsai DM (2003) Electroanalysis 15:1073– 1087
- Degefa TH, Chandravanshi BS, Alemu H (1999) Electroanalysis 11:1305
- Zare HR, Nasirizadeh N, Mazloum Ardakani M (2005) J Electroanal Chem 577:25–33
- 21. Shahrokhian S, Zare-Mehrjardi HR (2007) Sens Actuators B 121:530–537
- 22. Nalini B, Sriman Narayanan S (2000) Anal Chim Acta 405:93-97
- Raoof JB, Ojani R, Hosseinzadeh R, Ghasemi V (2003) Anal Sci 19:1251–1258
- 24. U. S. Pharmacopeia XX (1980) Mack Co., Easton, PA
- 25. Sharp M, Petersson M, Edstrom K (1979) J Electroanal Chem 95:123
- 26. Laviron E (1979) J Electroanal Chem 101:19
- 27. Bard AJ, Faulkner LR (2001) Electrochemical methods. Fundamentals and applications. Wiley, New York
- 28. Andrieux CP, Saveant JM (1978) J Electroanal Chem 93:163
- 29. Antoniadou S, Jannakoudakis AD, Theodoridou E (1989) Synth Met 30:295