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Electrochemical Characterization of Catechol-Dimethylamine Adduct at Different pH Values

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Abstract

Catechol, which underwent electrochemical oxidation to produce o-benzoquinone, as Michael acceptor, taking part in a nucleophilic attack by dimethylamine, has been studied in an aqueous solution, with various pH values, different electrodes and different dimethylamine concentrations, using cyclic voltammetry, controlled potential coulometry and differential pulse voltammetry. The participation of o-benzoquinone reaction with dimethylamine, at higher nucleophiles concentrations, in the second potential's scan, was observed. The products generated from the reaction were assumed to be 4-(dimethylamino)benzene-1,2-diol, which underwent electrons transfer at more negative potentials than those from catechol. Catechol pH effect, in dimethylamine presence, was studied by varying pH values from 3 to 9. The reaction was strongly influenced by pH, as well as by dimethylamine concentration. The reaction was mostly favorable in 150 mM of dimethylamine and 2 mM of catechol in a neutral medium. In both acidic and basic conditions, the reaction was not favored, due to amine protonation and hydroxylation. The reaction mechanism was of the ECE type, followed by the diffusion process.

Keywords: electro-oxidation, reaction condition, dimethylamine, catechol, cyclic voltammetry, differential pulse voltammetry and controlled potential coulometry.

Introduction

Catechol is one of the important building blocks in organic synthesis, and it is produced in industrial scales, as the precursor of pesticides, perfumes and pharmaceuticals [1]. The catechol skeleton also occurs in a variety of natural products, especially antioxidants [2]. The most well-known characteristic of catechol is that it can be easily oxidized, mainly due to its antioxidant activity and low oxidation potentials [3]. The oxidation products are the corresponding reactive and electron-deficient o-quinones. One of the most successful in situ generations of reactive o-quinones species is electrochemical oxidation [4].

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There are many reports on catechols electro-oxidation that produces o-quinones as reactive intermediates in many useful homogeneous reactions [5].
Dimethylamine is a precursor to several industrially significant compounds. It reacts with carbon disulfide to give dimethyldithiocarbamate, a precursor to a family of chemicals widely used in rubber vulcanization. Dimethylformamide and dimethylacetamide solvents are derived from dimethylamine. It is a raw material for the production of many agrichemicals and pharmaceuticals, such as dimefox and diphenhydramine, respectively. Tabun chemical weapon is derived from dimethylamine. Lauryl dimethylamine oxide surfactant is found in soaps and cleaning compounds. Unsymmetrical dimethylhydrazine, a rocket fuel, is prepared from dimethylamine [6-7].
Catechol electrochemical oxidation, in the presence of some other nucleophiles, such as methanol, aspartic acid, sulfanilic acid, glutamine, ethanol, 2-thiobarbituric acid, b-diketones, 4-hydroxy-6-methyl-2-pyrone, 2-thiouracil, dimedone, 4,7-dihydroxycoumarin, 4,5,7-trihydroxycoumarin, 4-hydroxy-6-bromocoumarin, 3-hydroxy coumarin, 4-hydroxy-6-methyl-a-pyrone, 4-hydroxy-6-methyl-2-pyridone and 4-hydroxycarbostyrile, has been studied [7–17]. A literature survey reveals that, although several papers have been published on catechols electrochemical oxidation, in the presence of secondary amines, and with the synthesis of quinones derivatives [7, 18-19], they only have studied catechol electro-catalytic effect with secondary amines, at a limited concentration. However, due to the great importance of these compounds in the pharmaceutical industry [20], and because of the increase in available data on catechol electro oxidation, in nucleophiles presence, we have investigated catechol electrochemical oxidation, in dimethylamine presence. In this paper, we have studied catechol electrochemical properties, in dimethylamine presence, with three different electrodes (Au, Gc and Pt), different dimethylamine concentrations (110-300 mM), pH values, and scan rates, using cyclic voltammetry (CV), differential pulse voltammetry (DPV), controlled potential coulometry (CPC) and chronoamperometry (CA) techniques.

Experimental section

Catechol, dimethylamine, acetic acid, sodium acetate, potassium chloride, sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate were of analytical grade (E-Merck). Catechol and catechol with dimethylamine solutions in different concentrations were prepared at different pH values, by using acetate or phosphate buffer solutions. Platinum and gold disks of 1.6 mm in diameter (BASi), and glassy carbon disks of 3 mm in diameter (BASi), were used as working electrode for voltammetry. The working electrode used in controlled potential coulometry was an assembly of three carbon rods (6 mm diameter and 4 cm length). The electrode surface was polished with 0.05 μm alumina before each run. The auxiliary electrode was a platinum coil (BASi). The reference electrode was an Ag|AgCl electrode (BASi). Materials could be adsorbed onto the working electrode surface, after each experiment. Then, the current response would degrade, and the electrode surface would need to be

cleaned. The working electrode surface was polished with 0.05 µm alumina before each run. A few drops of polish were placed on a polishing pad, and the electrode was vertically held, and polished by softly pressing the electrode against the polishing surface (0.05 µm alumina), for a period of 1-10 min, depending upon the electrode surface condition. The electrode was then thoroughly washed with deionized water. At this point, the electrode surface would look like a shiny mirror. The potentiostat/galvanostat was µStat 400 (DropSens, Spain). Nitrogen gas was bubbled from the one-compartment cell before the electrochemical run.

Results and discussion

Electrochemical behavior of catechol and dimethylamine

Catechol electrochemical properties were studied in the absence and presence of different dimethylamine concentrations, by cyclic voltammetry (CV), controlled potential coulometry (CPC) and differential pulse voltammetry (DPV). Fig. 1 (dashed line) represents the cyclic voltammogram of 2 mM catechol at the Gc electrode in a buffer solution of pH 7, and at a scan rate of 0.1 V/s. Catechol cyclic voltammogram indicates a pair of redox couple at 0.26 V/0.05 V, due to its inter conversion to o-quinone, and vice-versa. Pure dimethylamine is usually electrochemically inactive, having no redox peaks in the investigated potential range (Fig. 1, solid line). Fig. 1 (deep solid line) shows catechol's CV (2 mM) in dimethylamine presence (150 mM), in the second potential's scan, at the same conditions. In the second potential's scan, catechol with dimethylamine showed two anodic peaks at -0.1 V and 0.28 V, and a sharp cathodic peak at -0.18 V.

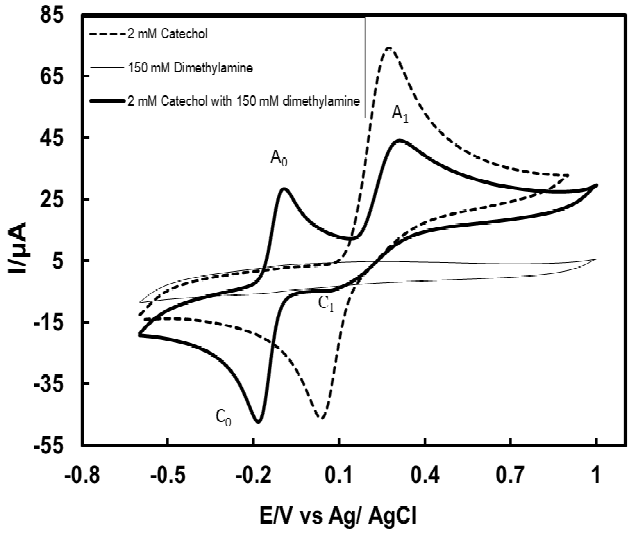
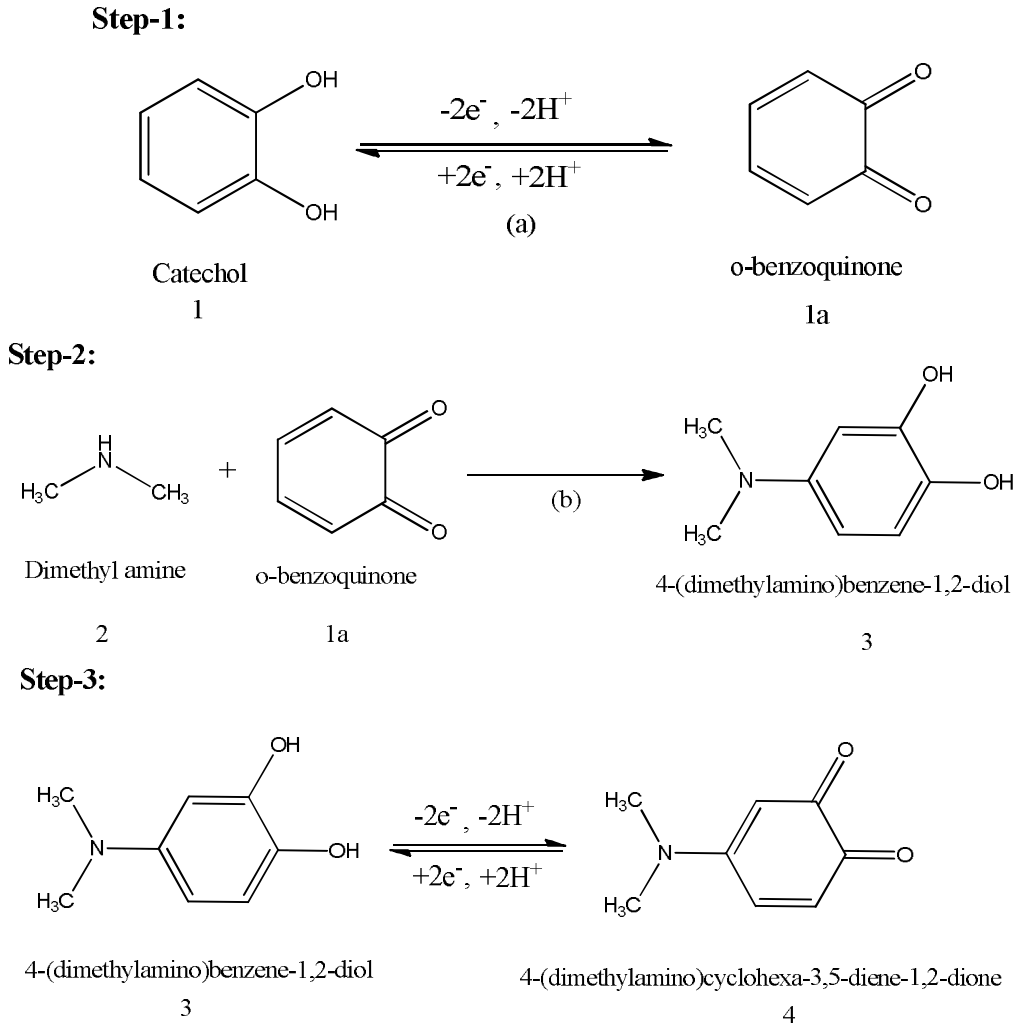


Figure 1. Cyclic voltammogram of 2 mM catechol, 150 mM dimethylamine and 2 mM catechol with 150 mM dimethylamine at Gc electrode in a buffer solution (pH 7), at a scan rate of 0.1 V/s (2nd cycle). A_0 and A_1 anodic peaks correspond to Co and C_1 cathodic peaks.

Upon dimethylamine addition to the catechol solution, A_1 and C_1 anodic and cathodic peaks gradually decreased, and new A_o and C_o anodic peaks appeared.

The newly appearance of A_o and C_o peaks, decreases in A_1 and C_1 peaks, and also shifting in the positions of A_1 and C_1 peaks, in dimethylamine presence, indicate that this was due to the follow up reaction of catechol with dimethylamine. This observation could be described by considering the nucleophilic attack of dimethylamine to o-benzoquinone. This attack reduced o-benzoquinone concentration in the reaction layer; simultaneously, A_1 and C_1 peaks were reduced, whereas, at the same time, the catechol-dimethylamine adduct was produced and, consequently, A_o and C_o peaks appeared at the low potential region. In the first potential's scan, the anodic catechol peak, in dimethylamine presence, was very similar to that of only catechol. But, in the second-potential's scan, A_1 peak current (deep solid line) significantly decreased compared to that of free catechol (dashed line). The peak current ratio for A_1 and C_1 (I_{pa1}/ I_{Pc1}) peaks noticeably decreased, which was indicative of a chemical reaction of dimethylamine (2) with o-quinone (1a) produced at the electrode surface. These observations may indicate the formation of 4-(dimethylamino)benzene-1,2-diol through a nucleophilic substitution reaction (Scheme 1).



Scheme 1.

If the constituent is such that the potential for the product oxidation is lower, then, further product oxidation is also lower, which is why further oxidation and addition may occur [21]. In catechol case, in dimethylamine presence, instead of o-benzoquinone, dimethylamine oxidation is easier than parent catechol oxidation. This behavior is in agreement with that reported by other research groups for similar electrochemically generated compounds, such as catechol and different nucleophiles [7-23]. In the absence of other nucleophiles, water or hydroxide ions often add to o-benzoquinone [24].

Fig. 2 (a) shows the CV of the second cycle of 2 mM catechol in the presence of 150 mM dimethylamine at Gc (3 mm) electrode in a buffer solution (pH 7), at different scan rates.

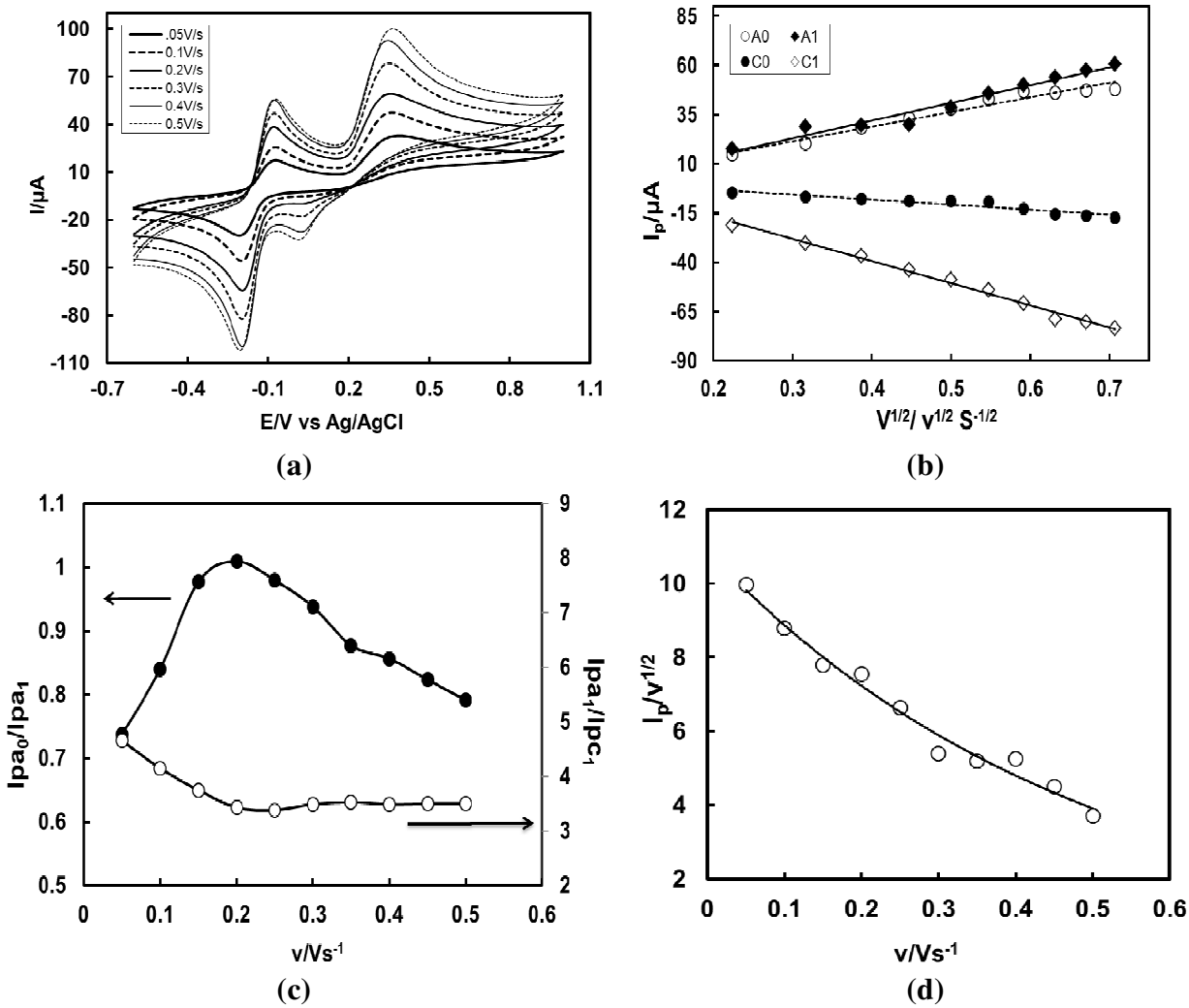


Figure 2. a) Cyclic voltammogram of 2 mM catechol with 150 mM dimethylamine in the second potential's scan at the Gc electrode in a buffer solution (pH 7), at a scan rate of 0.05 V/s-0.5 V/s. **b)** Plots of the peak current vs. the square root of the scan rate in the same condition. The legend shows the symbols of oxidation and reduction peaks. **c)** Variation of the peak current ratio of the corresponding peak (I_{pa1}/I_{pc1}) and anodic peak (I_{pa0}/I_{pa1}) vs. the scan rate in the same condition. **d)** Variation of the peak current function ($I_p/v^{1/2}$) versus the scan rate in the same condition.

The peak currents of both anodic and cathodic peaks gradually increased with the increase in the scan rates from 0.05 V/s to 0.5 V/s. By varying the scan rates, it can be seen that the cathodic peaks were shifted towards left, while the anodic peaks went towards right. Fig. 2 (b) shows plots of the anodic and cathodic net peak currents of 2 mM catechol with 150 mM dimethylamine, for the second cycle, against the square-root of the scan rates, where the net current means that the second peak was subtracted from the first one by the scan-stopped method [7]. Although the peak current proportionally increased with the increasing square root of scan rates, the line did not pass through the origin, so, the peak current of the reactant at each redox reaction was not purely controlled by the diffusion process; i.e., during the reaction, some surface related chemical complications occurred. At the scan rate of 0.05 V/s, the cathodic peak for o-benzoquinone reduction almost disappeared, as shown in Fig. 2a. By increasing the scan rate, the cathodic peak for o-benzoquinone reduction began to appear and increase. The corresponding peak current ratio (I_{pa1}/I_{pc1}) vs. scan rate, for a mixture of catechol and dimethylamine, firstly decreased with an increasing scan rate, and then, after 0.2 V/s, it was almost unchanged (Fig. 2c). The anodic peak current ratio (I_{pa0}/I_{pa1}) vs. scan rate, for a mixture of catechol and dimethylamine, firstly increased, and then, at 0.2 V/s, the scan rate remained constant, and it decreased above 0.2 V/s (Fig. 2c). On the other hand, the value of the current function ($I_p/v^{1/2}$) was found to decrease with an increasing scan rate (Fig. 2d).

The exponential nature of the current function versus the scan rate plot indicates the ECE mechanism for the electrode process [12]. This confirms o-benzoquinone (1a) reactivity towards dimethylamine (2), which firstly increased at a slow scan rate, and then, at a higher scan rate, it decreased. This behavior is in agreement with that reported by other research groups for similar electrochemically generated compounds, such as catechol and different nucleophiles [8, 15, 24].

The existence of a subsequent chemical reaction between o-benzoquinone 1a and dimethylamine 2 is supported by the following evidence.

(i) In dimethylamine presence, both I_{pa1} and I_{pc1} decreased during the second cycle (Fig. 1); this could be indicative of the fact that electrochemically generated o-benzoquinone (1a) is partially removed by the chemical reaction with dimethylamine (2).

(ii) The corresponding peak current ratio (I_{pa1}/I_{pc1}) varies with the potential sweep rate. For lower sweep rates, the peak current ratio (I_{pa1}/I_{pc1}) is lower than one, and increases with a decreasing sweep rate. This is indicative of a departure from the intermediate, and of an arrival to the diffusion region, with an increasing sweep rate [7].

(iii) An increase in the scan rate causes a decrease in the progress of the chemical reaction of 1a with 2, during the period of the cyclic voltammogram recording and, therefore, a decrease in the peak current ratio (I_{pa0}/I_{pa1}), at a higher scan rate.

(iv) The current function, $I_p/v^{1/2}$ for A_1, was found to exponentially decrease with an increasing scan rate. This indicates that the reaction mechanism of the system was of the ECE type (Scheme 1).

According to the results, it seems that the 1,4-Michael addition reaction of dimethylamine (2) to o-benzoquinone (1a) led to product 3. The oxidation of this compound (3) is easier than the oxidation of the parent molecule (1), by virtue of the electron donating amine group presence.
Pure catechol CV in a buffer solution (pH 7), at different scan rates, was also observed. The proportionality of the anodic and cathodic peak currents against the square-root of the scan rates suggests that the peak current of the reactant at each redox reaction was also controlled by the diffusion process.

Influence of pH

In the presence of 150 mM of dimethylamine, cyclic voltammogram of 2 mM catechol at Gc electrode was studied at different pH values ranging from pH 3 to pH 9 (Fig. 3a).
The electrochemical reaction of catechol occurring at pH below 7 is a two-proton, two-electron transfer process (Scheme 1), which was reported by research groups for catechol and its derivatives [22-23]. Accordingly to the electrochemical nature of catechol, in the presence of 150 mM dimethylamine at different pH values (3, 5, 7 and 9), it can be seen that a new A_0 anodic peak appeared after repetitive cycling, and that the A_1 peak started to shift at a lower potential, while pH increased. A small peak current of the catechol-dimethyl adduct at acidic media could be due to the inactivation of the amine group by protonation. In the basic medium, catechol cyclic voltammogram also showed a new peak, but the peak current intensity was lower. It was thus suggested that catechol oxidation was followed by an irreversible chemical reaction with hydroxyl ion, especially in alkaline solutions [23]. However, amines in this condition can also act as nucleophiles. The peak position of the redox couple was found to be dependent upon pH. Among these, we observed the maximum peak current at pH 7, at which o-benzoquinone was most favorable for the nucleophilic attack by the amine group.
Fig. 3 (b) reveals the plot of oxidation peak potential ($E_{p)}$ values against pH. The plot's slopes were graphically determined as the anodic peaks (26.4 mV/pH for A_0 appeared peak) at 0.1 V/s, which is close to the theoretical value of 30 mV/pH for the two-electron, two-proton transfer process. These values indicate that the catechol-dimethylamine adducts oxidation was preceded by the $2e^-/2H^+$ processes (Scheme 1). This also suggested that, during the reaction, not only electrons but also protons were released from the catechol-dimethylamine adduct. Similar behavior for catechol and its derivatives was also reported [25-26]. In both acidic and basic conditions, the peak current intensity of the A_0/C_0 redox couple was very small, whereas, in the neutral medium, a sharp peak was observed. This could be related to amine protonation and hydroxylation, and to its inactivation towards Michael addition reaction with o-benzoquinone (2a). This suggests that the coupling reaction rate is pH dependent, and enhanced by a neutral medium. The peak current of the redox couple was also found to be dependent upon pH. Fig. 3 (c) shows the plot of the oxidation peak (A_0) current ($I_{p)}$ against the solution's pH. From Fig. 3(c), it is seen that the maximum peak current was obtained at pH 7. At this pH, the difference between the peak current

ratio (I_{pa1}/I_{pc1}), in dimethylamine presence and absence, is maximum. Consequently, in this study, a buffer solution of pH 7 has been selected as a suitable medium for catechol electrochemical study, in dimethylamine presence. This can be ascribed to the fact that catechol electrochemical oxidation, in dimethylamine presence, is facilitated by a neutral media and, hence, the electron transfer rate is faster.

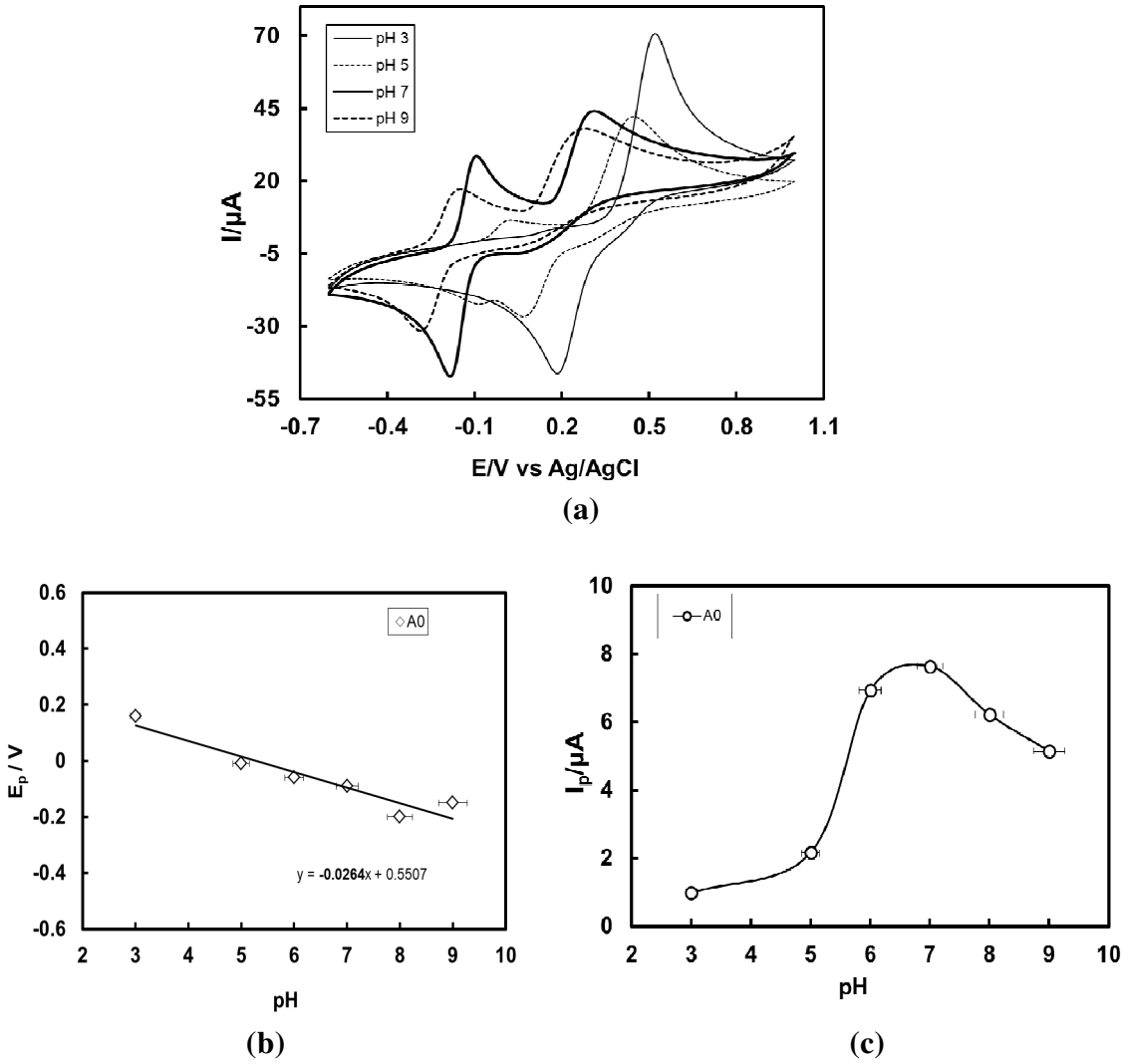


Figure 3. a) Cyclic voltammogram of 2 mM catechol with 150 mM dimethylamine at Gc electrode with different pH values (3, 5, 7 and 9), at a scan rate of 0.1 V/s. **b)** Plots of the peak potential vs. pH in the same condition. **c)** Plots of the peak current vs. pH in the same condition. The meaning of the A_0 symbol is similar to that of Fig. 1.

Concentration effect of dimethylamine

Fig. 4 (a) shows the effect of different dimethylamine (110, 130, 150, 170 and 300 mM) concentrations on fixed catechol concentrations (2 mM) at Gc electrode with pH 7, and at a scan rate of 0.1 V/s. A new peak appeared at -0.11 V, and the anodic peaks positively shifted upon dimethylamine addition, which suggests the formation of catechol-dimethylamine adduct. It can be seen that the net current intensity of the newly appeared anodic peak increases with the increase in dimethylamine composition up to 150 mM. After further addition of

dimethylamine (>150 mM), the anodic and cathodic peak currents slightly decreased (Fig. 4b). Catechol nucleophilic substitution reaction in dimethylamine presence was maximum favorable up to 150 mM of dimethylamine, at pH 7. The corresponding peak current ratio varied with dimethylamine concentration. This phenomenon was related to the increase in the homogenous reaction rate of the following chemical reaction between o-benzoquinone 1a and dimethylamine 2, with increasing dimethylamine concentrations up to 150 mM. At higher dimethylamine concentrations (>150 mM), the excess electro-inactive dimethylamine could be deposited on the electrode surface and, consequently, the peak current decreased.

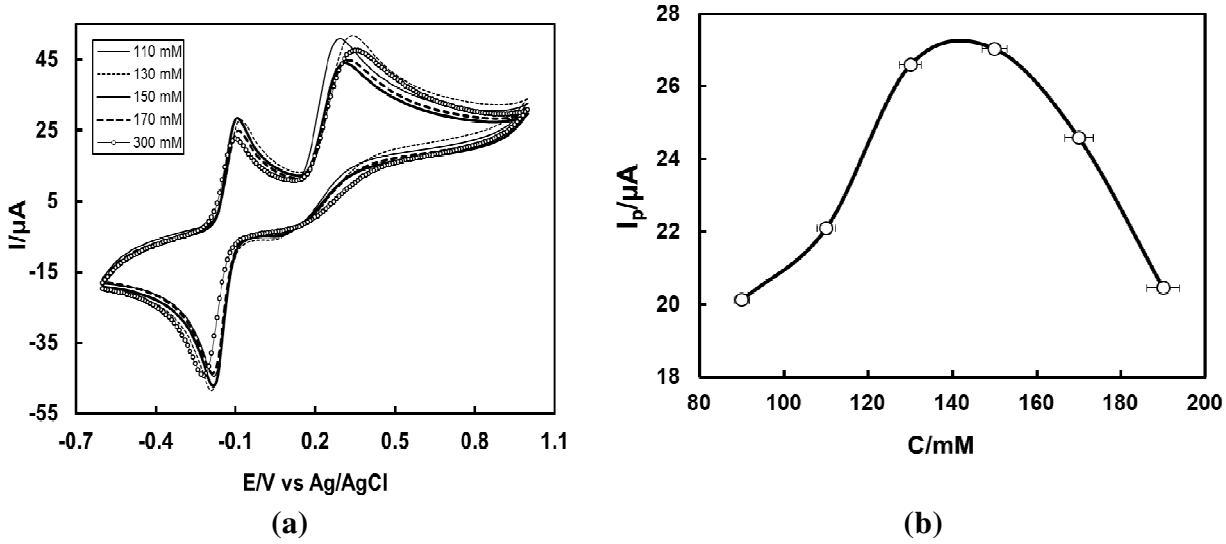


Figure 4. a) CV of dimethylamine changes in composition (110, 130, 150 and 170 mM) with fixed 2 mM catechol at Gc electrode with pH 7, and at a scan rate of 0.1 V/s. **b)** Plots of the anodic peak current (Ip) vs. dimethylamine concentrations (90, 110, 130, 150, 170 and 190 mM) with (fixed 2 mM catechol) in the same conditions. The meaning of A_0 is similar to that from Fig. 1.

Effect of electrode materials

Catechol electrochemical properties in dimethylamine absence and presence were examined by different electrodes, such as Gc, Au and Pt, at different pH values. The CV and DPV of 2 mM catechol with 150 mM dimethylamine, at Gc, Au and Pt electrodes, are shown in Fig. 5.

The nature of voltammograms, the peak position and current intensity of the studied systems are different for different electrodes, although the diameter of Gc electrode (3 mm) is higher than those of Au and Pt (1.6 mm) (Fig. 5a). The CV nature at Au electrode is slightly different from those of Gc and Pt electrodes. Au electrode shows two anodic and three cathodic peaks for the second scan. Gc electrode shows two anodic and two cathodic peaks for the second potential's scan, whereas Pt electrode shows two anodic and corresponding cathodic peaks. Voltammetric measurements, performed at Au electrode, in the buffer solution without catechol and dimethylamine, with pH 7, showed a reduction peak at 0.5 V, to the formation of Au(III) hydroxide. Similar behavior of Au electrode oxidation at different pH values has been reported [27]. In the case of Gc and Pt

electrodes, for the second potential's cycle, a new oxidation and reduction peak appeared at the lower oxidation potential, which can be attributed to the oxidation of the adduct formed between o-benzoquinone and dimethylamine.

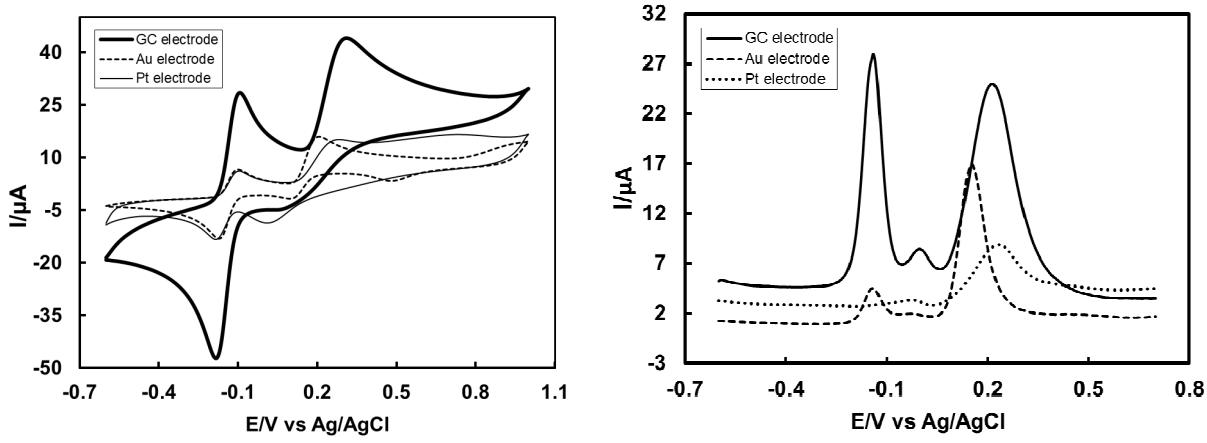


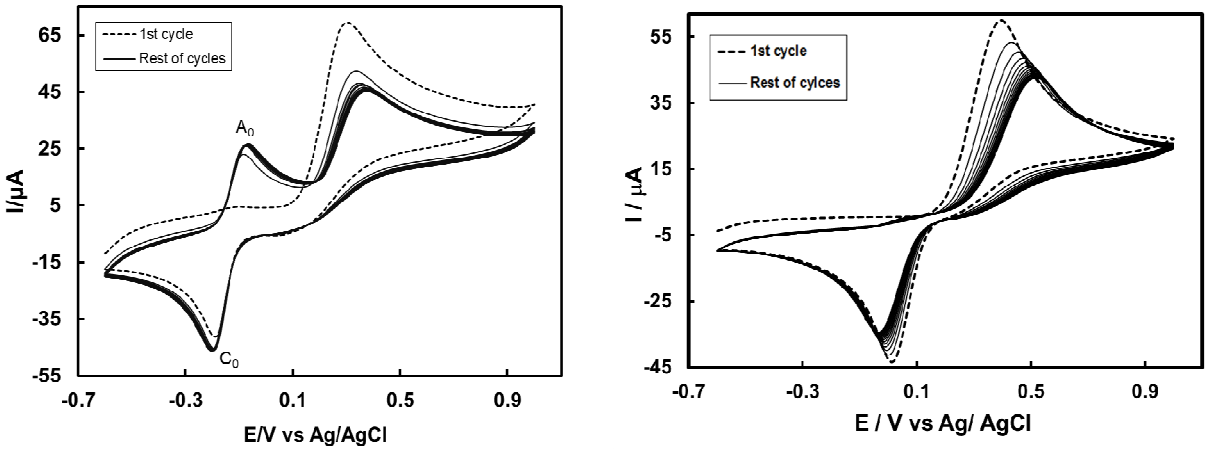
Figure 5. a) Cyclic voltammogram (CV). **b)** Differential pulse voltammogram (DPV) of 2 mM catechol with 150 mM dimethylamine at Gc electrode (3.0 mm), gold electrode (1.6 mm) and platinum electrode (1.6 mm), with pH 7, and at a scan rate of 0.1 V/s.

Fig. 5(b) shows better voltammetric response and extremely sharp adduct peak at -0.145 V, -0.025 V and 0.2 V. Catechol electrochemical properties with dimethylamine, for example, changes in pH, concentration, scan rate, etc., were studied in detail using Pt and Au electrodes. But, among the electrodes, the voltammetric response of Gc electrode was better than that of Pt and Au electrodes in the studied systems.

Subsequent cycles of catechol-dimethylamine CV

Fig. 6 (a) shows the cyclic voltammogram of the first 15 cycles of 2 mM catechol with 150 mM dimethylamine at Gc electrode, in a buffer solution with pH 7, for the potential range from -0.6 V to 1.0 V, at Gc electrode. The voltammogram at the 0.1 Vs^{-1} scan rate has one anodic peak at 0.28 V, and one cathodic peak at 0.18 V, when considered the first scan (dashed line). In the subsequent potential cycles, a new anodic peak appeared at ~ -0.08 V, and the intensity of the first anodic peak current progressively increased on cycling, but the second anodic peak current decreased, and positively shifted on cycling. This can be attributed to catechol-dimethylamine adduct production through the nucleophilic substitution reaction in the electrode surface (Scheme 1). The successive decrease in the height of the catechol oxidation and reduction peaks with cycling can be ascribed to the fact that the concentrations of the catechol-dimethylamine adduct formation increased by cycling, leading to the decrease in catechol or quinone concentrations at the electrode surface. The positive shift in the second anodic peak, in dimethylamine presence, is probably due to the formation of a thin product film at the electrode surface, inhibiting, to a certain extent, the electrode process performance. Along with the increase in the number of

potential cycles, the first anodic peak current increased up to 10 cycles and, then, the peak current was almost unchanged with subsequent cycles. This may be due to the blockage of the electrode surface by the newly formed electro-inactive species, after more cycling.



(a) **(b)**

Figure 6. **a)** CV of 150 mM dimethylamine with 2 mM catechol at Gc electrode in the buffer solution with pH 7 at the scan rate of 0.1 V/s (15 cycles). The appeared anodic peak current (A_0) and cathodic peak current (C_0) increased with the iteration scan from the first cycle. **b)** CV of 2 mM catechol in the buffer solution with pH 7 at the scan rate of 0.1 Vs^{-1} (15 cycles). For **(a)** and **(b)**, the first cycle is represented by the dashed line, and the rest of the cycles by the solid line.

Fig. 6 (b) shows the CV of the first 15 cycles of 2 mM catechol in a pH 7 buffer solution, at Gc electrode. The voltammogram at the 0.1 Vs^{-1} scan rate has one anodic peak at 0.38 V, and a cathodic peak at 0.03 V (dashed line). In the subsequent potential cycles, no new anodic peak appeared. This may be because catechol showed one anodic and corresponding cathodic peak related to its transformation to o-quinone (Scheme 1). During the repetitive potential's cycling, the anodic and cathodic peak current ratios are nearly unity (Fig. 6b); that can be considered as a criterion for the stability of o-quinone produced at the electrode surface [24], which is too slow. In other words, any hydroxylation [28-31] or dimerization [26, 30] reactions that are too slow can be observed in the time-scale of cyclic voltammetry [24]. A new reduction peak appeared at -0.19 V after the addition of 150 mM dimethylamine to the solution, at the first cycle (Fig. 6a). Conversely, the reduction peak's shift, due to catechol species, has diminished by dimethylamine addition. In the second-potential's scan (Fig. 6a), a new oxidation peak also appeared at -0.08 V, which can be attributed to the oxidation of the adduct formed between o-benzoquinone and dimethylamine, according to Scheme 1.

Controlled-potential coulometry was performed in an aqueous solution containing 1 mM of catechol and 75 mM of dimethylamine at 0.45 V, with pH 7. The electrolysis progress was monitored by CV (after 30 min of interval) (Fig. 7). As Fig. 7 shows, during the course of coulometry, A_0 and C_0 peaks appeared, and the height of the A_0 peak proportionally increased with the advancement of

coulometry, parallel to the decrease in height of the A_1 anodic peak. All anodic and cathodic peaks disappeared after the consumption of 4 electrons per catechol.

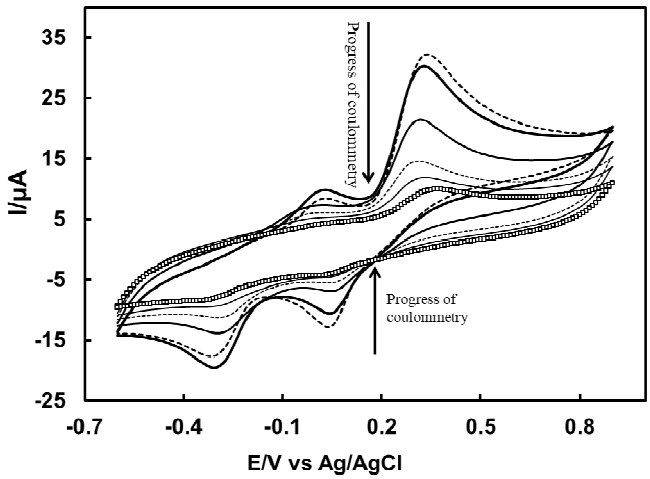


Figure 7. Cyclic voltammogram of 1 mM catechol in the presence of 75 mM dimethylamine at Gc electrode, during controlled potential coulometry (monitoring with 30 min of interval) at 0.50 V, with pH 7, at the scan rate of 0.1 V/s.

These observations allow us to propose the pathway in Scheme 1 for catechol electro-oxidation (1), in dimethylamine presence (2). According to our results, it seems that the 1,4 addition reaction of 2 to o-quinone (1a) (reaction (2)) is faster than other secondary reactions, leading to the 3 intermediate. The oxidation of this compound (3) is easier than the oxidation of the parent starting molecule (1), by virtue of the electron-donating group presence. Like o-quinone 1a, o-quinone 4 can also be attacked from the C-5 position by dimethylamine (2). However, no over reaction was observed during the voltammetric experiments, because of the low activity of the o-quinone 4 towards 1,4-(Michael) addition reaction with dimethylamine (2).

Differential pulse voltammetry (DPV)

DPV technique was employed to make the catechol-dimethylamine substitution reaction clearer. DPV obtained for 2 mM catechol in the presence of 150 mM dimethylamine, in the second scan, with different pH values (3-9), was shown in Fig. 8. In the buffer solution, with pH 7 and pH 9, catechol gave a well-developed wave in dimethylamine presence (Fig. 8). At pH 7, the first, second and third anodic peaks were showed at ~ -0.14 V, -0.02 and 0.2 V, respectively. But, at pH 3 and pH 5, the second potential's scan of the first anodic peak current intensity was very small. As it can be seen, two completely separated anodic peaks with high current intensity are observed at pH 7, which can be attributed to the oxidation of o-benzoquinone - dimethylamine new compound and o-benzoquinone, respectively.

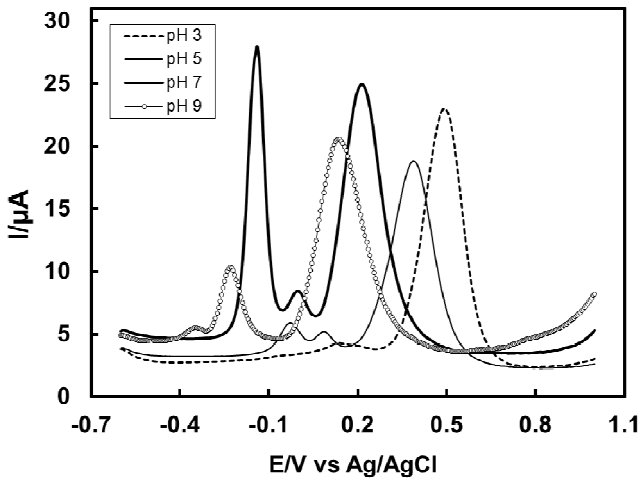


Figure 8. Differential pulse voltammogram (DPV) of 2 mM catechol with 150 mM dimethylamine, at Gc electrode, in the second scan, with different pH values (3, 5, 7 and 9), and at the scan rate of 0.1 V/s.

Fig. 9 shows the DPV of the deposition time change (0, 10, 30, 90, 120 and 150 s) of 2 mM catechol with 150 mM dimethylamine, with pH 7. From this figure, it is seen that the increase in the deposition time, from 0 to 30 s, led to the development of a new peak at -0.145 V. When the deposition time increased 30 s, more nucleophilic attacks occurred and, consequently, more catechol-dimethylamine adducts led to a decrease in o-benzoquinone concentration, and an increase in the catechol-dimethylamine adduct concentration at the electrode surface. At further increase in the deposition time, from 30 s to 150 s, the first anodic peak current decreased and the second anodic peak current decreased.

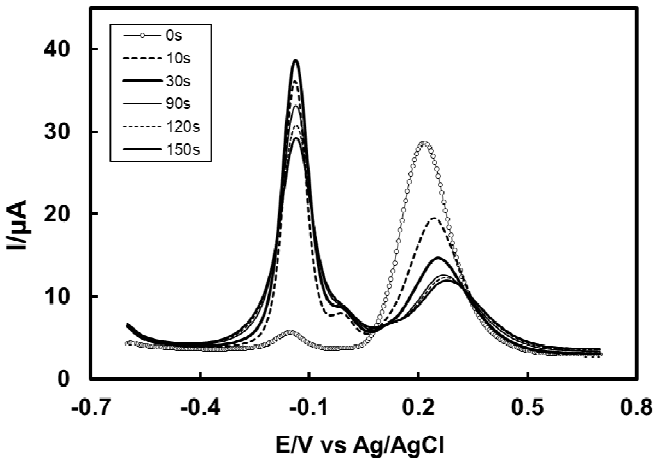


Figure 9. Differential pulse voltammogram (DPV) of the deposition time change (0, 10, 30, 90, 120 and 150 s) of 2 mM catechol with 150 mM dimethylamine with pH7, at *E*puls 0.02 V, tpuls 20 ms, and at a scan rate of 0.1 Vs^{-1}.

The effect of dimethylamine concentration on the differential pulse voltammogram of catechol was studied. Fig. 10 shows DPV for 2 mM of the catechol solution containing the buffer (pH 7), in the presence of various dimethylamine concentrations, from 110 to 300 mM, at the Gc electrode surface.

As indicated in this figure, two separated anodic peaks appeared again after dimethylamine addition into catechol, similar to what is shown in Fig. 8. In this case, the increase in dimethylamine concentration, from 110 mM to 150 mM, led to an increase in the first anodic peak current. At further increase in concentrations from >150 mM, the first and second anodic peak current gradually decreased. At lower dimethylamine (<110 mM) concentrations, the nucleophilic substitution reaction took place in a comparable degree, whereas an increase in dimethylamine concentration (150 mM) promoted the nucleophilic attack of dimethylamine towards o-benzoquinone generated at the electrode surface. At further dimethylamine (>150 mM) addition into the catechol solution, the excess electro-inactive dimethylamine was deposited on the electrode surface and, hence, the peak current decreased.

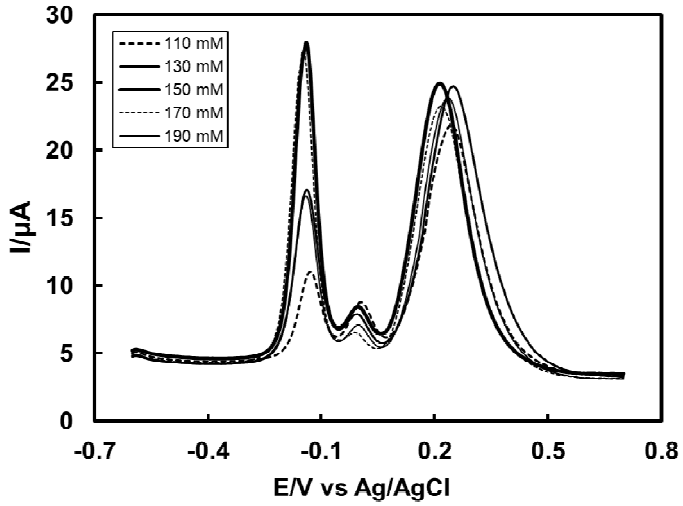


Figure 10. DPV of the composition change in dimethylamine (110, 130, 150, 170 and 190 mM) with the fixed composition of 2 mM catechol in the second scan, with pH 7, at *E*puls 0.02 V, tpuls 20 ms of Gc electrode, and at a scan rate of 0.1 Vs^{-1}.

In this study, comparatively, high dimethylamine concentrations (110-300 mM) were sequentially used to determine the optimum condition for the nucleophilic substitution reaction of catechol with dimethylamine. As the reaction occurred at high nucleophiles concentrations, the voltammetric peaks (CV and DPV) for the adduct noticeably appeared.

Spectral analysis of catechol with dimethylamine

The FTIR spectrum of the catechol-dimethylamine adduct vibrational modes has been shown in Fig. 11. The catechol-dimethylamine adduct shows a broad spectrum at 3450 cm^{-1}, due to the O-H band, whereas dimethylamine N-H stretching sharp band, at 3302 cm^{-1}, is absent. This indicates that –NH proton was replaced by the phenyl group, forming catechol-dimethylamine adduct. The peaks at 2906 cm^{-1} are characteristic of the C-H aromatic nuclei stretching vibration. In the catechol-dimethylamine adduct case, there is a more significant change in the finger print region than that with only catechol, and only dimethylamine.

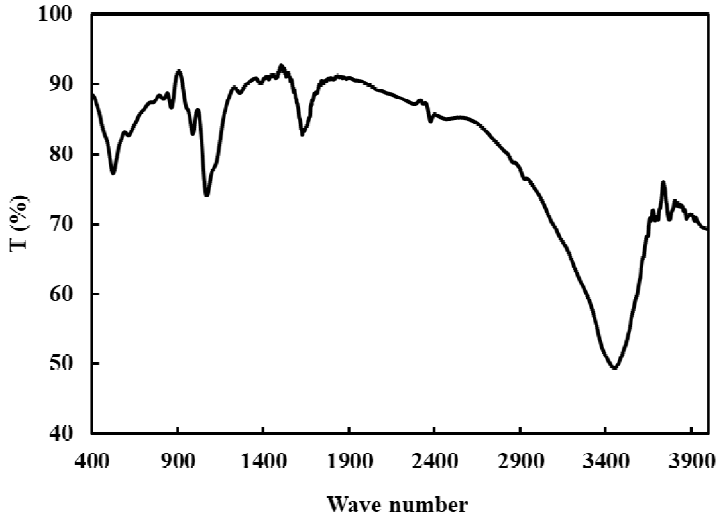


Figure 11. FTIR spectra of the catechol-dimethylamine adduct.

From the study, it is seen that dimethylamine properly functions as a nucleophile at pH 7. When the pH is below 7, the nucleophilic activity of dimethylamine reduces, due to amine protonation. When the pH value is above 7, other nucleophiles, such as –OH, are produced in the solution, therefore, amines activity decreases, and catechol oxidation is followed by an irreversible chemical reaction with hydroxyl ion [32].

Therefore, from the above discussion, it is clear that the nucleophilic substitution reaction of catechol in dimethylamine presence is most favorable at 150 mM of dimethylamine, and at pH 7, which is consistent with both CV and DPV. All above observations can be attributed to the reaction between dimethylamine and o-benzoquinone species produced at the electrode surface, with the new anodic peak being attributed to the oxidation of the newly formed o-benzoquinone-dimethylamine adduct.

Conclusions

Catechol electrochemical behavior, in dimethylamine absence and presence, was investigated by cyclic voltammetry, controlled potential coulometry and differential pulse voltammetry. Catechol anodic oxidation, which resulted in o-benzoquinone, was attacked by dimethylamine. The reaction products were transferred electrons at more negative potentials than those from catechol. The peak current of catechol- dimethylamine adduct at each redox reaction was controlled by the diffusion process. Catechol nucleophilic substitution reaction, in dimethylamine presence, was most favorable at 150 mM of dimethylamine, and at Gc electrode with pH 7. In this condition, it can be deduced that dimethylamine nucleophilic addition occurred through an ECE mechanism.

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