

Digital Simulation of the Cyclic Voltammetric Study of the Catechols Electrooxidation in the Presence of Thiourea

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Received: 18 September 2011 / Accepted: 16 October 2011 / Published: 1 November 2011

The present work explains the electrochemical behavior of catechols in the presence of thiourea as a nucleophile in aqueous solution, by means of cyclic voltammetry and controlled-potential coulometry. The results indicate that the participation of catechols in the Michael reaction with thiourea form the corresponding *o*-dihydroxybenz-thiourea adduct. Based on an *EC* mechanism, the observed homogeneous rate constants were estimated by comparing the experimental cyclic voltammetric responses with the digital simulated results. The calculated observed homogeneous rate constants (k_{obs}) was found to vary in order 2,3-Dihydroxybenzoicacid, Catechol, 3,4-Dihydroxybenzoicacid, 3-Methylcatechol, 3-Methoxycatechol, 4-Methylcatechol, 4-*Tert*-butylcatechol.

Keywords: Catechol, Cyclic voltammetry, Thiourea, Digital simulation, Michael reaction

1. INTRODUCTION

In the last fifteen years, considerable scientific attention has been paid to the electrooxidation of catechols in the presence of various nucleophiles. The quinones formed through this process are quite reactive and can be attacked by a variety of nucleophiles such as 2-thioracil [1], 4-amino-3-methyl-5-mercapto-1,2,4-triazole [2], 4,6-dimethylpyrimidine-2-thiol [3], indole [4] and 2-mercaptobenzoxazole [5]. Moreover, we have studied the electrochemical oxidation of catechol and some catechol derivatives in aqueous solutions and in the presence of a variety of nucleophiles such as 4-hydroxycoumarin [6,7] and benzenesulfinic acid [8]. Accordingly, because of the increase in available data concerning the electrooxidation of catechol in the presence of nucleophiles, the electrochemical oxidation of catechols in the presence of thiourea has been investigated using cyclic voltammetry and controlled-potential coulometry. The purpose of the investigation was to carry out a

quantitative detailed study of the electrochemical oxidation of catechols such as catechol, 3-methylcatechol, 4-methylcatechol, 3-methoxycatechol, 4-tert-butylcatechol, 2,3-dihydroxybenzoic acid and 3,4-dihydroxybenzoic acid in the presence of thiourea in aqueous solutions. Cyclic voltammetry is a powerful analytical technique that provides information about the characteristic electrochemical processes an analyte undergoes in solution, which is used to diagnose mechanisms of electrochemical reactions, for identification of the species present in solution and for the semi-quantitative analysis of reaction rates [9]. Controlled-potential coulometry is a useful method for studying the mechanisms of electrode reactions and for determining the n -value for an electrode reaction without prior knowledge of the electrode area or diffusion coefficient. However, because the time scale of coulometric measurements is at least one or two orders of magnitude longer than that of voltammetric methods, the perturbing homogeneous chemical reactions that follow the electrode transfer, which might not affect the voltammetric measurement, may be important in coulometry [10]. These methods provide a powerful independent route for quantitative characterization of complex electrode processes.

2. EXPERIMENTAL PART

2.1. Apparatus

Cyclic voltammetry and controlled-potential coulometry were performed using an Autolab model PGSTAT 302N potentiostat/galvanostat. The working electrode (WE) used in the voltammetry experiments was a glassy carbon disc (1.8 mm diameter) and platinum wire was used as a counter electrodes (CE). The working electrode (WE) used in controlled-potential coulometry was an assembly of 12 carbon rods (6 mm diameter and 11 cm length), and a large platinum gauze (2.5 cm width and 5 cm length) constituted the counter electrode (CE). The working electrode potentials were measured versus SCE (all electrodes from Radiometer analytical). The cell used was a simple and undivided cell.

2.2. Digital Simulation

The cyclic voltammograms have been analyzed by a commercial digital simulation program (DigiElch 6) [11-13] to estimate the observed homogeneous rate constants (k_{obs}) of the reaction of *o*-quinones derived from catechols with thiourea. To verify the reaction mechanism for the electrochemical oxidation of catechols in the absence and presence of the thiourea, the cyclic voltammograms have been analyzed by a commercial digital simulation program (DigiElch 6) to find the best-fit between experimental and simulated cyclic voltammograms.

2.3. Reagents

The catechols (catechol, 3-methylcatechol, 4-methylcatechol, 3-methoxycatechol and 4-tert-butylcatechol) were reagent-grade materials from Aldrich. Other catechols (2,3-dihydroxybenzoic acid and 3,4-dihydroxybenzoic acid) were used as a reagent-grade from Sigma. The thiourea, KH_2PO_4 ,

K_2HPO_4 and other acids and bases were of pro-analysis grade from E. Merck. These chemicals were used without further purification.

3. RESULTS AND DISCUSSION

3.1. Electrochemical oxidation of catechol (**1a**) in the presence of thiourea (**3**)

Fig. 1 (curve a) shows a cyclic voltammogram recorded for 2 mM catechol (**1a**) in aqueous solution containing 0.2 M phosphate buffer (pH 7.0). The voltammogram shows an anodic peak (A_1) in the positive scan and a cathodic counterpart peak (C_1) in the negative scan which corresponds to the transformation of catechol (**1a**) to *o*-benzoquinone (**2a**) and vice-versa within a quasi-reversible two-electron process. In these conditions, the peak current ratio (I_p^{C1} / I_p^{A1}) is nearly unity, particularly during the repetitive recycling of potential, which can be considered as a criterion for the stability of *o*-quinone produced at the surface of the electrode under the experimental conditions. In other words, any hydroxylation or dimerization reactions are too slow to be observed on the time scale of cyclic voltammetry [14-17]. The oxidation of catechol (**1a**) in the presence of thiourea (**3**) (2 mM) as a nucleophile was studied in some detail. (Fig. 1 curves b) shows the cyclic voltammogram obtained for a 2 mM solution of **1a** in the presence of thiourea (2 mM) in aqueous solution containing 0.2 M phosphate buffer (pH 7.0). In these conditions, the cathodic counterpart of the anodic peak A_1

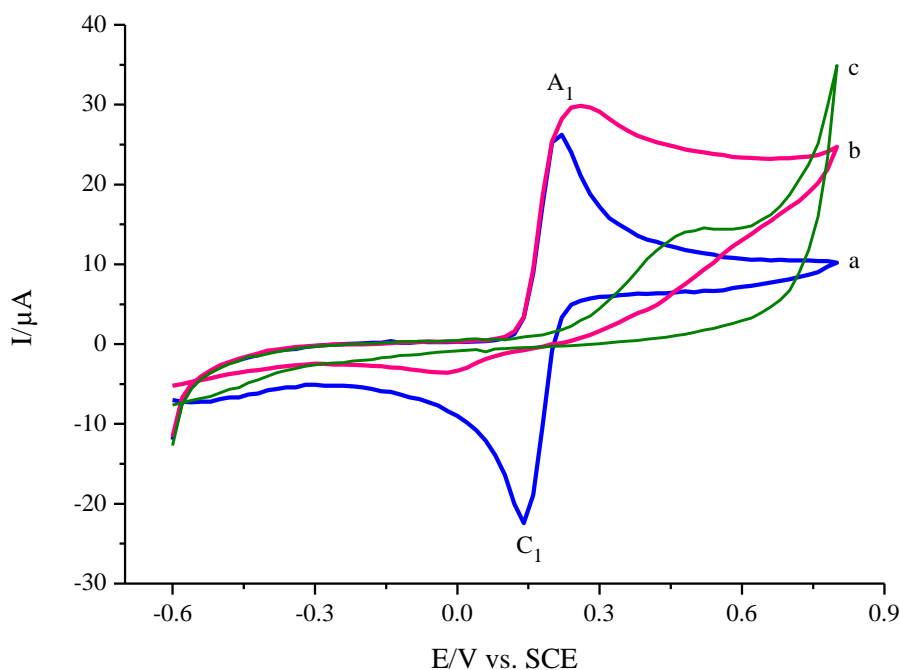


Figure 1. Cyclic voltammograms of 2 mM catechol (**1a**): (a) in the absence; (b) in the presence of 2 mM thiourea (**3**) and (c) 2 mM thiourea in the absence of catechol, at a glassy carbon electrode (1.8 mm diameter) in water containing of phosphates (KH_2PO_4/K_2HPO_4) as the buffer and supporting electrolyte (pH = 7.0); at scan rate: 100 mV s^{-1} ; $T=25 \pm 1 \text{ }^\circ\text{C}$.

disappears. Furthermore, it is seen that proportional to the augmentation of potential sweep rate, the current of peak C_1 increases (Fig. 2 curves a-g). A plot of peak current ratio (I_P^{C1} / I_P^{A1}) versus scan rate for a mixture of catechol (**1a**) and thiourea (Fig. 2 inset h) confirms the reactivity of **2a** towards thiourea (**3**), appearing as an increase in the peak current ratio (I_P^{C1} / I_P^{A1}) at higher scan rates. In comparison, the current function for A_1 peak, ($I_P^{A1}/v^{1/2}$) (Fig. 2 inset i), only changes slightly with the increasing scan rate and such a behavior is adopted as indicative of *EC* mechanism [10].

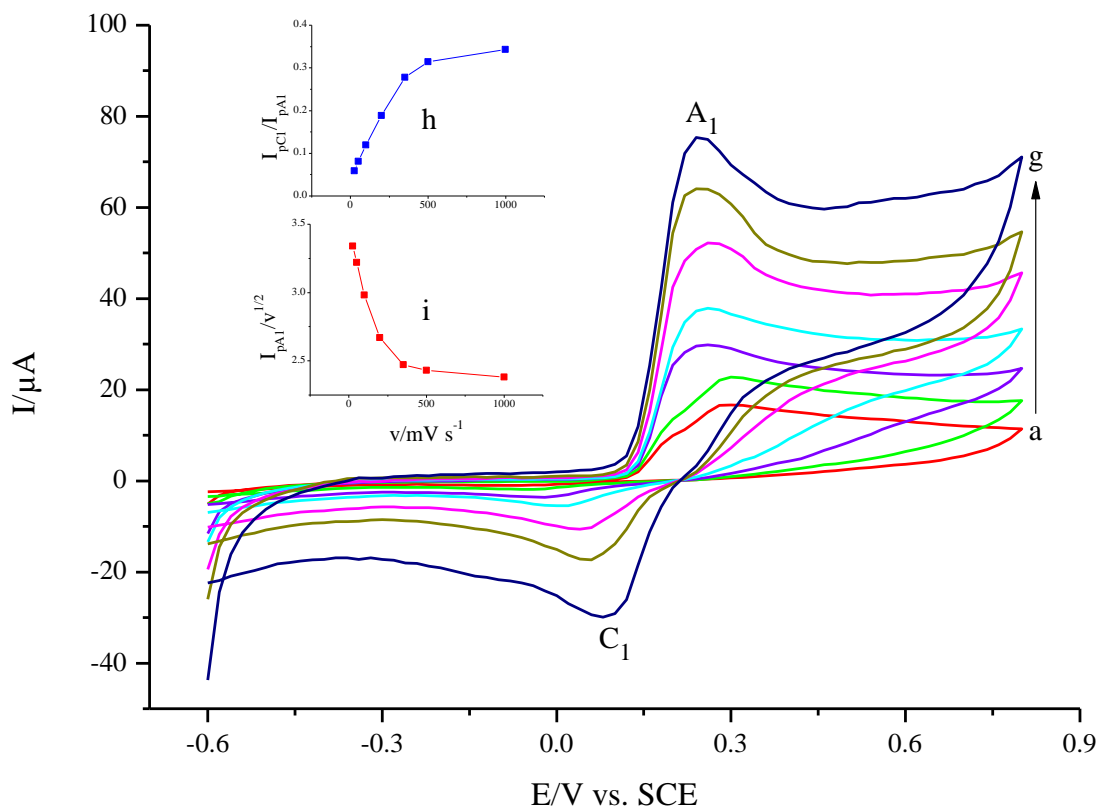


Figure 2. Typical cyclic voltammograms of 2 mM catechol (**1a**) in the presence of 2 mM thiourea (**3**) in water containing of phosphates (KH_2PO_4/K_2HPO_4) as the buffer and supporting electrolyte (pH = 7.0); at a glassy carbon electrode (1.8 mm diameter) and at various scan rates. Scan rate from (a) to (g) are: 25, 50, 100, 200, 350, 500, and 1000 $mV s^{-1}$, respectively; inset (h): variation of current ratio (I_P^{C1} / I_P^{A1}) versus scan rate for a mixture of catechol (**1a**) and thiourea (**3**); inset (i): variation of current function ($I_P^{A1}/v^{1/2}$) versus scan rate. $T=25 \pm 1$ °C.

Controlled-potential coulometry was performed in an aqueous solution containing 0.4 mmol of **1a** and 0.4 mmol of thiourea at 0.51 V versus SCE. The monitoring of electrolysis progress was carried out by cyclic voltammetry (Fig. 3). It is shown that, proportional to the advancement of coulometry, anodic peak A_1 decreases and disappears when the charge consumption becomes about $2e^-$ per molecule of **1a** (Fig. 3 inset).

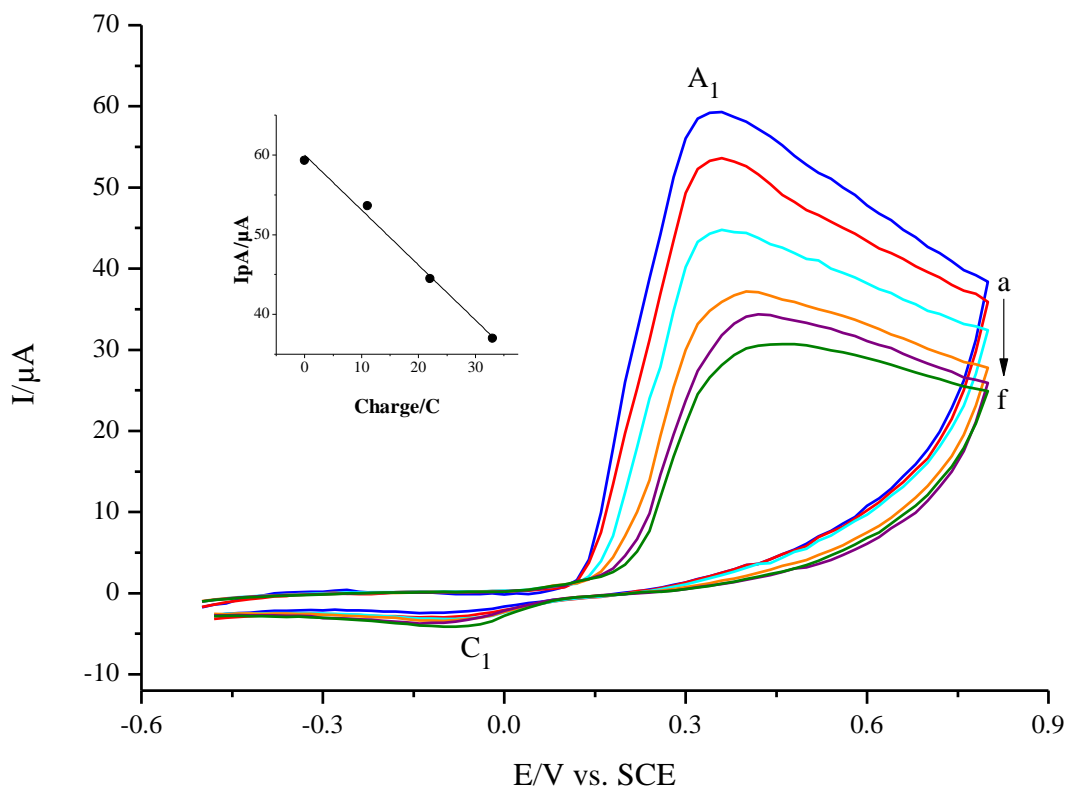


Figure 3. Cyclic voltammograms of 0.4 mmol catechol in the presence of 0.4 mmol thiourea during controlled-potential coulometry at 0.51 V versus SCE. After consumption of: (a) 0, (b) 12, (c) 34, (d) 57, (e) 67 and (f) 78 C. Inset: variation of A_1 peak current versus consumed charge. Scan rate 100 mVs^{-1} . $T=25 \pm 1 \text{ }^\circ\text{C}$.

These observations allow us to propose the pathway in Scheme 1 for the electrooxidation of **1a** in the presence of thiourea. According to the results obtained, it seems that the Michael addition reaction of thiourea (**3**) to *o*-quinone (**2a**) (Eq. 2) is faster than other secondary reactions, leading to the product **4a**. The oxidation of this compound (**4a**) is more difficult than the oxidation of the parent starting molecule (**1a**) by virtue of the presence of thiourea (**3**) with electron-withdrawing character on the catechol ring and therefore, the overoxidation of **4a** was circumvented.

3.2. Electrochemical oxidation of 3-methylcatechol (**1b**), 4-methylcatechol (**1c**), 3-methoxycatechol (**1f**) and 4-*tert*-butylcatechol (**1g**) in the presence of thiourea (**3**)

The electrooxidation of **1b,1c** and **1f-1g** in the presence of thiourea as a nucleophile in phosphate buffer (pH 7.0, 0.2 M) proceeds in a way similar to that of **1a**. The *o*-benzoquinone formed via oxidation can act as a Michael acceptor toward nucleophiles yielding substituted catechols. In the cases of **1b,1c**, and **1f-1g** the presence of methyl, methoxy or *tert*-butyl group as electron-donating substituents on molecular ring causes a diminution in activity of *o*-quinones **2b**, **2c**, and **2f-2g** as Michael acceptors toward the 1,4-addition reaction of thiourea. Such behavior is an indicator of an *EC* mechanism. These reactions can be followed by cyclic voltammetry. The height of the anodic peak in

the second cycle of catechols (**1b**, **1c**, and **1f-1g**) is significantly reduced and no new cathodic or anodic peak appears indicating that the product of the *EC* reaction is electroinactive in the accessible potential range by virtue of its insolubility in given solvent supporting electrolyte system. It is also deposited on the electrode surface, so that it inhibits the performance of the electrode process extensively. The presence of a methyl (and a methoxy) group with electron-donating character at the C-3 position of **1b** (and **1f**) causes the related Michael acceptor **2b** (and **2f**) respectively, to be attacked by **3** at both the C-4 and C-5 positions to yield two types of product. But, C-4 of *o*-benzoquinones **2b** (and **2f**) is less reactive than C-5 probably as a result of a combination of steric and electronic effects of electrode under the experimental conditions (Scheme 1).

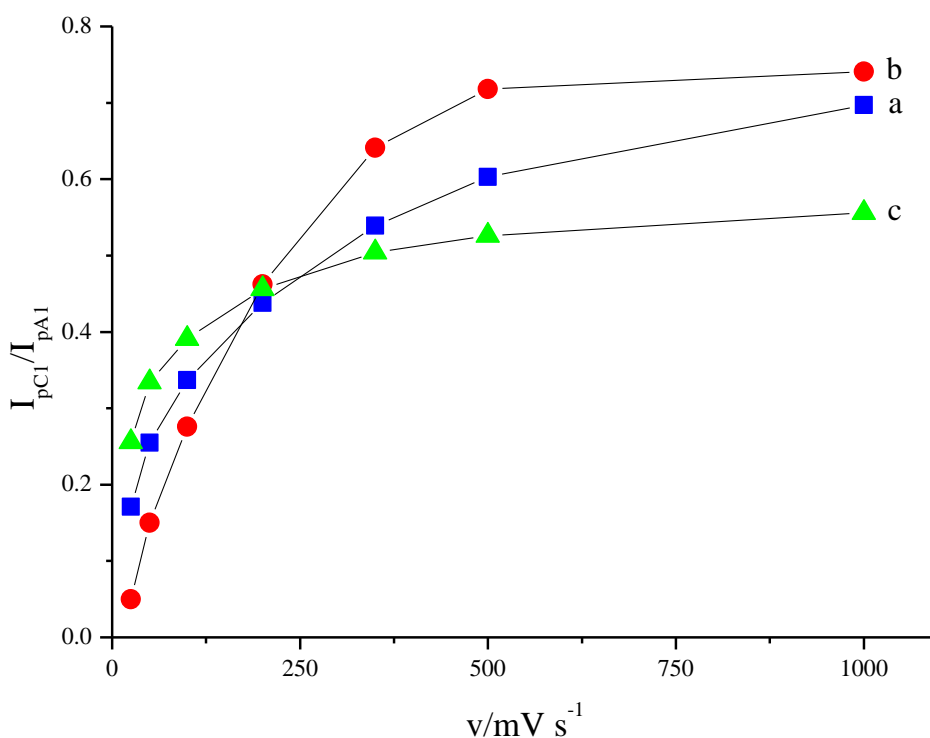


Figure 4. Variation of current ratio (I_p^{C1}/I_p^{A1}) versus scan rate for a mixture of catechols; (a) 3-methylcatechol (**1b**), (b) 4-methylcatechol (**1c**), (c) 3-methoxycatechol (**1f**) in the presence of thiourea (**3**). $T=25 \pm 1$ °C.

Fig. 4 shows the plot of the peak current ratio (I_p^{C1}/I_p^{A1}) versus scan rate for a mixture of catechols (**1b**, **1c** and **1f**) and thiourea confirming the reactivity of **2b**, **2c**, and **2f** towards thiourea. The presence of an electron donating group has little effect on the reactivity of *o*-benzoquinones (**2b**, **2c** and **2f**) formed. Similarly to **1a**, the occurrence of an *EC* mechanism is also confirmed by plotting the anodic peak current function, $I_p^{A1}/v^{1/2}$ versus scan rate. In addition, the current function changes of peak A₁, ($I_p^{A1}/v^{1/2}$) of **1b**, **1c**, and **1f** are shown with the increasing scan rate (Fig. 5).

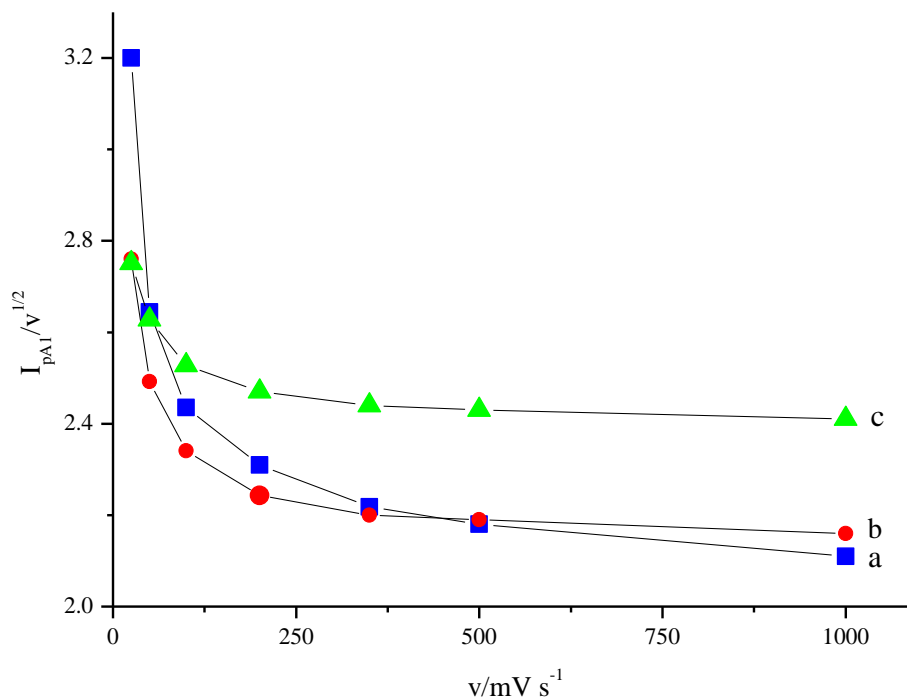


Figure 5. Variation of current function ($I_p^{A1}/v^{1/2}$) of catechols; (a) 3-methylcatechol, (b) 4-methylcatechol, (c) 3-methoxycatechol in the presence of thiourea versus scan rate. $T=25 \pm 1$ °C.

3.3. Electrochemical oxidation of 2,3-dihydroxybenzoic acid (**1d**) and 3,4-dihydroxybenzoic acid (**1e**) in the presence of thiourea (**3**)

In contrast, in the cases of **1d** and **1e** the presence of carboxylic group with electron-withdrawing character on the molecular ring causes an increase in activity of *o*-quinones **2d** and **2e** as Michael acceptors toward the 1,4-addition reaction of thiourea. At this condition, obtained voltammogram exhibit an anodic peak (A_1) in the positive scan and a cathodic counterpart peak (C_1) in the negative scan which corresponds to the transformation of 2,3-dihydroxybenzoic acid (**1d**) and 3,4-dihydroxybenzoic acid (**1e**) to *o*-benzoquinones (**2d,2e**). These observations are again in agreement with the occurrence of a following chemical reaction via an *EC* mechanism and also confirm the electrode surface fouling following the deposition of an electroinactive product formed during the electrooxidation process. The overall reaction mechanism for the anodic oxidation of **1d** and **1e** in the presence of thiourea (**3**) as a nucleophile is presented in Scheme 1. A peak current ratio (I_p^{C1}/I_p^{A1}) of nearly unity, particularly during the repetitive recycling of the potential, can be considered as a criterion for the stability of *o*-quinone produced at the surface of electrode under the experimental conditions. The peak current ratio (I_p^{C1}/I_p^{A1}) and the current function changes of peak A_1 , ($I_p^{A1}/v^{1/2}$) versus scan rate for a mixture of catechols (**1d,1e**) and thiourea are shown in (Figs. 6 and 7) in turn.

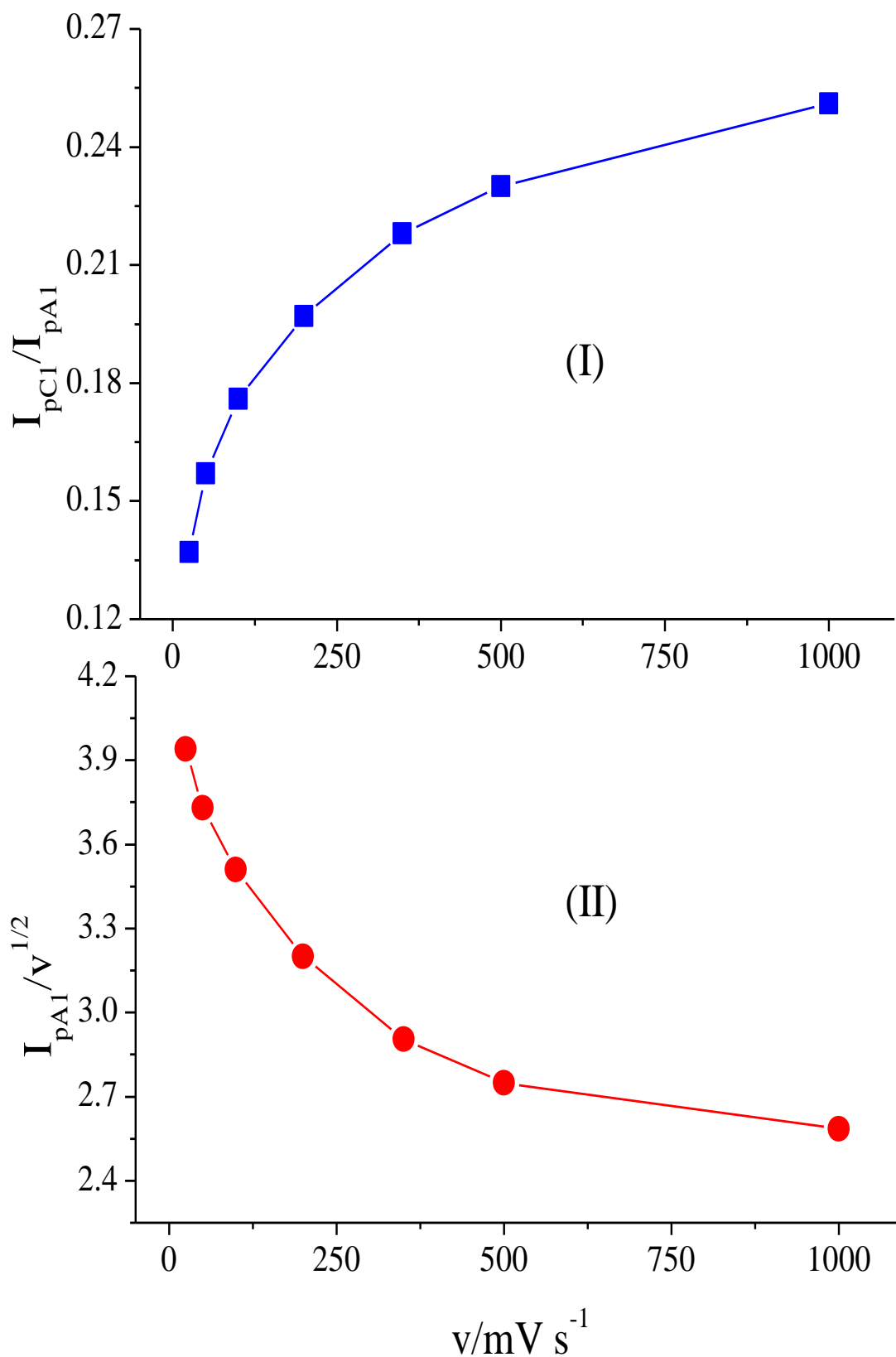


Figure 6. (I) variation of peak current ratio (I_{pCl}^{-1} / I_{pA}^1) versus scan rate for 2,3-dihydroxybenzoic acid (**1d**) in the presence of thiourea (**3**). (II) variation of peak current function ($I_{pA}^1 / v^{1/2}$) of 2,3-dihydroxybenzoic acid (**1d**) in the presence of thiourea (**3**) versus scan rate. $T=25 \pm 1$ °C.

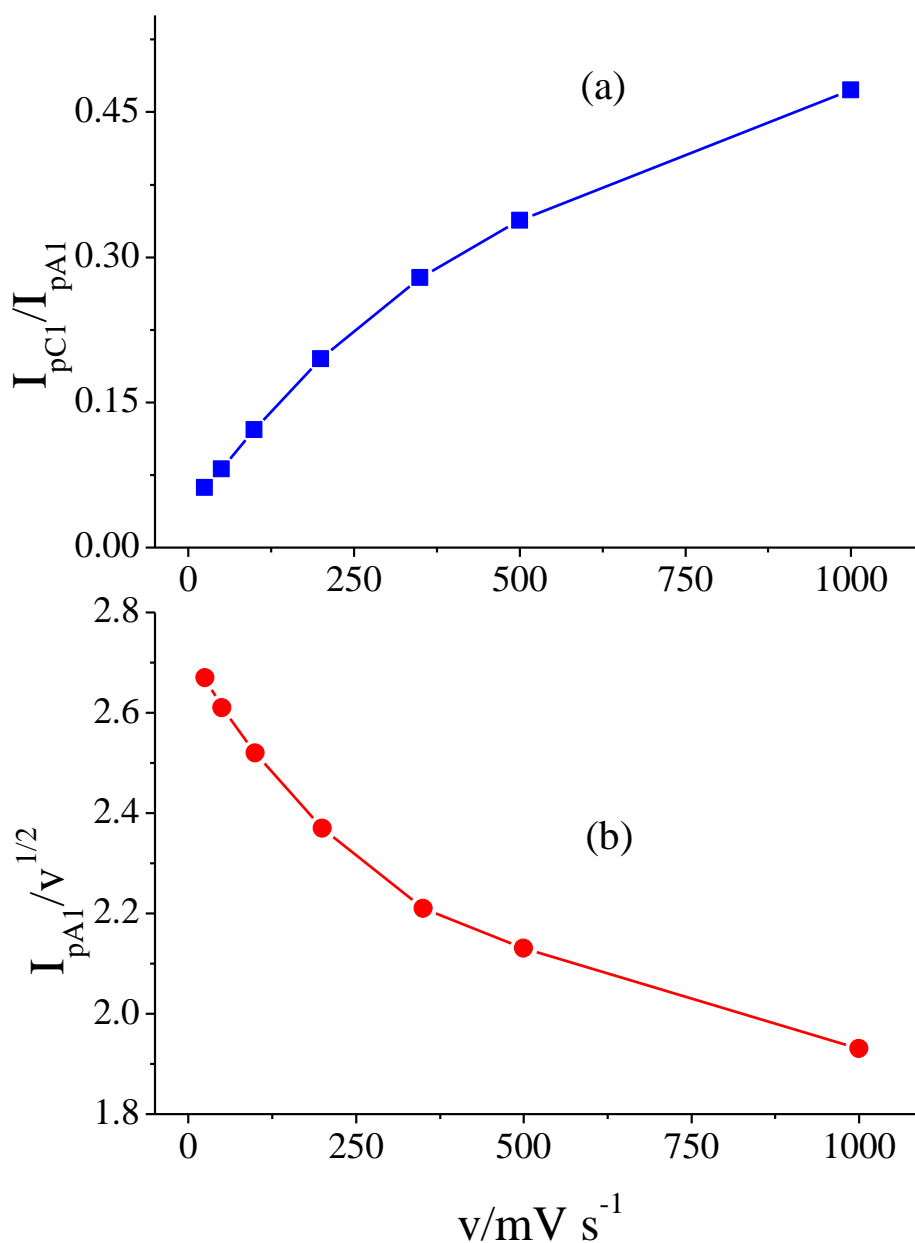
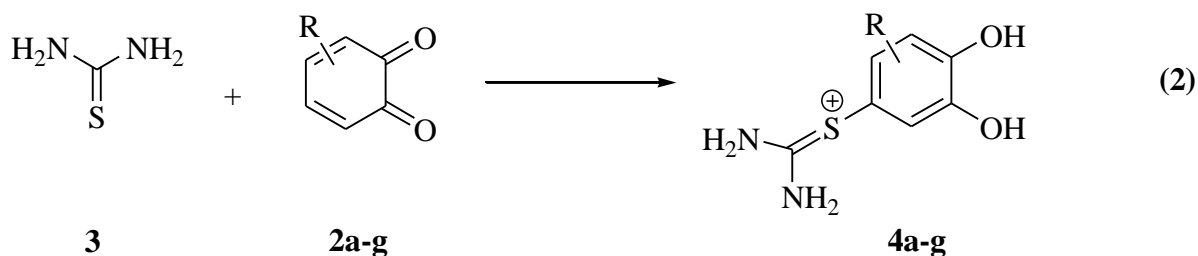
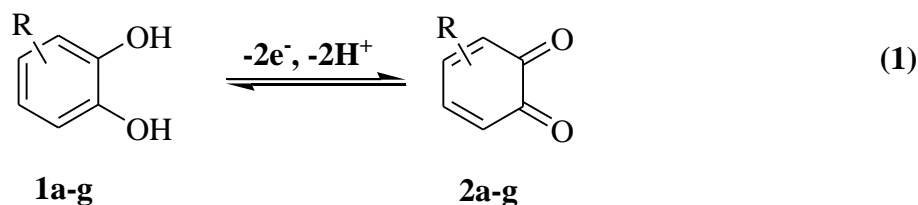


Figure 7. (a) variation of current ratio (I_p^{C1}/I_p^{A1}) versus scan rate for 3,4-dihydroxybenzoic acid (**1e**) in the presence of thiourea (**3**). (b) variation of current function ($I_p^{A1}/v^{1/2}$) 2,3-dihydroxybenzoic acid (**1e**) versus scan rate. $T=25 \pm 1$ °C.

The Scheme 1 for the electrochemical oxidation of catechols in the presence of thiourea is proposed and the validity of the reaction mechanism is tested by digital simulation. Based on an *EC* mechanism, the observed homogeneous rate constants (k_{obs}) of the reaction of *o*-benzoquinones with thiourea have been estimated by comparison of the simulation results (Fig. 8 curves b) with experimental cyclic voltammograms (Fig. 8 curves a). The calculated homogeneous rate constants are given in Table 1. As can be seen, the simulated voltammograms using the *EC* mechanism (Scheme 1) fit with the experimental voltammograms very well.



R=-H,	1a, 2a, 4a	R=-CH ₃ (in C-3),	1b, 2b, 4b
R=-CH ₃ (in C-4),	1c, 2c, 4c	R=-COOH (in C-3),	1d, 2d, 4d
R=-COOH (in C-4),	1e, 2e, 4e	R=-OCH ₃ (in C-3),	1f, 2f, 4f
R=-4- <i>tert</i> -butyl (in C-4),	1g, 2g, 4g		

Scheme 1. The mechanism for the electrooxidation of catechols in the presence of thiourea.

Table 1. Result of compare experimental cyclic voltammograms of catechol derivations in the presence of thiourea with simulated cyclic voltammograms.

Compound	Scan rate (mV s ⁻¹)	k_{obs} (M ⁻¹ s ⁻¹)
2,3-Dihydroxybenzoicacid	50-200-350	0.620 ± 0.0010
Catechol	100-200-500	0.550 ± 0.0070
3,4-Dihydroxybenzoicacid	100-200-350	0.500 ± 0.0100
3-Methylcatechol	100-200-350	0.095 ± 0.0009
3-Methoxycatechol	100-200-350	0.040 ± 0.0099
4-Methylcatechol	50-100-500	0.021 ± 0.0090
4- <i>Tert</i> -butylcatechol	100-200-350	0.001 ± 0.0001

The magnitude of observed homogeneous rate constants (k_{obs}) is dependent on nature and position of the substituted group on catechol ring. The most amounts of k_{obs} is calculated in electrochemical oxidation of 2,3-dihydroxybenzoicacid in the presence of thiourea and the less amounts of k_{obs} is electrochemical oxidation of 4-*tert*-butylcatechol in the presence of thiourea [Table 1].

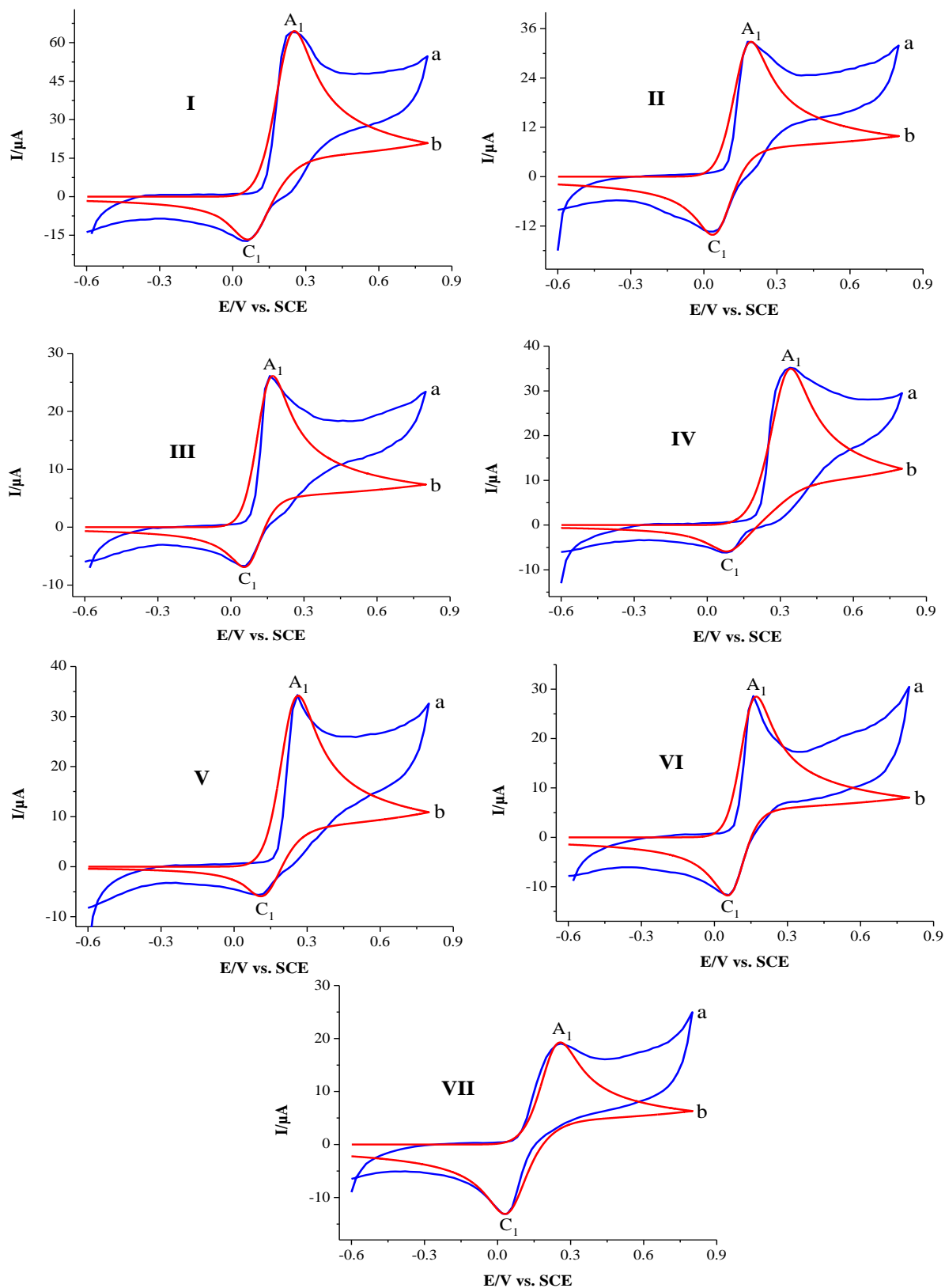


Figure 8. Cyclic voltammograms catechols (**1a-g**) in the presence of 2 mM thiourea (**3**) in various scan rates: (a) experimental, (b) simulated. (I) catechol 2 mM, (II) 3-methylcatechol 2 mM, (III) 4-methylcatechol 2 mM, (IV) 2,3-dihydroxybenzoic acid 2 mM, (V) 3,4-dihydroxybenzoic acid 2 mM, (VI) 3-methoxycatechol 4 mM, (VII) 4-*tert*-butylcatechol 8 mM, in phosphate buffer solution (pH = 7.0), at glassy carbon electrode. Scan rate from I to VII are: 500, 200, 100, 100, 200, 100, and 100 mVs^{-1} , respectively. $T=25 \pm 1$ °C.

4. CONCLUSIONS

The results of this work show that catechols (**1a-1g**) are oxidized in water to their respective *o*-benzoquinones. The quinones are then attacked by thiourea to form *o*-dihydroxybenz-thiourea adduct. The overall reaction mechanism for the anodic oxidation of catechols in the presence of thiourea as a nucleophile is presented in Scheme 1. According to our results, it seems that the Michael reaction of this nucleophile to *o*-quinones formed leads to the formation of new *o*-dihydroxybenz-thioureas as final products. In addition, we examined the kinetic for the reactions of the electrogenerated *o*-benzoquinones with thiourea by cyclic voltammetric technique. The cyclic voltammograms were digitally simulated under *EC* mechanism. The simulated cyclic voltammograms show good agreement with those obtained experimentally.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of this work by Universiti Kebangsaan Malaysia (UKM) Bangi, Selangor, Malaysia for the Grant (Research University Grant UKM-OUP-FST 2011) and Arak Islamic Azad University Markazi, Iran. We would like to thank Dr. Mohammad Alimoradi (Department of Chemistry, Islamic Azad University, Arak branch) for his valuable suggestions.

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