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# Electrocatalytic Oxidation of Hydroxylamine at a Quinizarine Modified Glassy Carbon Electrode: Application to Differential Pulse Voltammetry Detection of Hydroxylamine

**Mohammad MAZLOUMARDAKANI[1,*], Payam EBRAHIMI KARAMI[1], Hossein NAEIMI[2], Bibifatemeh MIRJALILI[1]**

[1] *Department of Chemistry, Faculty of Science, Yazd University, Yazd-IRAN*

[2] *Department of Chemistry, Faculty of Science, Kashan University, Kashan-IRAN*

*e-mail: mazloum@yazduni.ac.ir*

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The electrocatalytic behavior of hydroxylamine was studied on a glassy carbon electrode modified by electrodeposition of quinizarine, using cyclic voltammetry, chronoamperometry, and rotating disk voltammetry as diagnostic techniques. Cyclic voltammetry showed that the catalytic current of the system depends on the concentration of hydroxylamine. The magnitude of the peak current for quinizarine increased sharply in the presence of hydroxylamine and proportional to hydroxylamine concentration. The diffusion coefficient of hydroxylamine and the catalytic rate constant for the catalytic reaction of quinizarine with hydroxylamine were also estimated using a rotating disk electrode experiment. The kinetics parameters of this process were calculated, and the apparent electron transfer rate constant $k_s$ and $\alpha$ (charge transfer coefficient between glassy carbon electrode and quinizarine) were 4.44 $s^{-1}$ and 0.66, respectively. Chronoamperometry and cyclic voltammetry studies were also used to determine the overall number of electrons involved in the catalytic oxidation of hydroxylamine, which was found to be 1. Hydroxylamine in the range of 1-10 $\mu$M could be determined by differential pulse voltammetry.

**Key Words:** Electrocatalytic oxidation; hydroxylamine; chemically modified electrode; quinizarine.

## Introduction

Electrochemical methods are more and more widely used for the determination of electroactive compounds in pharmaceutical forms and physiological fluids due to their simple, rapid, and economical properties. As

*Corresponding author

an electroactive substance, hydroxylamine has also attracted much interest from electrochemists.[1] Hydroxylamine and its derivatives lead to the formation of methemoglobin in humans and animals.[2] Hydroxylamine has been identified as an intermediate in the nitrogen cycle[3] and in nitrogen fixation.[4] Heterotrophic nitrification[5] is involved in the production of hydroxylamine. Hydroxylamine has also been detected in bacterial media and in tissues of a number of organisms.[6] It induces point mutation by reaction with cytosine, but in the presence of trace metal ions and oxygen it also produces radicals that rapidly inactivate DNA.[7] Hydroxyl ammonium salts are also used in many branches of chemical industries like paints, pharmaceuticals, plastics, textiles, nuclear industries, and photography.[8] It has been reported that millimolar solutions of hydroxylamine are stable for several hours at pH 4.0, but only for 60 min at pH 7.8 in the presence of air.[9] Hence the determination of hydroxylamine in low concentration levels is very important in both industrial and biological samples. Many methods have been developed for the determination of hydroxylamine because of its toxicity, biological functions, and broad industrial utilizations. Kolasa has reviewed traditional methods.[10] In recent years, many methods have been reported for the determination of hydroxylamine in pharmaceutical and biological samples such as electrochemical detection (ECD),[11−13] spectrophotometric,[14−16] and chromatographic[17−19] methods, and some combinations of them, such as HPLC-ECD[20] and CE (capillary electrophoresis)-ECD,[20] have been successfully applied to the determination of hydroxylamine. However, most of these methods are complicated because they need derivatization or combination with various detection methods. The known method for the spectrophotometric determination of low concentration of hydroxylamine is the Blom method,[22] which is based on oxidation of hydroxylamine to nitrite by iodine.

Electrochemical analysis has become of growing importance in industrial process control, environmental monitoring, and different applications in medicine and biotechnology. The use of bare electrodes for electrochemical detection has a number of limitations, such as low sensitivity and reproducibility, slow electron transfer reaction, low stability over a wide range of solution composition, and high overpotential at which the electron transfer process occurs. The chemical modifications of inert substrate electrodes with redox active thin films offer significant advantages in the design and development of electrochemical sensors. In operation, the redox active sites shuttle electrons between the analyte and the electrodes with significant reduction in activation overpotential.

A further advantage of chemically modified electrodes is that they are less prone to surface fouling and oxide formation compared to inert substrate electrodes. A wide variety of compounds have been used as electron transfer mediators for modification of electrode surfaces with various procedures.[23] In this study, a quinizarine modified glassy carbon electrode was used as an electrochemical sensor for hydroxylamine based on electrocatalytic oxidation, and some parameters influencing the performances of this electrode in the determination of hydroxylamine are discussed.

# Experimental

## Chemicals

Quinizarine (1,4-dihydroxyanthraquinone) was synthesized from hydroquinone and phthalic anhydride in our laboratory and characterized by physical and spectroscopic data (Scheme 1). Other reagents and solvents used in this study were prepared from Merck. All solutions were freshly prepared with double-distilled water. Before use, flasks and containers were soaked in 6 M $HNO_3$ for at least 24 h and then rinsed with deionized water. Nitrogen gas was used to remove dissolved oxygen in the solutions prior to voltammetric experiments.

Hydroxylamine solutions were freshly prepared in deoxygenated buffer solutions. Working solutions were prepared by successive dilution of the stock solutions.

## General procedure for synthesis of 1, 4-dihydroxyanthraquinone

Phthalic anhydride (1 g, 6.75 mmol, from Merck, chromatographic pure) and 1, 4-dihydroxybenzene (hydroquinone) (0.74 g, 6.75 mmol, from Merck, analytical pure) were mixed with together and then aluminum chloride and concentrated sulfuric acid (0.67 mmol) were added to this mixture. The reaction mixture was heated at 105 °C with stirring for 25 min. The progress of the reaction was followed by TLC. After the completion of the reaction, the reaction mixture was poured on crushed ice and extracted with dichloromethane (3 × 30 mL). The organic layer was washed with 5% sodium bicarbonate solution (100 mL) and dried with $CaCl_2$. The solvent was evaporated to give 1, 4-dihydroxyanthraquinone as a red crystalline solid, which was recrystallized from acetone/distillated water, and the pure product was obtained in 98% yield.

**1,4-Dihydroxyanthraquinone;** $C_{14}H_8O_4$, red solid, 98% yield, MW 240, mp 194-196 °C; IR(KBr), $\upsilon/cm^{-1}$: 2919 (w), 2847 (w), 1629 (m), 1588 (m), 1454 (m), $^1$H-NMR (400 MHz), $CDCl_3/\delta$ ppm: 7-7.3 (2 H, s), 7.6-7.8 (2 H, s), 8.1-8.3 (2 H, s), 12.6-12.8 (2 H, s); $^{13}$C-NMR (100 MHz), $CDCl_3/\delta$ ppm: 114, 128, 131, 135, 136, 159, 188.

## Apparatus

Voltammetric measurements were carried out using a computerized potentiostat/galvanostat computerized potentiostat / galvanostat model $\mu$ Autolab, type III (Eco Chemie B. V.A). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. All electrochemical studies were performed at 25 ± 1 °C with a 3-electrode assembly that included a 50 mL glass cell and a silver/silver chloride electrode as reference electrode. A personal computer was used for data storage and processing. The auxiliary electrode was a platinum electrode. A glassy carbon disk electrode with a diameter of 3 mm was used as the working electrode. All potentials were measured and reported vs. the Ag/AgCl reference electrode. A rotating electrode system, from Pine Instruments, was employed.

## Modified electrode preparation

The procedures of GC electrode pretreatment and modification were as follows. Prior to use, the working electrode was polished mechanically with 0.05 $\mu$m alumina powder to obtain a mirror-like surface and then it was washed with distilled water and acetone. Electrochemical activation of the electrode was performed by continuous potential cycling from -1.1 to 1.6 V at a sweep rate of 100 mV $s^{-1}$ in sodium bicarbonate (0.1 M) solution until a stable voltammogram was obtained. After rinsing with doubly distilled water, the activated electrode was modified subsequently as follows. It was placed in a 0.1 M phosphate buffer solution containing 1.2 mM quinizarine and was modified by cycling the potential between 600 and 800 mV at a scan rate of 60 mV $s^{-1}$ for 18 cycles. Finally, the electrode was rinsed thoroughly with water and dipped into the buffer solution to test its electrochemical behavior. The surface coverage of the quinizarine modified glassy carbon electrode was determined from cyclic voltammograms recorded and by integration of anodic and cathodic peaks.

# Results and Discussion

## Electrochemical behavior

Quinizarine can be electrodeposited oxidatively onto glassy carbon electrodes activated previously in bicarbonate solution. The mechanism of electrodeposition appears to involve oxidation of the quinizarine, followed by nucleophilic attack of the oxidized form of quinizarine by active groups present on the activated glassy carbon electrode surface. This process can be influenced by the presence of other nucleophilic species that exist in the electrolyte and are capable of competing with the reactive groups present at the electrode surface.[24–27] The coverage determination was carried out in all cases using the equation[23]

$$\Gamma_{\text{quinizarine}} = Q/nFA \tag{1}$$

where Q is the charge from the area under the quinizarine anodic peak corrected for the baseline; and n is the number of electrons exchanged per reactant molecule (n = 2). The results were not corrected for surface roughness, which was assumed constant. The optimum conditions for preparation of the quinizarine modified glassy carbon electrode in various pH media, different concentrations of quinizarine, scan rate, and number of cycles of cyclic voltammetry could be easily observed from cyclic voltammograms. The maximum coverage of the quinizarine modified glassy carbon electrode is obtained when the modification is carried out in a quinizarine solution at pH 3; therefore this was selected in the subsequent modification process. At higher pH, probably the deposition process is inhibited by other competing Michael reactions. This is due to the fact that the quinizarine is in deprotonated form or because of the competing effect of interfering species reacting as preferred nucleophiles rather than the electrode surface groups.[28] At lower pH, possibly the hydroxyl groups at an activated electrode surface are blocked by protons, and this inhibits the deposition of quinizarine. Moreover, the influence of the concentration of the quinizarine on cyclic voltammetry behaviors of quinizarine modified glassy carbon electrode in the concentration range of 0.3-1.5 mM was examined. The experimental results showed that in 1.2 mM quinizarine solution the modified glassy carbon electrode has a maximum surface coverage. The voltammetric behavior of the quinizarine modified glassy carbon electrode at the scan rate range of 10-100 mV/s was investigated. The experimental results show that a scan rate of 60 mV/s has the best surface coverage. The calculated value of $\Gamma_{quinizarine} = 9.9 \times 10^{-10}$ mol cm$^{-2}$ corresponds to the coverage of the voltammogram recorded after 18 cycles of potential. The surface coverage ($\Gamma$) of the quinizarine modified glassy carbon electrode at the optimum condition decreases rapidly at first by potential recycling between 600 and 800 mV and then remains almost constant (Figure 1, curve a). Such behavior is also observed during the time when the freshly quinizarine modified glassy carbon electrode is kept in phosphate buffer (pH 2, Figure 1, curve b). The quinizarine modified glassy carbon electrode prepared under optimum conditions was characterized by cyclic voltammetry (CV). The representative cyclic voltammograms obtained for the quinizarine modified glassy carbon electrode are shown in Figure 2 for various scan rates (10-100 mV s$^{-1}$). The observation of well-defined and persistent cyclic voltammetric peaks indicates that the immobilized quinizarine exhibits electrochemical responses that are characteristic of the redox species confined on the electrode. Inset A of Figure 2 shows the magnitudes of peak potentials ($E_{pa}$) as a function of potential scan rate. For the quinizarine modified glassy carbon electrode the peak-to-peak separation potential ($\Delta E_p = E_{pa} - E_{pc}$) of the cyclic voltammogram recorded at low scan rate (10 mV/s) in the presence of phosphate buffer as the supporting electrolyte is about 12 mV. In addition, the formal potential [$E^{\circ\prime} = (E_{p.a} + E_{p.c})/2$] is almost independent of the potential scan

rate for sweep rates, suggesting facile charge transfer kinetics over this range of scan rate. However, for scan rates above 600 mV $s^{-1}$, the peak separations begin to increase, indicating the limitation arising from charge transfer kinetics (Figure 2, inset B). Laviron derived general expressions for the linear potential sweep voltammetric response for the case of surface-confined electroactive species with a concentration small enough[29]

$$E_{pc} = E^{\circ} + A \ \ln[(1-\alpha)/m] \tag{2}$$

$$E_{pa} = E^{\circ} + B \ \ln[\alpha/m] \tag{3}$$

For $E_{pa}$ – $E_{pc} = \Delta E_p > 200/n$ mV:

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nF\nu) - \alpha(1-\alpha)nF\Delta E_p/2.3RT \tag{4}$$

where A = RT/(1 – $\alpha$)nF, B = RT/$\alpha$nF, and m = (RT/F) ($k_s/n_\alpha$). From these expressions it is possible to determine the transfer coefficient ($\alpha$) by measuring the variation in the peak potentials with scan rate ($\nu$) as well as the apparent charge transfer rate constant ($k_s$) for electron transfer between the electrode and the surface deposited layer. A plot of Ep = f(log$\nu$) yields 2 straight lines with slopes equal to –2.3RT/$\alpha$nF and 2.3RT/(1 – $\alpha$)nF for the anodic and cathodic peaks, respectively. We found that for scan rates above 600 $mVs^{-1}$ the values of $\Delta E = (Ep - E^{\circ\prime})$ were proportional to the logarithm of scan rate as was indicated by Laviron. The plots are shown in the inset of Figure 2. Using such a plot and Eq. (4), the values of $\alpha$ and $k_s$ (in potential limit of between 1 and 5 V $s^{-1}$) were 0.66 and 4.44 $s^{-1}$, respectively, for the quinizarine modified glassy carbon electrode in the presence of 0.1 M phosphate buffer. The plots of anodic and cathodic peak currents as a function of potential scan rate are shown in inset C of Figure 2, indicating that the immobilized quinizarine exhibits electrochemical responses that are characteristic of the redox species confined on the electrode surface. Electron transfer kinetics is of fundamental importance in analytical and mechanistic electrochemistry for several reasons. First, the shape and magnitude of voltammograms depend on $k_s$, as does the slope of a current versus concentration plot. Second, the range of useful scan rates is ultimately limited by $k_s$, with higher scan rates and correspondingly short time scales requiring higher $k_s$. A summary of electrochemical data for the modifier obtained at the glassy carbon electrode is presented in Table 1.

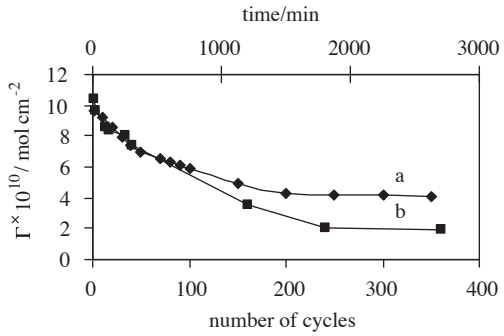


**Figure 1.** Variation in $\Gamma_{quinizarine}$, a) during the repetitive recycling of the potential between 600 and 800 mV, b) during the storage time of the modified electrode in buffer solution (pH 2).

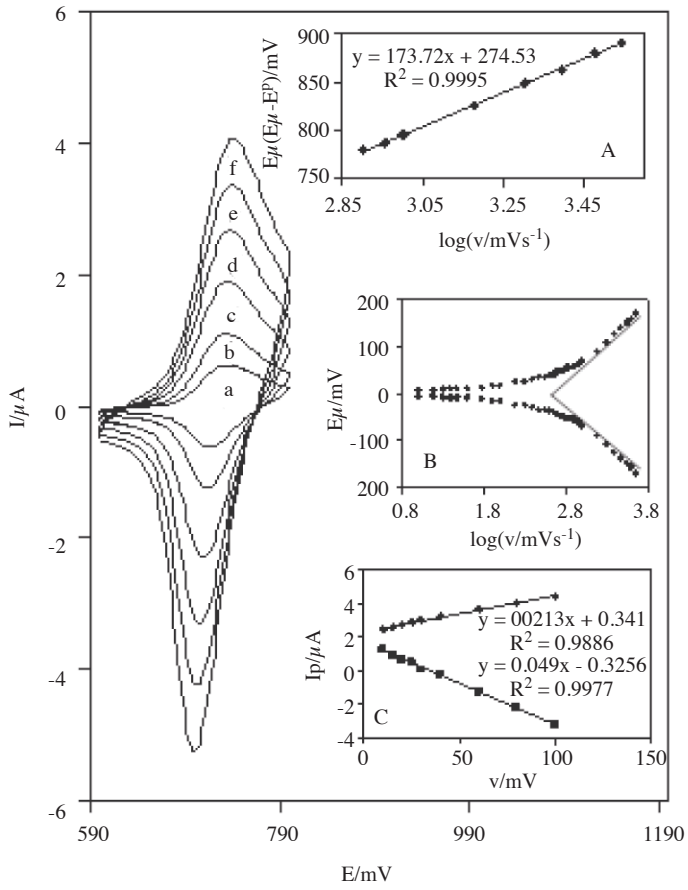


**Figure 2.** Cyclic voltammogram of a quinizarine modified glassy carbon electrode in 0.1 M phosphate buffer solution of pH 2.0 at various scan rates a) 10, b) 20, c) 40, d) 60, e) 80, f) 100 $mVs^{-1}$, A) plot of $E_{pa}$ vs. log$\upsilon$, B) plot of Ep vs. log$\upsilon$, C) plot of $I_p$ vs. $\upsilon$.

**Table 1.** Electrochemical data for quinizarine modified glassy carbon electrode.

| $E^\circ$ / mV | $\alpha$ | $k_s$ / $s^{-1}$ | $pk_a$ |
|---|---|---|---|
| 725 | 0.66 | 4.44 | 8 |

## Effect of pH on the peak potential

The voltammetric behavior of the quinizarine modified glassy carbon electrode was characterized at various pHs by cyclic voltammetry. Figure 3 shows peak currents of solution buffers at various pH values ranging from 2 to 9. As illustrated in Figure 3, the formal potential ($E^{o\prime}$) of the surface redox couple and anodic peak surface coverage were pH dependent. Curve A (Figure 3 inset) shows $E^{o\prime}$ as a function of pH. The results showed that the slope ($E^{o\prime}$/pH) is 58.6 mV/pH unit over a pH range from 2 to 8. This slope was close to the Nernstian value of 59.2 mV for a 2-electron, 2-proton process. However, such a process can be regarded as a simple reaction with 2 successive 1-electron exchanges as indicated by Laviron for the conditions at which the transfer coefficients of the electrochemical reactions are about 0.5 and protonations are at equilibrium.[30] The change in the slope for pH values above 8 can be attributed to the deporotonation

of the deposited quinizarine. The value obtained for the $pK_a$ of surface deposited quinizarine was 8. The slope of the 31 mV/pH unit was anticipated for pH values more than 8, which is very close to the Nernstian value of 29.6 mV for a 2-electron, 1-proton process. As can be seen in curve B of inset Figure 3, there was a decrease in surface coverage with an increase in pH values. The loss of coverage could be due to the displacement of surface-confined quinizarine by solvent molecules,[29] or could be related to the deprotonation of surface-attached material.[29]

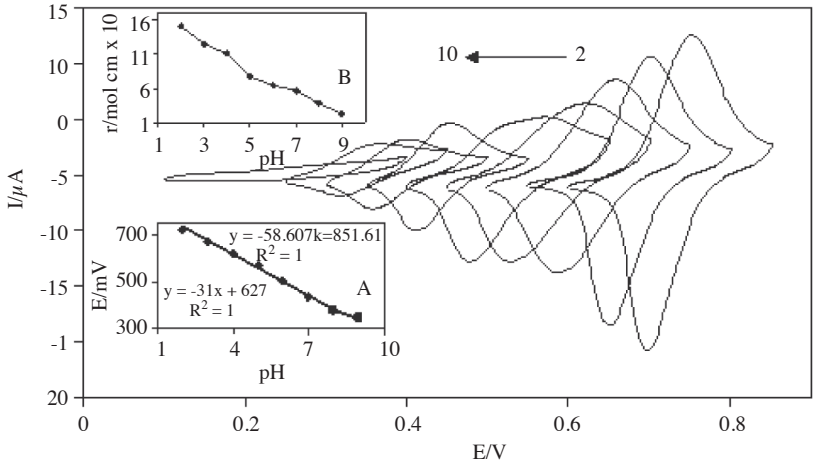


**Figure 3.** Cyclic voltammograms of quinizarine modified glassy carbon electrode in 0.1 M phosphate buffer solution of pH a) 2.0, b) 3.0, c) 4.0, d) 5.0, e) 6.0, f) 7.0, g) 8.0, h) 9.0 and, A) plot of $E^o$ vs. pH, B) plot of surface coverage vs. pH.

## Electrocatalytic oxidation of hydroxylamine at a quinizarine modified electrode

The cyclic voltammetric responses of a bare glassy carbon electrode in 0.1 M phosphate buffer (pH 2), without and with hydroxylamine in solution, are shown in Figure 4 (curves c and d respectively). If the electrode is modified with quinizarine and then placed into the same hydroxylamine-containing electrochemical cell, a large anodic peak is observed (Figure 4, curve b). That the current observed is associated with hydroxylamine oxidation and not the oxidation of surface-attached quinizarine is demonstrated by comparing the current in Figure 4 curve a with those in Figure 4 curve b, which shows the cyclic voltammetric behavior of an electrode modified with quinizarine in a hydroxylamine free electrolyte (0.1 M phosphate buffer with pH 2). It is apparent that the anodic current associated with the surface attached materials is significantly less than that obtained in the solution containing hydroxylamine. These voltammograms were recorded after several preliminary scans at the surface of the unmodified glassy carbon electrode in the potential range of 0.6 to 1.0 V vs.Ag/AgCl reference electrode. There was no measurable wave for the unmodified electrode in 1.0 mM and absence of hydroxylamine in the potential range studied (Figures 4c, d). As can be seen, electroactivity toward hydroxylamine on the modified electrode was significant (Figures 4a, b), with strongly defined peak potential, around 745 mV vs. Ag/AgCl electrode. The cyclic voltammograms obtained for a series of hydroxylamine solutions with various concentrations are illustrated in Figure 5. The inset shows the calibration curve constructed from the above-mentioned voltammograms. The logarithmic dependence of anodic peak current to the logarithm of concentration of hydroxylamine was linear in the range of 0.1-1 mM hydroxylamine.

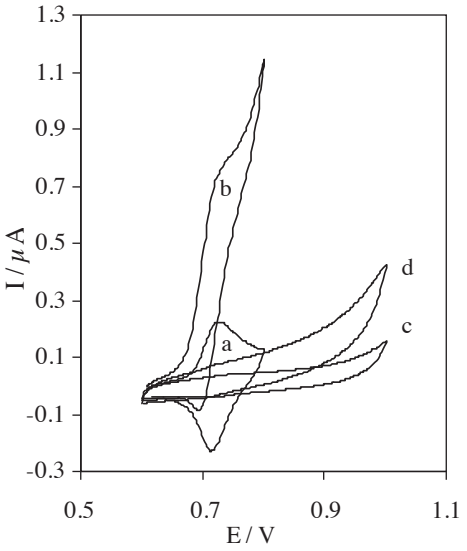


**Figure 4.** Cyclic voltammograms of quinizarine modified glassy carbon electrode in 0.1 M phosphate buffer solution of pH 2.0, a) in absence of, b) in 1 mM hydroxylamine and bare glassy carbon electrode, c) as a and d) as b.

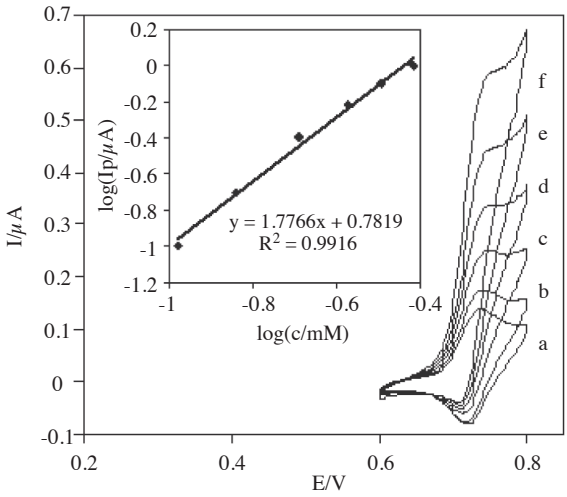


**Figure 5.** Cyclic voltammograms of different concentrations of hydroxylamine at quinizarine modified glassy carbon electrode with scan rate 6 mV $s^{-1}$ in (0.1) M phosphate buffer (pH 2). a to f) 0.1, 0.2, 0.4, 0.6, 0.8, and 1 mM respectively. Inset represents the variations in peak currents vs. hydroxylamine concentration.

Figure 6 shows the cyclic voltammograms of a quinizarine modified glassy carbon electrode at various scan rates obtained in 0.1 M phosphate buffer solution (pH 2) containing 0.5 mM hydroxylamine. The peak current for the anodic oxidation of hydroxylamine is proportional to the square root of scan rate (Figure 6, inset A), which indicates that the reaction involves mass transport. The calculated slope of $I_p$ vs. $\nu^{1/2}$ is 0.1332 $\mu AmV^{-1/2}$ $s^{1/2}$ and according to $I_p = 3.01 \times 10^{-10}$ n $[(1\text{-}\alpha)n_\alpha]^{1/2}$ A c $D^{1/2}\nu^{1/2}$, which is for a totally irreversible diffusive process;[31] it can be estimated that (Figure 6, inset A) the total number of electrons involved in the anodic oxidation of hydroxylamine is 0.94, assuming $[(1-\alpha)n_\alpha] = 0.66$, D = 1.36 $\times 10^{-6}$ $cm^2$ $s^{-1}$ (see section rotating disc electrode voltammetry) and A = 0.0314 $cm^2$. A Tafel plot from

data of the rising part of the current–voltage curve at a scan rate of 8 mV $s^{-1}$ is illustrated in Figure 6 (inset B) and can be used to obtain information on the rate-determining step. A slope of 88.98 mV $decade^{-1}$ is obtained, which indicates that the rate-limiting step is 1-electron transfer (assuming a transfer coefficient of $\alpha = 0.34$).

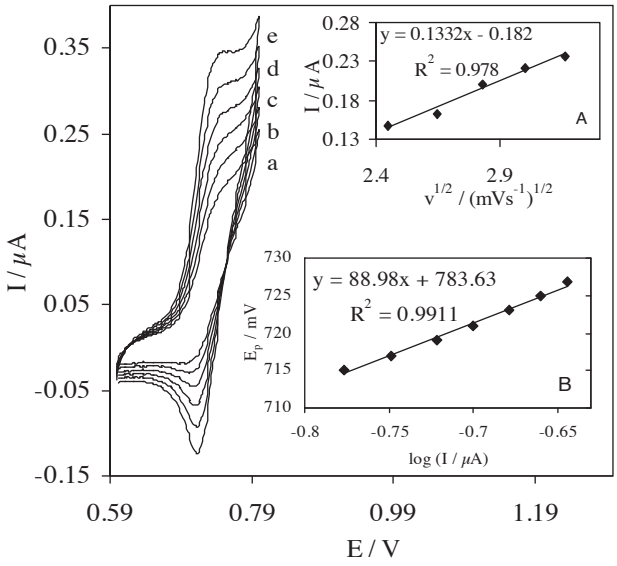


**Figure 6.** Cyclic voltammograms of a quinizarine modified glassy carbon electrode in 0.1 M phosphate buffer solution of pH 2.0 containing 0.5 mM hydroxylamine at various scan rates a) 6, b) 7, c) 8, d) 9, e) 10 $mVs^{-1}$. A) plot of I vs. $v^{1/2}$, B) plot of E vs. log I (Tafel plot).

## Chronoamperometric measurements

The quinizarine was applied to the electrocatalytic oxidation of hydroxylamine using the chronoamperometric method. Figure 7 (inset A) shows the chronoamperograms that were obtained for a series of hydroxylamine solutions with various concentrations (0.2-1.0 mM). The results show that an increase in concentration of hydroxylamine was accompanied by an increase in anodic current obtained for a potential step of 800 mV vs. Ag/AgCl. The level of the Cottrell current was measured at 40 s. By using the Cottrell equation,

$$I_{(t)} = nFAC^*(D/\pi t)^{1/2} \tag{5}$$

number of electrons involved in the catalytic oxidation of hydroxylamine can be evaluated, where D and $C^*$ are the diffusion coefficient ($cm^2$ $s^{-1}$), and the bulk concentration (mol $cm^{-3}$), respectively, A is the effective electrode area and n is the number of electrons transferred. The slopes of the charge (Q) versus $t^{1/2}$ plot (Figure 7, inset B) were then plotted versus the hydroxylamine concentration (Figure 7, inset C). According to the integrated Cottrell equation, the charge was calculated as

$$Q = 2nFAD^{1/2}t^{1/2}C^*/\pi^{1/2} \tag{6}$$

where A = 0.0314 $cm^2$ and D = $1.36 \times 10^{-6}$ $cm^2$ $s^{-1}$. From the slope of the linear plot of Q vs. $t^{1/2}$ (Figure 7, inset B) or the slope of the linear plot of inset C of Figure 7, the mean value of n for 0.2, 0.4, 0.6, 0.8, and 1 mM of hydroxylamine was calculated as 0.97.

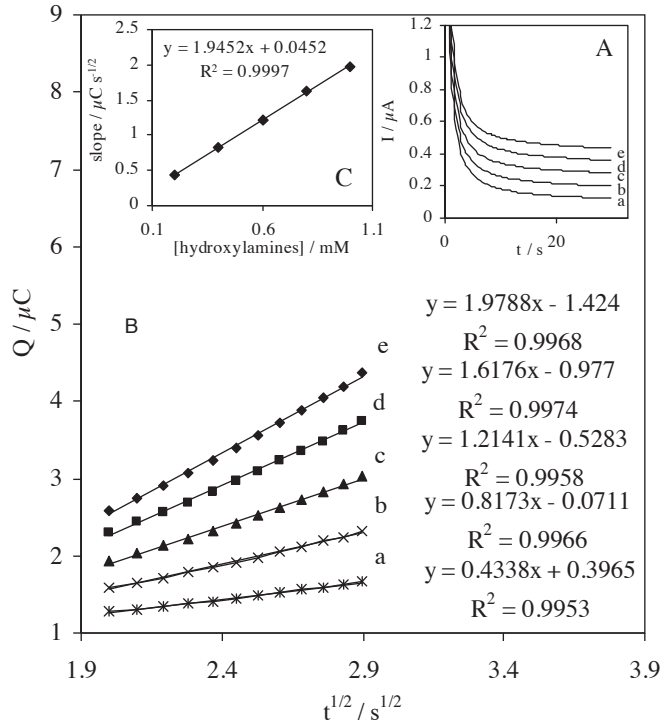


**Figure 7.** A) Chronoamperograms of quinizarine modified glassy carbon electrode in 0.1 M phosphate buffer solution containing a) 0.2, b) 0.4, c) 0.6, d) 0.8, e) 1.0 mM hydroxylamine, B) Plot of Q vs. $t^{1/2}$ obtained from chronoamperometric experiments for a quinizarine modified glassy carbon electrode in 0.1 M phosphate buffer solution (pH 2) containing hydroxylamine at concentrations of a) 0.2, b) 0.4, c) 0.6, d) 0.8, e) 1.0 mM hydroxylamine. C) The slopes of the resulting straight line of inset B versus the hydroxylamine concentration.

## Rotating Disk Electrode (RDE) voltammetry

The rotating disk electrode voltammograms (Figure 8) were recorded for 1 mM concentration of hydroxylamine in 0.1 M phosphate buffer (pH 2) and at various rotation rates using a quinizarine modified glassy carbon rotating disk electrode. Since the rate of electron transfer between quinizarine and the electrode substrate can be considered fast, this would suggest that the oxidation of hydroxylamine is the rate-determining step. However, under these conditions, there is a linear relationship between the inverse of the limiting current and the inverse of the square root of the rotation speed of the electrode according to the Koutecky–Levich equation, which is formulated as follows:

$$[I_l]^{-1} = [nFAC^*k\Gamma]^{-1} + [0.62nFAD^{2/3}\nu^{-1/6}C^*\omega^{1/2}]^{-1} \tag{7}$$

where C is the bulk concentration of quinizarine (mol $cm^{-3}$), $\omega$ is the angular frequency of rotation (rad $s^{-1}$), D is the diffusion coefficient ($cm^2$ $s^{-1}$), $\nu$ is the kinematic viscosity ($cm^2$ $s^{-1}$), k is the reaction rate constant (cm $s^{-1}$), and all other parameters have their conventional meanings. The Koutecky–Levich plots, obtained from the data in Figure 8 (inset A), are shown in Figure 8 (inset B). These plots show the anticipated linear dependence between $1/I_{lim}$ and $1/\omega^{1/2}$ in 0.77 V. The rate constant, k, can be calculated from the intercept of the Koutecky–Levich plot. From the value of the intercept, the k value was found to be 3.96 ×

$10^3$ $M^{-1}s^{-1}$. The diffusion coefficient of hydroxylamine, D, may be obtained from the slope of Koutecky–Levich plots. The value of D was found to be $1.36 \times 10^{-6}$ $cm^2$ $s^{-1}$. In Table 2, the characteristics of the quinizarine modified glassy carbon electrode are compared with the other reported modified electrode.[32−34] It is noteworthy that the transfer coefficient electron between the electrode surface and quinizarine and surface coverage of the proposed electrode are also improved with respect to those of the previously reported modified electrodes.

**Table 2.** Comparison of the parameters of the proposed quinizarine modified glass carbon electrode with the other modified electrodes.

| Parameters | Quinizarine Modified Glassy Carbon Electrode | 32 | 33 | 34 |
|---|---|---|---|---|
| The apparent electron transfer rate constant ($k_s$), $s^{-1}$ | 4.44 | - | - | - |
| Heterogeneous rate constant for the reduction of hydroxylamine at the surface of the modified electrode ($k_h$), $M^{-1}$ $s^{-1}$ | $3.96 \times 10^3$ | - | - | $4.6 \times 10^3$ |
| Transfer coefficient for electron transfer between the electrode surface and immobilized Compound($\alpha$) | 0.66 | 0.6 | - | 0.52 |
| Transfer coefficient for electron transfer between hydroxylamine and immobilized compound ($\alpha$) | 0.34 | - | 0.31 | - |
| $\Gamma$, mol $cm^{-2}$ | $9.9 \times 10^{-10}$ | $1.2 \times 10^{-10}$ | - | $2.8 \times 10^{-9}$ |
| D, $cm^2/s$ | $1.36 \times 10^{-6}$ | $1.4 \times 10^{-5}$ | $2.16 \times 10^{-5}$ | $1.3 \times 10^{-5}$ |

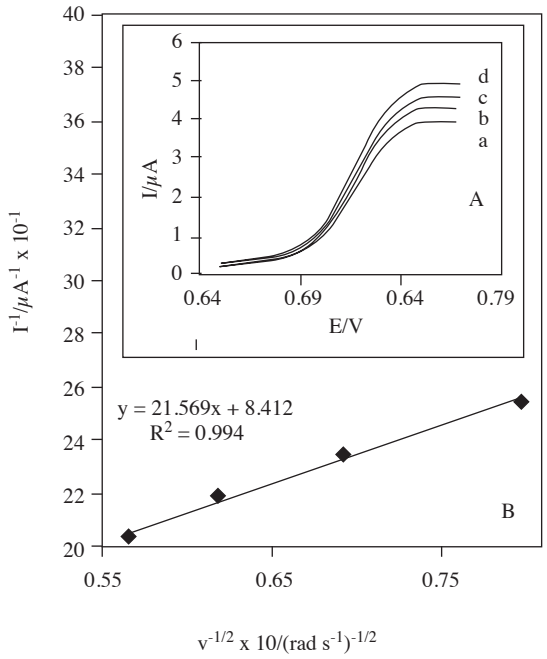


**Figure 8.** A) Typical example of rotating disk voltammograms for 1 mM concentration of hydroxylamine reduction in 0.1 M phosphate buffer (pH 2) at quinizarine modified glassy carbon electrode. The rotation speed is in rpm: a) 1500, b) 2000, c) 2500, and d) 3000, potential sweep rate: 5 mV $s^{-1}$, B). Koutecky–Levich plots of limiting currents at 770 mV.

## Differential pulse voltammetry investigations

Electrocatalytic oxidation of hydroxylamine at a quinizarine modified glassy carbon electrode was investigated for its determination in solution. Sensitivities in differential pulse voltammetry (DPV) are better than other techniques of voltammetry, in view of the fact that the improvement comes from a reduced contribution from background currents. The differential pulse voltammograms (Figure 9) were recorded for various

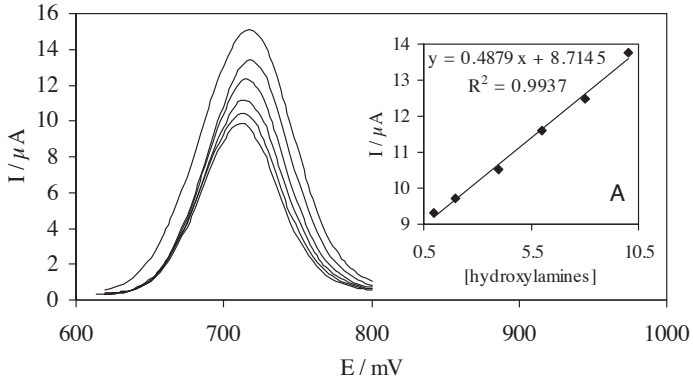


**Figure 9.** Differential pulse voltammograms of different concentrations of hydroxylamine at quinizarine modified glassy carbon electrode in (0.1) M phosphate buffer (pH 2). a to f) 1, 2, 4, 6, 8, and 10 $\mu$M, respectively. Inset represents the variations of peak currents vs. hydroxylamine concentration.

concentrations of hydroxylamine in 0.1 M phosphate buffer (pH 2). The electrocatalytic peak current of hydroxylamine at the surface of the quinizarine modified glassy carbon electrode was linearly dependent on the hydroxylamine concentration by the DPV method (Figure 9, inset A). Results show that the anodic peak current was linearly dependent on the hydroxylamine concentration in the range 1 to 10 $\mu$M; with a correlation coefficient better than 0.994. Thus the catalytic oxidation of hydroxylamine can readily be applied for the determination of hydroxylamine.

## Conclusions

This work showed that quinizarine can oxide hydroxylamine catalytically. The kinetic process of the catalytic oxidation can be explained using cyclic voltammetry, chronoamperometry, and rotating disk electrode (RDE) voltammetry. The results obtained for rate constant, k, diffusion coefficient of hydroxylamine, D, and number of electrons in the rate determining step by different approaches are in good agreement.

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