Int. J. Electrochem. Sci., 6 **(2011)** 2509 - 2525

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Voltammetric Behaviour and Determination of 8-Hydroxyquinoline Using a Glassy Carbon Paste Electrode and the Theoretical Study of its Electrochemical Oxidation Mechanism

Milica C. Stević[1,*], *Ljubiša M. Ignjatović*[1], *Gordana Ćirić-Marjanović*[1], *Svetlana M. Stanišić*[1], *Dalibor M. Stanković*[2] *and Jiři Zima*[3]

[1] Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11158 Belgrade, Serbia
[2] Faculty of Chemistry, University of Belgrade, Studentski Trg 12-16, 11158 Belgrade, Serbia
[3] UNESCO Laboratory of Environmental Electrochemistry, Department of Analytical Chemistry, Charles University, Albertov 6, CZ-128 43 Prague 2, Czech Republic
[*]E-mail: milica@ffh.bg.ac.rs

Received: 1 May 2011 / *Accepted:* 6 May 2011 / *Published:* 1 July 2011

The 8-Hydroxyquinoline (8HQ) oxidation process has been investigated by Cyclic Voltammetry using a Glassy Carbon Paste Electrode (GCPE) as a working electrode. The theoretical study of the mechanism of electrochemical oxidation of 8HQ has been based on the AM1 semi-empirical quantum chemical computations of the heats of formation of the reaction intermediates, taking into account the influence of pH and solvation effects. We proposed that a two-electron irreversible process, controlled by diffusion of electroactive species, is responsible for an oxidation peak of 8HQ that appears in all cyclic voltammograms recorded on a clean electrode in the solutions of pH in the range 2–12 with a supporting electrolyte of Britton-Robinson Buffer/methanol. A single-electron oxidation of 8HQ leads, depending on pH, to the formation of various free radical species that combine to make dimers which, after being oxidized once more, give quinonoid-type compounds. Recording continuous cyclic voltammograms on the GCPE, pre-peaks appear as a consequence of dimer and quinonoid compounds formation. By applying Differential Pulse Voltammetry for 8HQ determination it was calculated that the limit of detection was 5.2×10^{-8} mol/L. For more sensitive quantitative determination of the investigated substance Adsorptive Stripping Differential Pulse Voltammery can be used since it was found that after 300s-deposition time at 0.0 V *vs.* Saturated Calomel Electrode, a 2.1 times higher peak current than without deposition was obtained.

Keywords: 8-Hydroxyquinoline, Glassy Carbon Paste Electrode, Cyclic Voltammetry, Differential Pulse Voltammetry, Computational method

1. INTRODUCTION

The heterocyclic aromatic compound, 8-Hydroxyquinoline (8HQ), Figure 1, is often found as an environmental pollutant due to its widespread use in industry, medicine and agriculture. Well-known as one of the most commonly used complexing agents in analytical chemistry [1−3], 8HQ itself or in the form of a metal complex, such as copper 8-Hydroxyquinoline, $Cu(8HQ)_2$, exhibits fungicidal activity [4–6], being applied, for example, as a pesticide [7], a mildew-resisting agent [8] or as a preservative, bactericide and disinfector in different cosmetics [9]. Of increasing importance in display technology is the use of the 8HQ complex compound, Tris(8-hydroxyquinolato) aluminium, in the manufacture of organic light-emitting diodes [10]. Recent pharmacological studies indicate that 8HQ may find an important use as a drug for shortening the course of treatment for both active and latent tuberculosis [11].

The electrochemical characteristics, behaviour and determination of 8HQ have been extensively studied using different working electrodes: carbon paste electrode [12], glassy carbon electrode [12], multiwall carbon nanotube/Nafion [13], hanging mercury drop electrode [14] and dropping mercury electrode [15]. To our knowledge, there is no report related to the quantum chemical study of the electrochemical oxidation of 8HQ.

In the present work, using Cyclic Voltammetry, we described the electrochemical characterization of 8HQ behaviour on a glassy carbon paste electrode [16] as a working electrode, in supporting electrolyte mixtures Britton Robinson buffer/methanol, since this electrode is compatible with high content of methanol [17, 18]. In addition, Differential Pulse Voltammetry was used for establishing optimum conditions for its determination and finding the limits of detection (LOD). It was further confirmed that Adsorptive Stripping Differential Pulse Voltammetry can be used as a technique for more sensitive quantitative analysis. We also presented the theoretical study of 8HQ electro-oxidation mechanism that successfully explained some experimental observations, e.g., the peak potential-pH relationship, and proposed the possible 8HQ dimers formed throughout the investigated pH range.

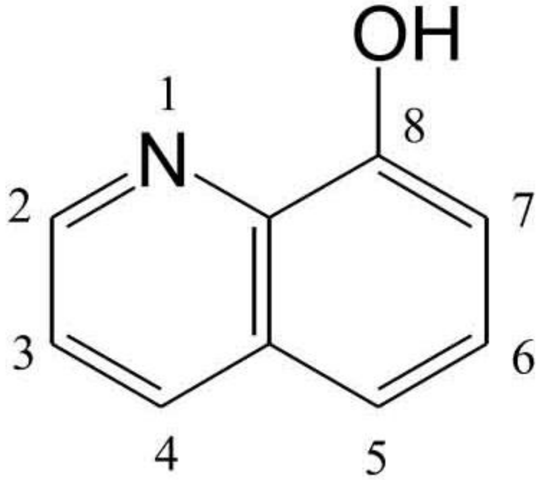


Figure 1. Structural formula of 8HQ.

2. EXPERIMENTAL

2.1. Reagents and Chemicals

8HQ (99%) and glassy carbon powder, comprising spherical particles with diameters in the range 2−12 μm, were supplied by Sigma-Aldrich (Poole, UK). Methanol (HPLC grade) was purchased from J. T. Baker (Deventer, The Netherlands). Paraffin oil (liquid petrolatum; white mineral oil; Nujol), ortho-phosphoric acid, boric acid, acetic acid and sodium hydroxide, all of analytical grade purity, were obtained from Merck (Darmstadt, Germany). Deionized water, produced by an Ultra Clear Basic SG Water apparatus (SG Wasseraufbereitung GmbH, Germany), was used.

2.2. Apparatus

All voltammetric measurements were carried out using a computerized voltammetric analyzer CH Instruments (Austin, USA) driven by voltammetric software CHI (Version 4.03). A three electrode measurement system comprising a Glassy Carbon Paste Electrode (GCPE), as a working electrode, a Saturated Calomel Electrode (SCE), as a reference electrode, in respect to which all measured potentials are given, and a Platinum wire, as an auxiliary electrode, was used. The electrodes were in triangular geometry. For pH measurements, a pH meter, model 744, equipped with combined glass pH electrode and temperature sensor, all from Metrohm (Herisau, Switzerland) was used.

2.3. Solutions and Glassy Carbon Paste Electrode Preparation

The stock standard solution (1×10^{-2} M) of the investigated substance was prepared by dissolving accurately weighted amounts of 8HQ in methanol. More dilute solutions were prepared by serial dilution of the stock solution with methanol. All solutions were stored in a dark place. A spectrophotometric study demonstrated that the stock standard solution was stable for at least three months. The more dilute solutions (1×10^{-3} M and 1×10^{-4} M) were prepared weekly.

The Britton-Robinson (BR) buffer solutions were prepared by mixing appropriate volumes of acidic and basic buffer components. The acidic buffer component comprises 0.04 M ortho-phosphoric acid, 0.04 M boric acid and 0.04 M acetic acid. The basic buffer component is 0.2 M sodium hydroxide solution. Supporting electrolytes were made by mixing the BR buffer of appropriate pH and methanol in the ratio 80:20 (v/v).

The GCPE was prepared by hand-mixing 250 mg of glassy carbon powder with 90 μL of mineral oil in a mortar and pestle until a completely homogeneous stiff paste was obtained. The resulting paste was pressed firmly into the 2 mm-internal diameter and 20 mm long Teflon electrode body cylinder, to produce the GCPE.

2.4. Procedures

As a start, cyclic voltammograms (CVs), using different scan rates, and differential pulse voltammograms (DPVs), using different pulse amplitudes, of the supporting electrolyte at pH 2.02

were recorded. The scan rates used for CV measurements in this study were 10, 20, 50, 100 and 200 mV/s. All DPVs were obtained at a constant scan rate of 20 mV/s and using the following different pulse amplitudes 5, 10, 25, 50 and 100 mV.

After recording these blank voltammograms, using 20 ml of the supporting electrolyte at pH 2.02 in the voltammetric cell, 200 μL of the 8HQ stock standard solution was added thus producing 1×10^{-4} M solution of 8HQ. The solution mixing was achieved by nitrogen bubbling and, after allowing the solution to equilibrate for 10 s, CV measurements at above-mentioned scan rates and DPV measurements using above-mentioned pulse amplitudes were carried out. The GCPE had to be cleaned after every measurement by wiping its surface on a filter paper wetted with deionized water.

After recording all CVs and DPVs for the supporting electrolyte and for the 1×10^{-4} M 8HQ solution at pH 2.02, the whole procedure was repeated using supporting electrolyte in the pH range 2−12. For CV determinations of 8HQ the starting potential was −0.5 V and the final potential was +1.3 V, while for DP measurements the starting potential was 0.0 V and the final potential was +1.2 V.

Continuous recording of fifty CVs was done for 1×10^{-4} M 8HQ solutions of pH 2.95, 4.96, 7.10, 9.00 and 11.93 in BR buffer/methanol supporting electrolyte, containing 20% of methanol (v/v). The scan rate used here was 50 mV/s and, as opposed to the previously described procedure, the GCPE surface was not cleaned after measuring each cycle.

The 8HQ calibration curves were determined in triplicate in the concentration range 1×10^{-7} to 1×10^{-5} M and evaluated by the least-squares linear regression method. The limit of detection (LOD) for 8HQ was obtained in the widely-accepted conventional way [19]. All the above mentioned measurements were made at laboratory temperature (20 ± 1) ºC.

2.5. Computational Methods

A semi-empirical AM1 method [20] (included in the molecular orbital package MOPAC 97 [21], a part of the Chem3D Pro 5.0 package, CambridgeSoft Corporation) has been used to obtain the heats of formation (ΔH_f) of individual species. This method is accurate enough to have useful predictive power, and is fast enough to allow the processing of oligomers [22−25]. Solvation effects were taken into account using the conductor-like screening model (COSMO) to approximate the effect of water surrounding the analyzed molecule [26]. Conformational analysis of intermediates was done. The steric energy was minimized using the MM2 molecular mechanics force-field method [27]. Input files for the semi-empirical quantum-chemical computations of dimeric 8HQ intermediates were the most stable conformers of the investigated molecular structures. The geometry optimization was performed by the EigenFollowing procedure [28, 29].

3. RESULTS AND DISCUSSION

3.1. Oxidative Electrochemical Behaviour of 8HQ and Theoretical Study of its Oxidation Mechanism

CV measurements were performed in order to understand the oxidative electrochemical processes of 8HQ taking place at the surface of the GCPE. Under the investigated conditions 8HQ yields a single well-defined anodic peak whose potential changes in the following way: with increasing pH of the supporting electrolyte, the peak potential becomes more negative as is depicted in Figures 2 and 3, while increasing the scan rate causes the peak potential to become more positive and peak current to increase (Figure 4).

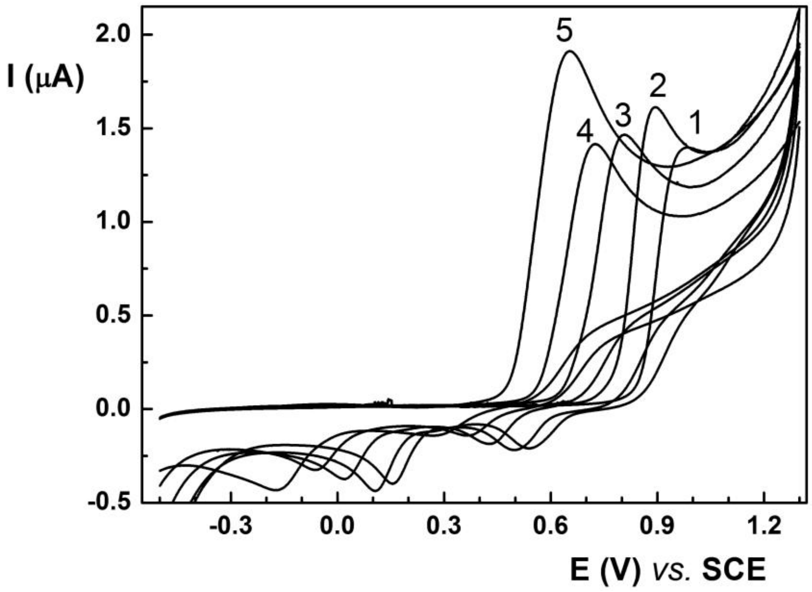


Figure 2. Cyclic voltammograms of 1×10^{-4} M 8HQ on GCPE, in BR buffer/methanol, containing 20% of methanol (v/v), pH: 2.02 (1); 2.95 (2); 3.99 (3); 4.96 (4); 6.03 (5); scan rate 50 mV/s.

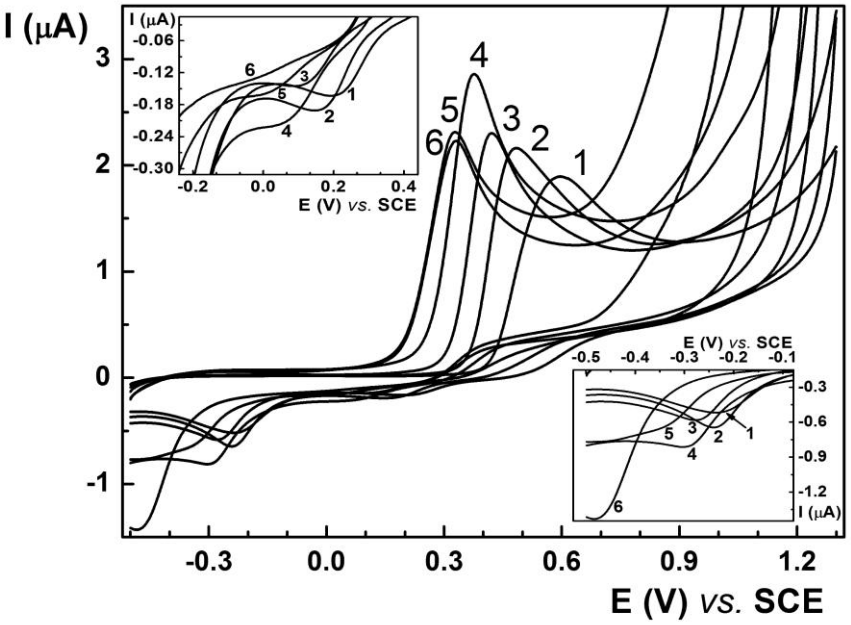


Figure 3. Cyclic voltammograms of 1×10^{-4} M 8HQ on GCPE, in BR buffer/methanol, containing 20% of methanol (v/v), pH: 7.10 (1); 8.09 (2); 9.00 (3); 9.95 (4); 11.05 (5) and 11.93 (6); scan rate 50 mV/s. The enlarged cathodic peaks are shown in the insets: first cathodic peaks (left top corner); second cathodic peaks (right down corner).

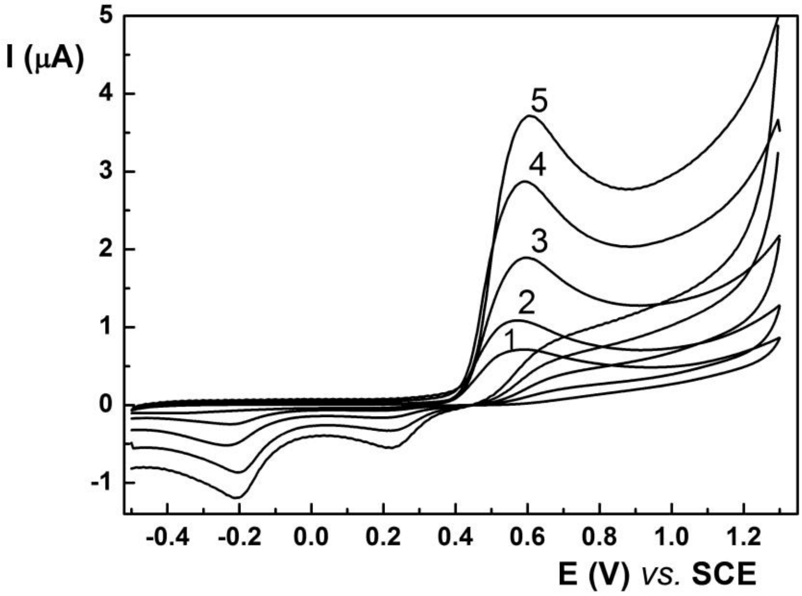


Figure 4. Cyclic voltammograms of 1×10^{-4} M 8HQ, obtained at a clean GCPE surface, in BR buffer/methanol, containing 20% of methanol (v/v), pH 8.09, at different scan rates: 10 mV/s (1); 20 mV/s (2); 50 (mV/s) (3); 100 mV/s (4) and 200 mV/s (5).

The influence of the supporting electrolyte pH on the CV anodic peak potential, Ep-pH, is depicted in Figure 5 where the two intercepts that can be detected at pH 4.79 and pH 9.81 correspond well to pK_{a1} (NH^+/N) and pK_{a2} (OH/O^-) values of 8HQ, respectively [30].

The linear parts of the Ep-pH dependence in the particular pH regions are expressed by the following equations:

$$\text{pH} < 4.79\text{: Ep (V)} = 1.181 - 0.091\ \text{pH}$$

$$4.79 < \text{pH} < 9.81\text{: Ep (V)} = 1.088 - 0.072\ \text{pH}$$

$$\text{pH} > 9.81\text{: Ep (V)} = 0.713 - 0.033\ \text{pH}$$

In order to interpret the electrochemical oxidation of 8HQ, the possible initial single-electron and two-electron transfer reaction pathways have been computationally analyzed. The known acid–base equilibria of 8HQ (**1** → **2**, $pK_{a1} = 4.85$; **2** → **3**, $pK_{a2} = 9.95$ [30], Scheme 1) indicate the initial formation of monoprotonated 8HQ di-cation radicals $[\text{H-8HQ}]^{\bullet 2+}$ (**4**), 8HQ cation radicals $[\text{8HQ}]^{\bullet +}$ (**5**) and deprotonated 8HQ neutral radicals $[\text{8HQ(-H)}]^{\bullet}$ (**6**) during the single-electron oxidation of monoprotonated 8HQ (**1**), 8HQ (**2**), and deprotonated 8HQ (**3**), respectively (Scheme 1). AM1/COSMO computations of ionization energy (E_i) of different acid-base forms of 8HQ have proved that the oxidizability of 8HQ increases in the following order: monoprotonated 8HQ ($E_i = 9.37$ eV) < 8HQ ($E_i = 9.07$ eV) < deprotonated 8HQ ($E_i = 8.03$ eV), i.e., the oxidizability of 8HQ increases with increasing pH, which is in accordance with the experimental observations.

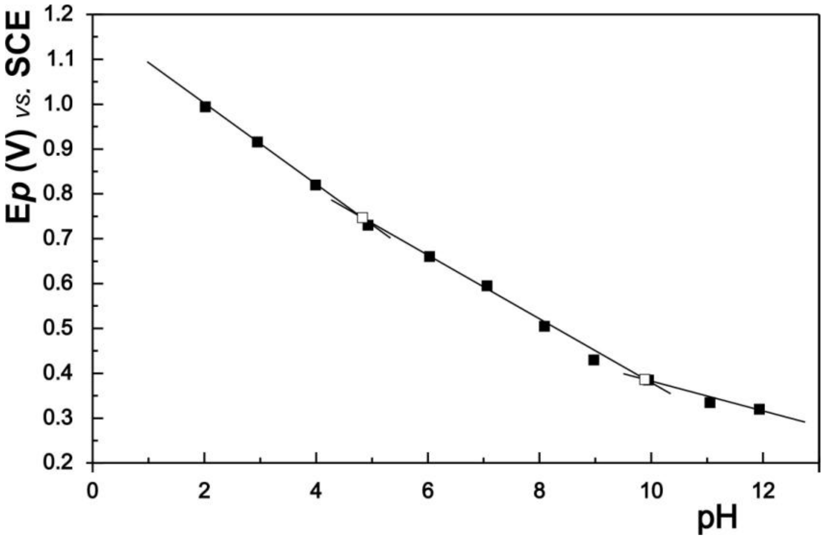
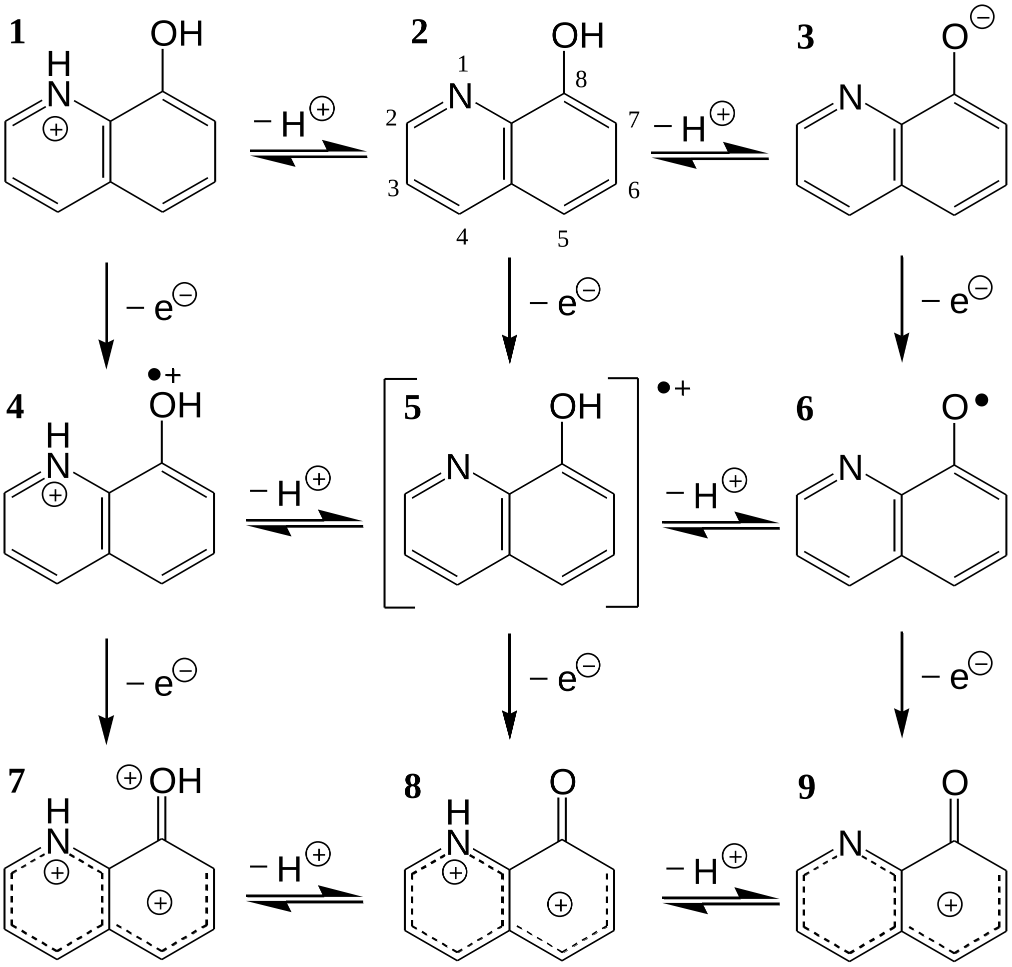


Figure 5. Influence of the supporting electrolyte pH on the CV anodic peak potential; scan rate 100 mV/s; 8HQ concentration 1×10^{-4} M. White squares represent pK_{a1} and pK_{a2} values, left to right, respectively.



Scheme 1. The acid-base equilibria of 8HQ (**1**–**3**) and its single-electron (**4**–**6**) and two-electron oxidation products (**7**–**9**).

By analyzing the CVs obtained after continuous cycling on GCPE the following has been concluded: (I) apart from the main oxidation peak in the anodic region, two pre-peaks appear at pH 2.95, 4.96, 7.10 and 9.00 (Figure 6), whereas at pH 11.93 only one pre-peak is found (Figure 7); (II) the main oxidation peak current decreases with increasing number of cycles (Figures 6 and 7). We proposed that pre-peaks in the CVs appear as a consequence of a quite complex electro-oxidation process that leads to dimerization and polymerization taking place on the GCPE surface.

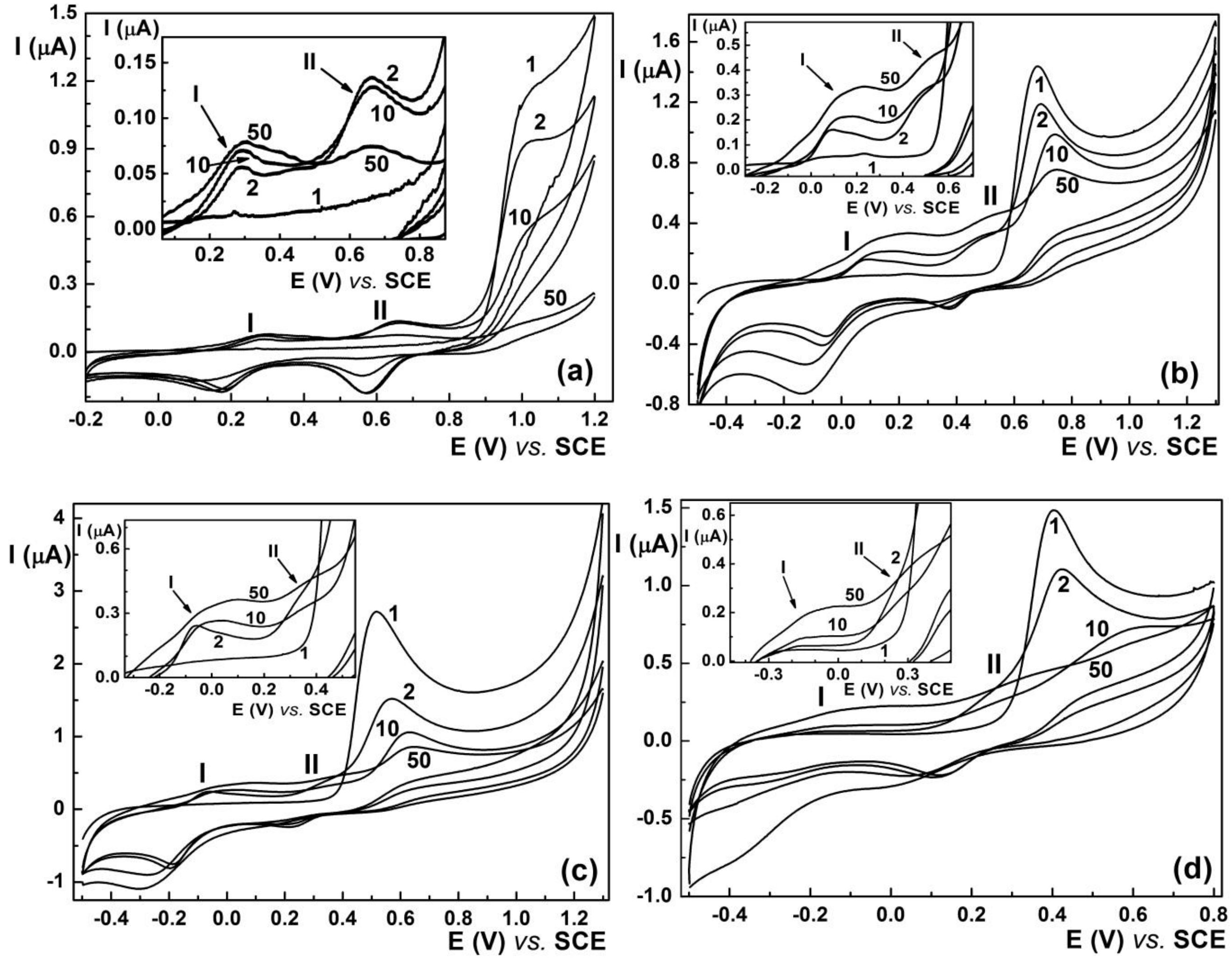


Figure 6. Continuous cyclic voltammograms of 1×10^{-4} M 8HQ on GCPE in BR buffer/methanol, containing 20% of methanol (v/v), at different pH: 2.95 (a); 4.96 (b); 7.10 (c); 9.00 (d), recorded after different number of cycle(s): one (1), two (2), ten (10) and fifty (50); scan rate 50 mV/s. The positions of pre-peaks (I) and (II) are indicated. The enlarged areas with pre-peaks are shown in the insets.

In order to determine the number of electrons exchanged during the 8HQ oxidation process coulometric analysis, using a GCPE as a working electrode, was attempted. However, due to the very strong adsorption of electrochemically-formed species on the electrode surface a non-conducting surface layer develops, blocking the electrode/supporting electrolyte contact and preventing further electrolysis. It was, therefore, impossible to use coulometry to determine the number of electrons involved in the 8HQ oxidation process on GCPE.

The regioselectivity of 8HQ dimer formation through the recombination of $[H\text{-}8HQ]^{\bullet 2+}$, $[8HQ]^{\bullet +}$, and $[8HQ(\text{-}H)]^{\bullet}$ is analyzed by the AM1/COSMO computational method. According to the Hammond postulate [31], the regioselectivity of these reactions is not controlled by the stability of final products (**11**, **14**, and **17**, Scheme 2) but it is governed by the stability of intermediates (**10**, **13**, and **16**, Scheme 2) resembling structurally the corresponding transition states. It is proved that C5–C5 coupling is the prevalent 8HQ dimerization route in the case of $[H\text{-}8HQ]^{\bullet 2+}$ recombination reaction in an acidic aqueous solution (Scheme 2, Table 1) as well as in the case of $[8HQ]^{\bullet +}$ recombination (Scheme 2, Table 2). The C7–C7 coupled 8HQ dimers accompanied by C5–C5 coupled 8HQ dimers are found to be dominant in the case of $[8HQ(\text{-}H)]^{\bullet}$ recombination in an alkaline aqueous solution (Scheme 2, Table 3).

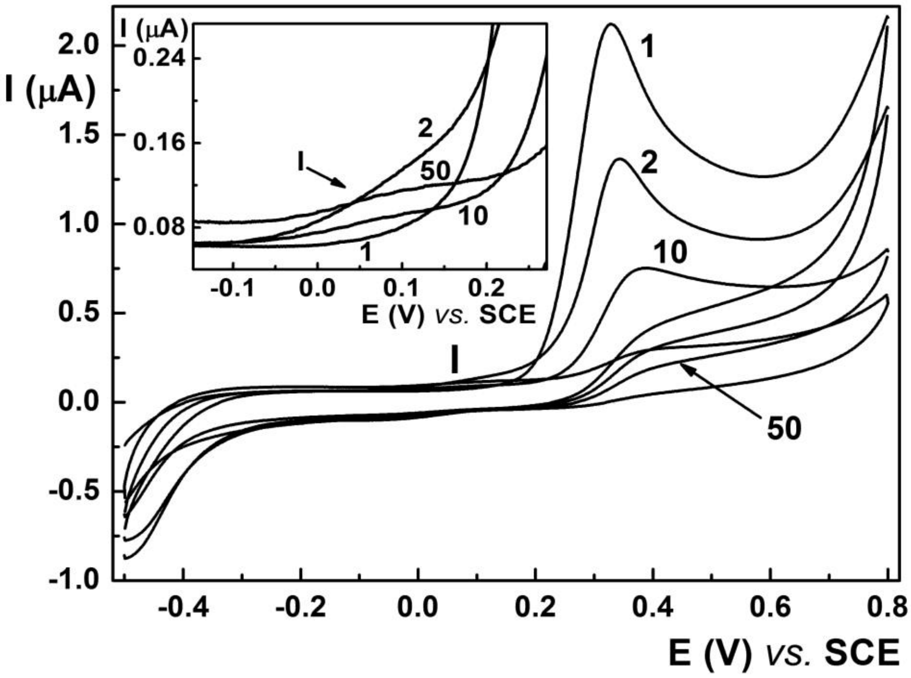


Figure 7. Continuous cyclic voltammograms of 1×10^{-4} M 8HQ on GCPE in BR buffer/methanol, containing 20% of methanol (v/v), pH 11.93, recorded after different numbers of cycle(s): one (1), two (2), ten (10) and fifty (50); scan rate 50 mV/s. The position of pre-peak (I) is indicated. The enlarged area with pre-peak is shown in the inset.

The two-electron oxidation of the prevalent 8HQ dimers, which are more oxidizable than 8HQ, leads to the formation of corresponding quinonoid compounds (**12**, **15**, and **18**, Scheme 2). We propose that the single-electron oxidation of 8HQ in a broad pH range, accompanied by both the dimerization of the resultant radical species and subsequent oxidation of 8HQ dimers to quinonoid compounds, is responsible for the first oxidation peak in cyclic voltammograms. This complex electro-oxidation process represents the overall two-electron transfer per 8HQ molecule.

Table 1. The heat of formation, ΔH_f, of 8HQ dimer tetra-cation intermediates formed by the radical recombination reaction of $[H\text{-}8HQ]^{\bullet 2+}$, computed by AM1/COSMO method.

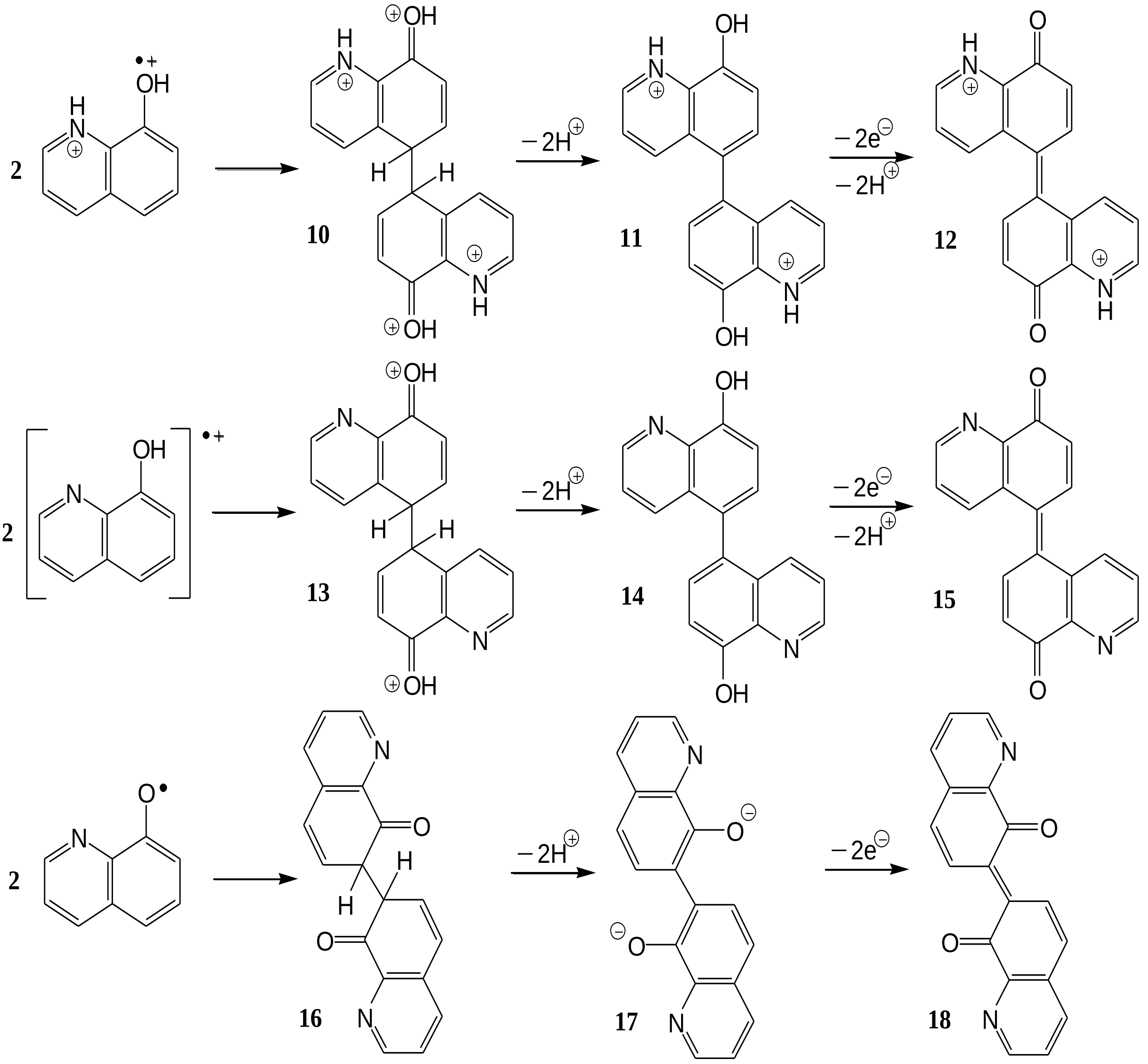
Coupling mode	ΔH_f kcal mol^{-1}	Coupling mode	ΔH_f kcal mol^{-1}	Coupling mode	ΔH_f kcal mol^{-1}
C2–C2	554.1	C4–C4	541.4	C5–C7	489.6
C2–C4	551.3	C4–C5	511.3	C5–O	521.4
C2–C5	525.6	C4–C7	522.0	C7–C7	500.3
C2–C7	525.7	C4–O	543.5	C7–O	531.3
C2–O	587.0	C5–C5	487.2	O–O	571.4

Table 2. The heat of formation, ΔH_f, of 8HQ dimer di-cation intermediates formed by the radical recombination reaction of $[8HQ]^{\bullet +}$, computed by AM1/COSMO method.

Coupling mode	ΔH_f kcal mol^{-1}	Coupling mode	ΔH_f kcal mol^{-1}	Coupling mode	ΔH_f kcal mol^{-1}
C2–C2	303.1	C4–C5	281.3	C5–O	297.5
C2–C4	302.5	C4–C7	285.2	C7–C7	276.9
C2–C5	282.4	C4–N	284.9	C7–N	266.6
C2–C7	289.4	C4–O	314.8	C7–O	302.8
C2–N	288.2	C5–C5	264.0	N–O	347.5
C2–O	318.0	C5–C7	265.9	N–N	293.3
C4–C4	300.4	C5–N	264.9	O–O	346.1

Table 3. The heat of formation, ΔH_f, of 8HQ dimer intermediates formed by the radical recombination reaction of $[8HQ(\text{-}H)]^{\bullet}$, computed by AM1/COSMO method.

Coupling mode	ΔH_f kcal mol^{-1}	Coupling mode	ΔH_f kcal mol^{-1}	Coupling mode	ΔH_f kcal mol^{-1}
C2–C2	67.8	C4–C5	43.0	C5–O	33.1
C2–C4	64.2	C4–C7	45.2	C7–C7	21.2
C2–C5	43.6	C4–N	72.8	C7–N	45.5
C2–C7	47.8	C4–O	53.5	C7–O	33.1
C2–N	71.1	C5–C5	22.1	N–O	90.4
C2–O	56.2	C5–C7	24.2	N–N	101.7
C4–C4	63.5	C5–N	47.0	O–O	100.6



Scheme 2. The formation of the prevalent 8HQ dimers (**11**, **14**, and **17**) via radical recombination, and subsequent two-electron oxidation of 8HQ dimers.

In the cathodic area two peaks appear in the investigated pH range 2−12 (Figure 2 and Figure 3, inset). Taking into account that the 8HQ oxidation on GCPE is a two-electron process according to theory, the following facts were apparent: (I) the anodic and first cathodic peak potential differences are much bigger than 56/n mV (28 mV in this case), Figures 2 and 3; (II) the anodic and cathodic peak current height ratio (i_{pa}/i_{pc}) after a certain number of cycles is much higher than unity; (III) peak potential is a function of the scan rate (Figure 4). Unambiguously it has been concluded, in accordance with computational predictions, that the electrode process is irreversible [32] due to the fast subsequent chemical reaction.

The rate of the electrochemical oxidation of 8HQ is controlled by the diffusion of the electroactive species (as the slowest step in the electrochemical process). The diffusion nature of the 8HQ voltammetric peaks is confirmed by the linear dependence of the CV anodic peak current logarithm, on the scan rate logarithm, log I*p*=f (log v), (Figure 8), with r=0.9946 and slope 0.4960 (theoretically diffusion controlled process has a slope 0.5 [32]).

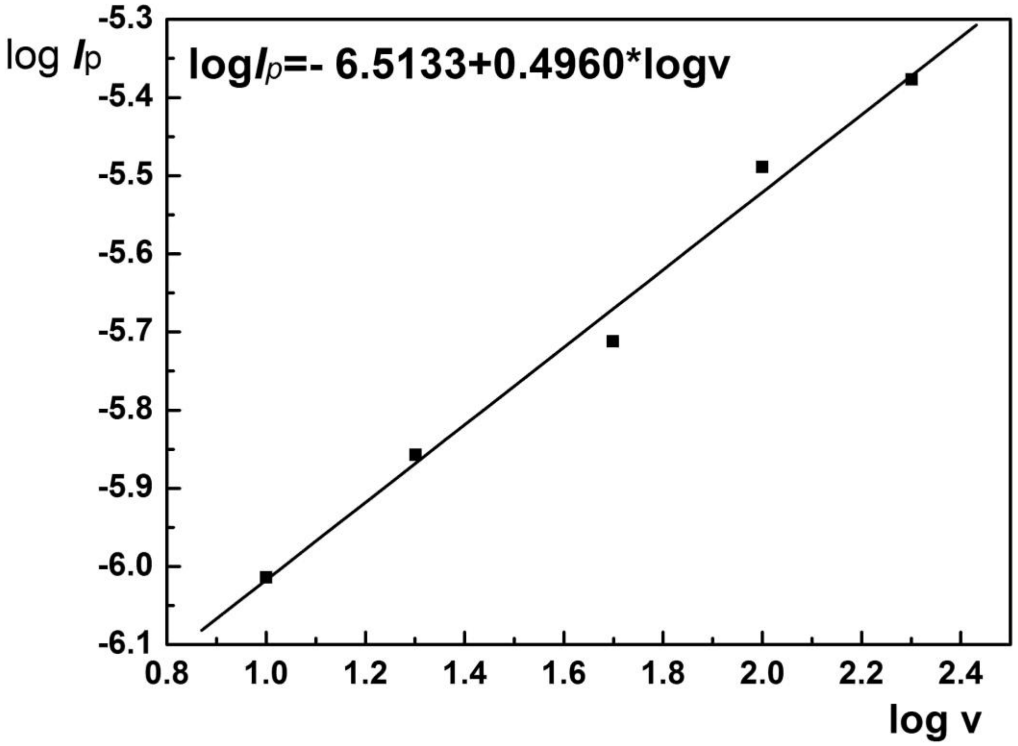
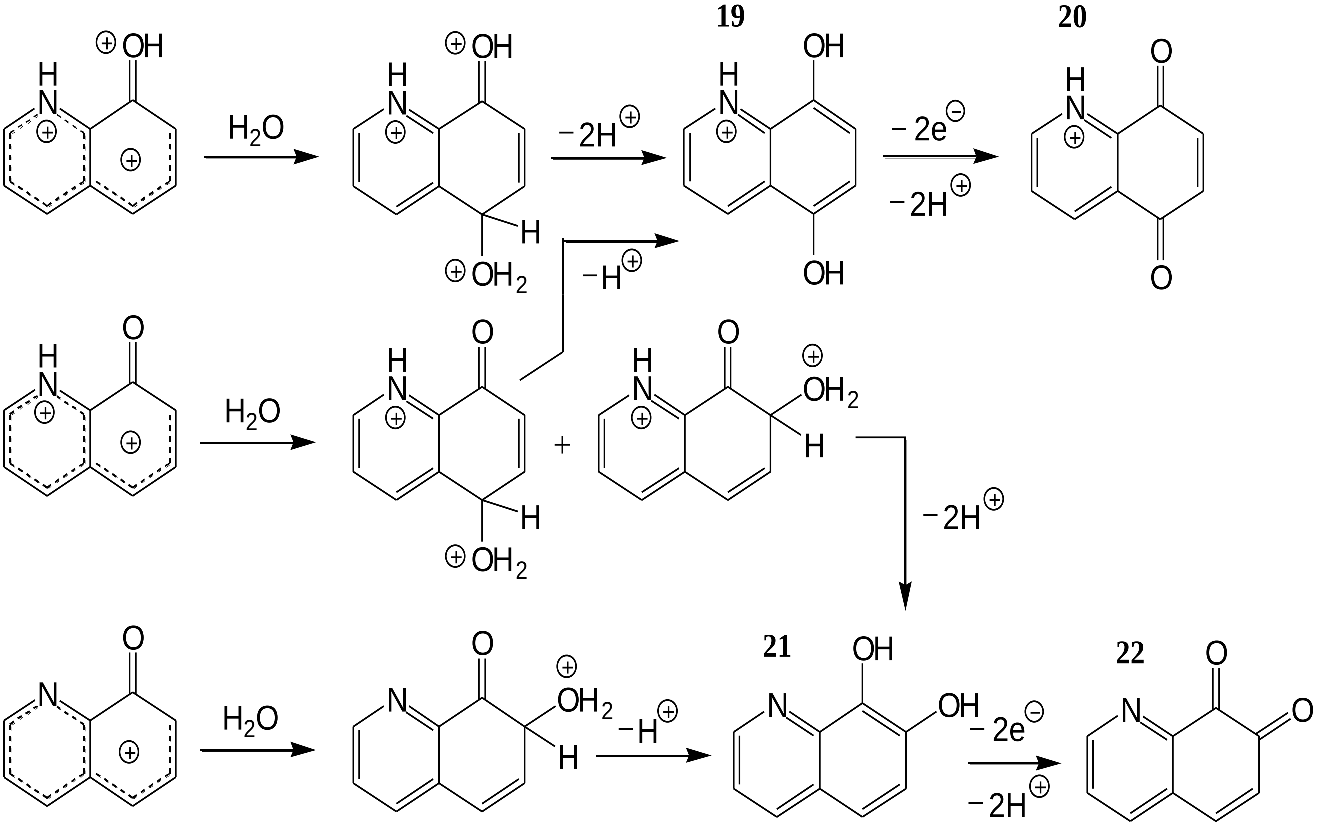


Figure 8. Dependence of CV anodic peak current logarithm, log I*p*, of 1×10^{-4} M 8HQ on GCPE in BR buffer/methanol, containing 20% of methanol (v/v), pH 9.00, on the scan rate logarithm, log v.

Significantly lower oxidizability of radical/cation radical species (**4**, **5**, and **6**, Scheme 1) in comparison with parent 8HQ molecular species (**1**, **2**, and **3**, Scheme 1), as proved by our semi-empirical quantum chemical computations, indicates that the oxidation potential onsets corresponding to the formation of 8HQ phenoxonium cations **7**, **8**, and **9** (Scheme 1) are higher for ~1 V in comparison with oxidation potential onsets corresponding to the formation of radical/cation radical species **4**, **5**, and **6**, respectively. The resultant 8HQ phenoxonium cations, as highly reactive electrophilic species, can react further with unoxidized 8HQ and water molecules thus forming 8HQ dimers and dihydroxyquinolines, respectively. Our AM1/COSMO computational study of the reactions between different acid-base forms of 8HQ phenoxonium cation and water molecule indicates the prevalent formation of 5,8-dihydroxyquinoline (**19**) in acidic aqueous solution and 7,8-dihydroxyquinoline (**21**) in an alkaline aqueous solution (Scheme 3). The two-electron oxidation of the prevalent dihydroxyquinolines, which are more oxidizable than 8HQ, leads to the formation of corresponding naphthoquinone-like compounds (**20** and **22**, Scheme 3). Based on our semiempirical quantum chemical computations and cyclovoltammetric experimental results, we propose that the formation of 8HQ phenoxonium cations, accompanied with complex chemical/electrochemical processes, occur at oxidation potentials higher than 1.2 V *vs.* SCE in aqueous solutions in the pH range

2–12. It is expected that the formation of 8HQ phenoxonium cations is also pH dependent, similarly to the formation of corresponding 8HQ radical/cation radical species.



Scheme 3. Reactions of the 8HQ phenoxonium cation in different acid-base forms with water.

3.2. Determination of 8HQ using Differential Pulse Voltammetry

The DP voltammetric behaviour of 8HQ in supporting electrolytes comprising mixtures BR buffer/methanol, containing 20% of methanol (v/v), of pH 2–12, was studied. The analyte concentration was 1×10^{-4} M. Under these conditions one well developed peak appears in all DPVs of 8HQ. For the purpose of illustration DPVs obtained by applying 25 mV pulse amplitude and 20 mV/s scan rate, in the studied pH range, are presented in Figure 9.

The influence of the supporting electrolyte pH on the DPV peak currents, I*p*, of 8HQ is given in Figure 10. The highest and best developed peak is obtained in supporting electrolyte pH 9.00 so that medium was used for measuring the calibration dependences on GCPE in concentration range 1×10^{-7}–1×10^{-4} M. The parameters of the calibration plots - the slope, A, and its standard deviation, S(A), the intercept, B, and its standard deviation, S(B), correlation coefficient, r, with the calculated limits of detection, LOD, for 8HQ are summarized in Table 4.

In order to improve the sensitivity of 8HQ determination we have conducted a preliminary investigation applying Adsorptive Stripping Differential Pulse Volammetry (AdSDPV). The analyte concentration in the investigated solution was 1×10^{-7} M. In Figure 9 it can be seen that the 8HQ DPV peak potential at pH 9.00 is +376 mV.

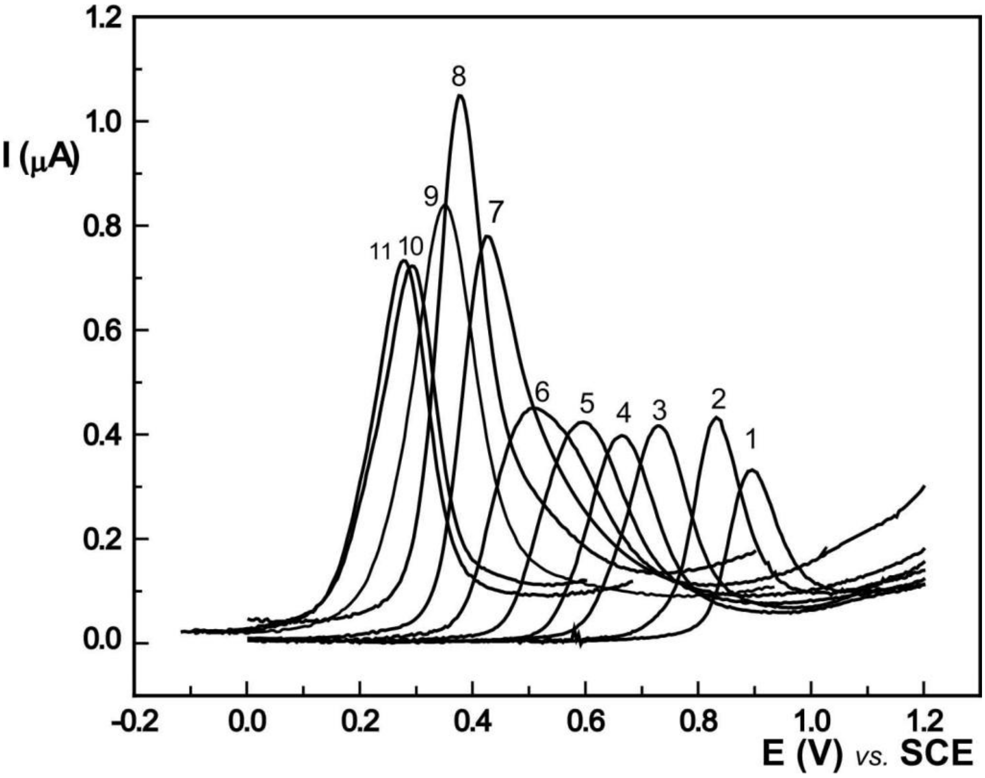


Figure 9. DP voltammograms of 1×10^{-4} M 8HQ on GCPE, in BR buffer/methanol, containing 20% of methanol (v/v), pH: 2.02 (1); 2.95 (2); 3.99 (3); 4.96 (4); 6.03 (5); 7.10 (6); 8.09 (7); 9.00 (8); 9.95 (9); 11.05 (10) and 11.93 (11); scan rate 20 mV/s, pulse amplitude 25 mV.

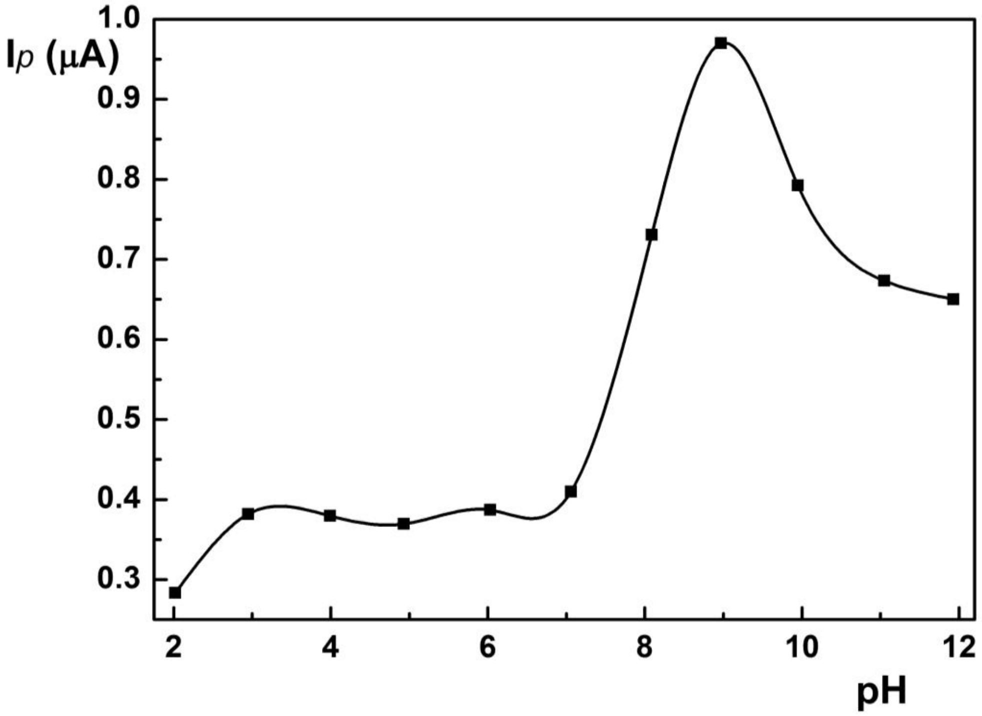


Figure 10. The influence of the supporting electrolyte pH, BR buffer/methanol, containing 20% of methanol (v/v), on the DP anodic peak current, I*p*, of 1×10^{-4} M 8HQ; scan rate 20 mV/s, pulse amplitude 25 mV.

Table 4. Parameters of the calibration plots for DP voltammetric determination of 8HQ in BR buffer/methanol, containing 20% of methanol (v/v), pH 9.00, on GCPE.

C mol L^{-1}	A±S(A) nA	B±S(B) mA/molL^{-1}	r	LOD molL^{-1}
$(1-10)\times10^{-5}$	−45.7 ± 8.5	31.0 ± 1.4	0.9947	-
$(1-10)\times10^{-6}$	−15.1 ± 8.5	31.9 ±0.4	0.9967	8.5×10^{-7}
$(1-10)\times10^{-7}$	−0.9 ± 0.1	33.8 ±1.8	0.9955	5.2×10^{-8}

In order to determine the best deposition potential, i.e. the potential with the highest DPV peak current, DP voltammograms were recorded after 1 minute deposition time at the following potentials: 300, 200, 100 and 0 mV [33]. It was found that the highest DP peak current was obtained by applying a 1 minute deposition time at 0.0 V, so this potential was selected as the optimum deposition potential. Afterwards, at potential 0.0 V, different deposition times: 0, 50, 150, 200, 300, 400 and 500 s, were applied. After each deposition time DPV was recorded in 0.0–0.9 V range.

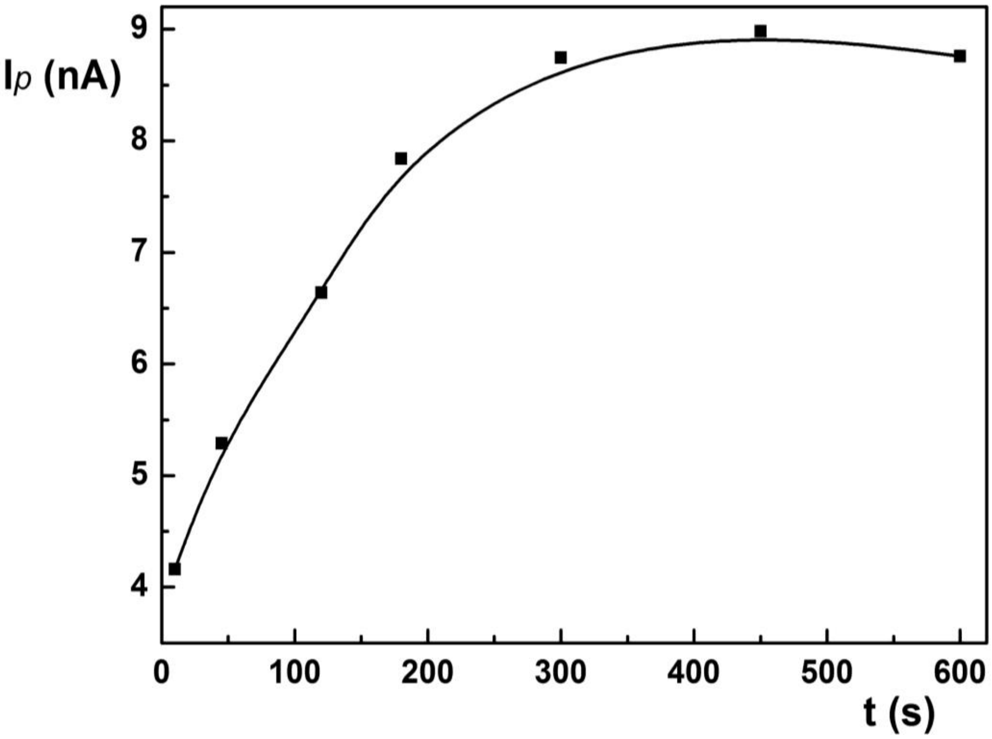


Figure 11. The influence of the deposition time on DP peak current, I*p*, in 1×10^{-7} M 8HQ in BR buffer/methanol, containing 20% of methanol (v/v), pH 9.00, on GCPE; scan rate 20 mV/s, pulse amplitude 25 mV, deposition potential 0.0 V.

The obtained respective peak heights were presented as a function of deposition time in Figure 11, where it can be seen that the optimal accumulation time is 300 s at 0.0 V. Under these conditions a 2.1 times higher current peak was produced than without any deposition period. We, therefore, concluded that AdSDPV is at least two times more sensitive for 8HQ quantitative determination than DPV. The further study of the AdSDPV of 8HQ is going to be one of our subsequent investigation topics.

4. CONCLUSION

In this study the oxidative behaviour of 8HQ on GCPE was investigated voltammetrically, using CV and theoretically, using the semi-empirical computational method. It was confirmed that 8HQ oxidizability increases with increasing pH of the supporting electrolyte. Molecular orbital AM1 computations, combined with MM2 molecular mechanics force-field method and conductor-like screening model of solvation, indicated that a complex two-electron process is responsible for the single peak that appears in CVs in a wide pH range, 2–12, in the anodic area. The pre-peaks that appear in CVs after continuous cycling are consequences of dimerization and polymerization which take place on the GCPE surface. The optimum conditions for DPV determinations are established and it was shown that for more sensitive quantitative determinations AdSDPV can be used.

ACKNOWLEDGEMENT
This study was supported by the Serbian Ministry of Science and Technological Development (projects 172030 and 172043).

References

1. V. Aranciba, M. Zúñiga, M. C. Zúñiga, R. Seruga and M. Esteban, *J. Braz. Chem. Soc*, 21 (2010) 255
2. E. R. de Sousa, E. P. Marques, E. N. Fernandes, J. Zhang and A. L. B. Marques, *J. Braz. Chem. Soc*, 17 (2006) 177
3. J. P. Phillips, *Chem. Rev*, 56 (1956) 271
4. N. E. Rigler and G. A. Greathouse, *Ind. Eng. Chem*, 33 (1941) 693
5. J. L. Stauber and T. M. Florence, *Mar. Biol*, 94 (1987) 511
6. R. Musiol, M. Serda, S. Hasel-Bielowka and J. Polanski, *Curr. Med. Chem*, 18 (2010) 1960
7. N. Parthasarathy, M. Pelletier and J. Buffle, *J. Membr. Sci*, 355 (2010) 78
8. L. Fishbein, *Potential industrial carcinogens and mutagens*, Elsevier Scientific Publishing Company, The Netherlands (1979)
9. R. S. Yamamoto, G. M. Williams, H.H. Frankel and J. H. Weisburger, *Toxicol. Appl. Pharmacol* 19 (1971) 687
10. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett*, 51 (1987) 913
11. C. M. Darby and C. F. Nathan, *J. Antimicrob Chemother*, 65 (2010) 1424
12. Z. P. Yang, M. Alafandy, K. Boutakhrit, J. M. Kauffmann and J. Arcos, *Elecroanalysis*, 8 (1996) 25
13. S. Guo, X. Wu, J. Zhou, J. Wang, B. Yang and B. Ye, *J. Electroanal. Chem*, 655 (2011) 45
14. J. Claret, C. Muller, J. M. Feliu and J. Virgili, *Electrochim. Acta*, 27 (1982) 1475
15. J. T. Stock, *J. Chem. Soc* (1949) 586
16. J. Wang, U. A. Kirgoz, J. Mo, J. Ju, A. N. Kawde and A. Muck, *Electrochem. Comm*, 3 (2001) 203

17. I.Svancara, K. Vytras, J. Barek and J. Zima, *Crit. Rev. Anal. Chem*, 31 (2001) 311
18. J. Zima, I. Svancara, J. Barek and K. Vytras, *Crit. Rev. Anal. Chem*, 39 (2009) 204
19. J. N. Miller and J. C. Miller, *Statistics and chemometrics for analytical chemistry*, Pearson Education Limited, England (2005)
20. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc*, 107 (1985) 3902
21. J. J. P. Stewart, *J. Comput. Aid. Mol. Des*, 4 (1990) 1
22. L. Y. Dávila and M. J. Caldas, *J. Comput. Chem*, 23 (2002) 1135
23. G. Ćirić-Marjanović, M. Trchová and J. Stejskal, *Collect. Czech. Chem. Commun*, 71 (2006) 1407
24. G. Ćirić-Marjanović, M. Trchová, E. N. Konyushenko and J. Stejskal, *Synth. Met*, 168 (2008) 200
25. G. Ćirić-Marjanović, M. Trchová, E. N. Konyushenko, P. Holler and J. Stejskal, *J. Phys. Chem. B*, 112 (2008) 6976
26. A.Klamt and G. Schüürmann, *J. Chem. Soc. Perkin. Trans*, 2 (1993) 799
27. U. Burkert and N. L. Allinger, *Molecular Mechanics*, ACS, Washington DC (1982)
28. A.Banerjee, N. Adams, J. Simons and R. Shepard, *J. Phys. Chem*, 89 (1985) 52
29. J. Baker, *J. Comp. Chem*, 7 (1986) 385
30. H. A. Mottola and H. Freiser, *Talanta*, 13 (1966) 55
31. G. S. Hammond, *J. Am. Chem. Soc*, 77 (1955) 334
32. A.J. Bard and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, 2nd Edition, John Wiley & Sons, Inc., New York (2001)
33. H. Benadikova and R. Kalvoda, *Anal. Lett*, 17 (1984) 1519

© 2011 by ESG (www.electrochemsci.org)