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 benzenesulfonic 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$_2$PO$_4$, KH$_2$PO$_4$, KH$_2$PO$_4$, KH$_2$PO$_4$. KH$_2$PO$_4$. KH$_2$PO$_4$. KH$_2$PO$_4$.
K₂HPO₄ 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 (A₁) in the positive scan and a cathodic counterpart peak (C₁) 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 \( \frac{I_{p1}}{I_{p1}} \) 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 A₁

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 (KH₂PO₄/K₂HPO₄) as the buffer and supporting electrolyte (pH = 7.0); at scan rate: 100 mV s⁻¹; T=25 ± 1 ºC.
disappears. Furthermore, it is seen that proportional to the augmentation of potential sweep rate, the current of peak C₁ increases (Fig. 2 curves a-g). A plot of peak current ratio \( \frac{I_p^{C1}}{I_p^{A1}} \) 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 \( \frac{I_p^{C1}}{I_p^{A1}} \) at higher scan rates. In comparison, the current function for A₁ peak, \( \frac{I_p^{A1}}{v^{1/2}} \) (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 (KH₂PO₄/K₂HPO₄) 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 \( \frac{I_p^{C1}}{I_p^{A1}} \) versus scan rate for a mixture of catechol (1a) and thiourea (3); inset (i): variation of current function \( \frac{I_p^{A1}}{v^{1/2}} \) versus scan rate. T=25 ± 1 ºC.

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 A₁ decreases and disappears when the charge consumption becomes about 2e⁻ per molecule of 1a (Fig. 3 inset).
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 seem 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 \( \frac{I_{PC}^{C1}}{I_{PA}^{A1}} \) 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 ± 1 °C.

Fig. 4 shows the plot of the peak current ratio \( \frac{I_{PC}^{C1}}{I_{PA}^{A1}} \) 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, \( I_{PA}^{A1}/\nu^{1/2} \) versus scan rate. In addition, the current function changes of peak A1, \( I_{PA}^{A1}/\nu^{1/2} \) of 1b, 1c, and 1f are shown with the increasing scan rate (Fig. 5).
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 (A1) in the positive scan and a cathodic counterpart peak (C1) 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 \( \frac{I_{p1}}{I_{p2}} \) 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 \( \frac{I_{p1}}{I_{p2}} \) and the current function changes of peak A1, \( \frac{I_{p1}/\sqrt{v}}{I_{p2}/\sqrt{v}} \) 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 ($I_{pC1}/I_{pA1}$) versus scan rate for 2,3-dihydroxybenzoic acid (1d) in the presence of thiourea (3). (II) Variation of peak current function ($I_{pA1}/ν^{1/2}$) of 2,3-dihydroxybenzoic acid (1d) in the presence of thiourea (3) versus scan rate. $T=25 \pm 1 \, ^\circ C$. 
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.
\[
\text{HO} \quad \text{-}2e-, \quad -2\text{H}^+ (1)
\]

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

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Scan rate (mV s(^{-1}))</th>
<th>(k_{\text{obs}}) (M(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-Dihydroxybenzoic acid</td>
<td>50-200-350</td>
<td>(0.620 \pm 0.0010)</td>
</tr>
<tr>
<td>Catechol</td>
<td>100-200-500</td>
<td>(0.550 \pm 0.0070)</td>
</tr>
<tr>
<td>3,4-Dihydroxybenzoic acid</td>
<td>100-200-350</td>
<td>(0.500 \pm 0.0100)</td>
</tr>
<tr>
<td>3-Methylcatechol</td>
<td>100-200-350</td>
<td>(0.095 \pm 0.0009)</td>
</tr>
<tr>
<td>3-Methoxycatechol</td>
<td>100-200-350</td>
<td>(0.040 \pm 0.0099)</td>
</tr>
<tr>
<td>4-Methylcatechol</td>
<td>50-100-500</td>
<td>(0.021 \pm 0.0090)</td>
</tr>
<tr>
<td>4-Tert-butylicatechol</td>
<td>100-200-350</td>
<td>(0.001 \pm 0.0001)</td>
</tr>
</tbody>
</table>

The magnitude of observed homogeneous rate constants \(k_{\text{obs}}\) is dependent on nature and position of the substituted group on catechol ring. The most amounts of \(k_{\text{obs}}\) is calculated in electrochemical oxidation of 2,3-dihydroxybenzoic acid in the presence of thiourea and the less amounts of \(k_{\text{obs}}\) is electrochemical oxidation of 4-tert-butylicatechol 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-methylecatechol 2 mM, (III) 4-methylecatechol 2 mM, (IV) 2,3-dihydroxybenzoic acid 2 mM, (V) 3,4-dihydroxybenzoic acid 2 mM, (VI) 3-methoxycatechol 4 mM, (VII) 3-tert-butylandecatechol 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 mV s\(^{-1}\), respectively. T=25 ± 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.

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