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Poly(o-toluidine) Modified Platinum Electrode As an Electrocatalyst for Benzyl Alcohol Oxidation in Acid Media

Mohamed EL-Deeb[1,2,*] *and Hamed Alshammari*[1]

[1] Chemistry Department, Faculty of Science, Ha'il University, 81451 Hail, P.O. Box 2440, KSA
[2] Chemistry Department, Faculty of Science, Beni-Suef University, 62514 Beni-Suef, Egypt
[*]E-mail: eldeebm@yahoo.com

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The heterogeneous electrocatalytic behavior of poly (o-toluidine) modified platinum electrode (Pt/o-CH_3) towards benzyl alcohol oxidation in acid medium is investigated using a cyclic voltammetry technique under different experimental conditions. Electrode modification is carried out by the electrodeposition of poly (o-toluidine) films on platinum surface and the obtained films are characterized using FTIR and UV-visible spectroscopy as well as the mechanism of the electrodeposition process is discussed. Data shows that, the oxidation potential of benzyl alcohol at modifying electrode (Pt/o-CH_3) is shifted to more negative value compared with that at the platinum electrode (Pt) under the same conditions and the anodic current densities of the electrooxidation process enhances with increasing the monomer and alcohol concentrations. The electrocatalytic activity of the modified electrode can be explained as a result of the synergistic effects of the conducting polymer film coated platinum surface. Also, the electrooxidation process at modified electrode is described partially by a diffusion-controlled process

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Keywords: Electrooxidation, Electrodeposition, Polymer Modified Electrode, Benzyl Alcohol, Cyclic Voltammetry, spectroscopic characterization.

1. INTRODUCTION

The selective electrocatalytic oxidation of small organic molecules such as methanol, ethanol and benzyl alcohol to corresponding carbonyl compound is one of the most important reactions in drugs, dyes and fine chemicals as well as the potential fuel reactions in fuel cells [1-4]. Selective oxidation of benzyl alcohol to benzaldhyde is considered as a one of the most important alcohol oxidation because the product serves as the multilateral intermediates in synthetic chemical industries used in flavors, manufacture of pharmaceuticals, pesticides, dyes, perfumes and flavoring agents [5,6]

The oxidation of alcohol is traditionally occurred using transition metal oxidants such as $Cr_2O_7^{2-}$, MnO_4^- [7], but these oxidants produce equivalent metal wastes and cause some environmental pollutions as well as the oxidation reactions are carried out in halogenated organic solvents that be considered as an environmental unfriendly [8,9]. Therefore, from the economic and environmental point of view, developing green, selective and efficient catalysts for the chemical and electrochemical oxidation of benzyl alcohol are particularly interesting [10-13].

Preparation of conducting polymers is an interesting field of scientific and industrial research because of their many potential applications [14-18]. The applications of the conducting polymers as a support for the selective electrocatalytic process subject of numerous investigations, being polyaniline and polypyrrole particularly attractive host media [19]. A thin layer of a conducting polymer electrodeposited onto the surface of the substrate electrode (platinum, graphite, glassy carbon and other substrate) is able to enhance the kinetics of electrode processes of some solution species, these electrocatalytic processes occurred at conducting polymer electrodes present a fast growing area of investigation.

Lu et. al. [20] studied the effect of modified PPy-TEMPO electrode on the electrooxidation of benzyl alcohol in $NaClO_4$-CH_3CN solution using cyclic voltammetry and in situ FTIR techniques. Results show that PPy-TEMPO modified electrode exhibits high electrocatalytic activity towards benzyl alcohol oxidation in the presence of 2,6-lutidine as compared with the platinum electrode under the similar conditions.

Electrodeposition of PPyATEMPO on platinum electrode was carried out from PyATEMPO/$NaClO_4$/CH_3CN solution using cyclic Voltammetry technique [21]. Modified Pt/PPyATEMPO electrode showed high electrocatalytic activity for benzyl alcohol oxidation in the presence of Lewis base which improve the rate of benzyl alcohol oxidation to benzaldhyde.

The goal of the present work is to electrodeposition of poly(o-toluidine) films on platinum electrode using cyclic voltammetry technique as well as investigate the electrocatalytic activity of poly(o-toluidine) modified platinum electrode towards benzyl alcohol electrooxidation under some experimental conditions.

2. EXPERIMENTAL

2.1. Materials

Benzyl alcohol (98%), o-toluidine, sulphuric acid, methanol, acetone and chloroform are obtained from Merck Chemical Co., (Germany) and a platinum working electrode (area = 1.0 cm^2) is supplied from Metron Co., prior to each experiment, the working electrode is polished, rinsed with acetone and finally washed with deionized water (18.2 µs) that be used to prepare all solutions.

2.2. Electrochemical Measurements:

Electrochemical measurements are performed on standard three-electrode glass cell with platinum as working and counter electrodes while a Ag/AgCl electrode as a reference electrode.

Electrochemical measurements are performed using the Potentiostat / Galvanostat (AUTOLAB PGSTAT 128N) supplied from Metrohm Autolab and NOVA 1.10 software is used for recording and fitting the obtained data.

2.3. Spectroscopic Characterization:

Infrared and UV-Visible spectroscopic analysis of o-toluidine monomer and the as-deposited polymer film are measured using Thermo Nicolet 6700 FTIR Spectrometer and Thermo Scientific^{TM} Evolution 300 UV-Vis Spectrophotometer respectively at room temperature.

3. RESULTS AND DISCUSSIONS

3.1. Modification of a platinum electrode:

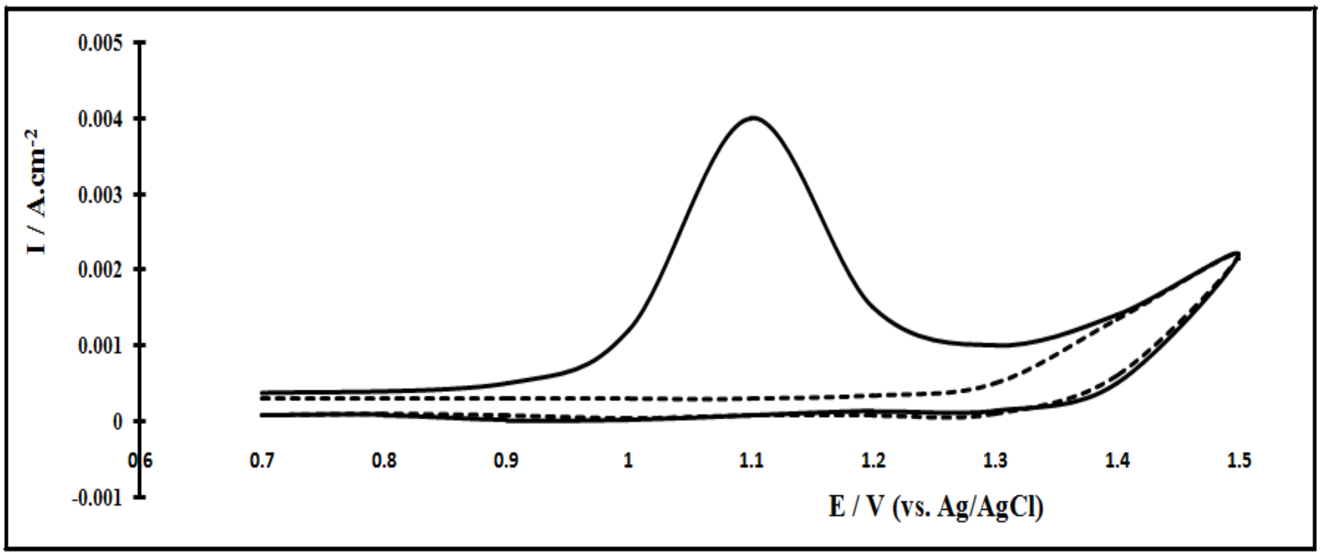
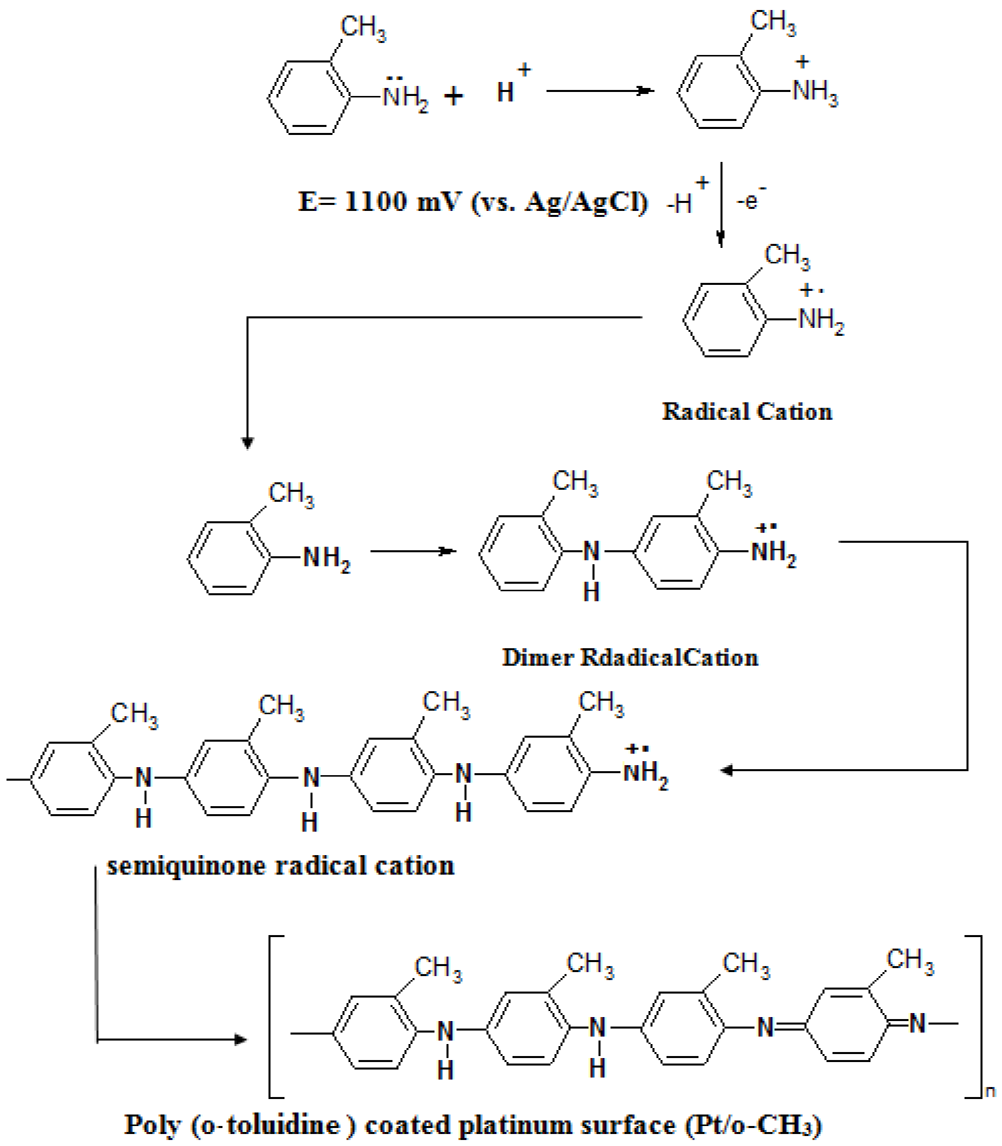


Figure 1. Cyclic voltammograms of aqueous solution (5 : 95 v/v Methanol : H_2O) containing 0.5 M sulphuric acid in the absence (dashed line) and presence (solid line) of 0.03 M o-toluidine monomer at 25 ^oC with scan rate of 100 mV.s^{-1}

Poly (o-toluidine) modified platinum electrode is carried out through the electrodeposition of poly (o-toluidine) film on a platinum surface from aqueous solution (5 : 95 v/v Methanol : H_2O) containing 0.5 M sulphuric acid and 0.03 M o-toluidine monomer using cyclic voltammetry technique at a potential between 700 and 1500 mV (vs. Ag/AgCl) with a scan rate of 100 mVs^{-1} at 25 ^oC and the data are graphically represented in Figure (1). The obtained data clearly shows that, the basic curve (dashed line) doesn't contain any oxidation or reduction peaks in the studied potential range while in the presence of 0.03 M monomers (solid line), a distinct anodic peak in the anodic excursion at 1100 mV (vs. Ag/AgCl) is obtained as a result of the oxidation of o-toluidine monomer and the formation of well-adhering, homogeneous brown poly (o-toluidine) film deposited on the platinum surface.

3.1.1. Mechanism of the electropolymerization process:



Scheme 1.

Electrodeposition of poly (o-touilidine) film on platinum surface is formed electrochemically through the anodic oxidative electropolymerization of o-touilidine monomer to radical cation that interact with another monomer molecule to form dimer radical cation which is followed by a further reaction with a monomer molecules to give a trimmer radical cation and finally the semiquinone radical cation that be transformed to the quinone imine structure as shown in Scheme (1). The suggested mechanism of the electrodeposition process and the structure of the as-deposited polymer film are acceptable in our previous works [22 – 26].

3.1.2. Characterization of the as-deposited poly(o-toluidine):

In order to confirm the structure of the as-deposited poly (o-toluidine) film on a platinum surface, infrared spectra for o-toluidine monomer and the as-deposited polymer film are shown in Figure (2). From the Figure, the characteristic peak at 756 cm^{-1} for 1,2-disubstituted benzene ring in case of monomer is disappeared and appears as two peaks at 867 and 1694 cm^{-1} for 1,2,4-trisubstituted benzene ring in polymer spectrum. The absorption band appears at 1374 cm^{-1} in case of polymer (disappears in the case of monomer) is assigned to the stretching vibration of C=N in a quinoide structure [27].

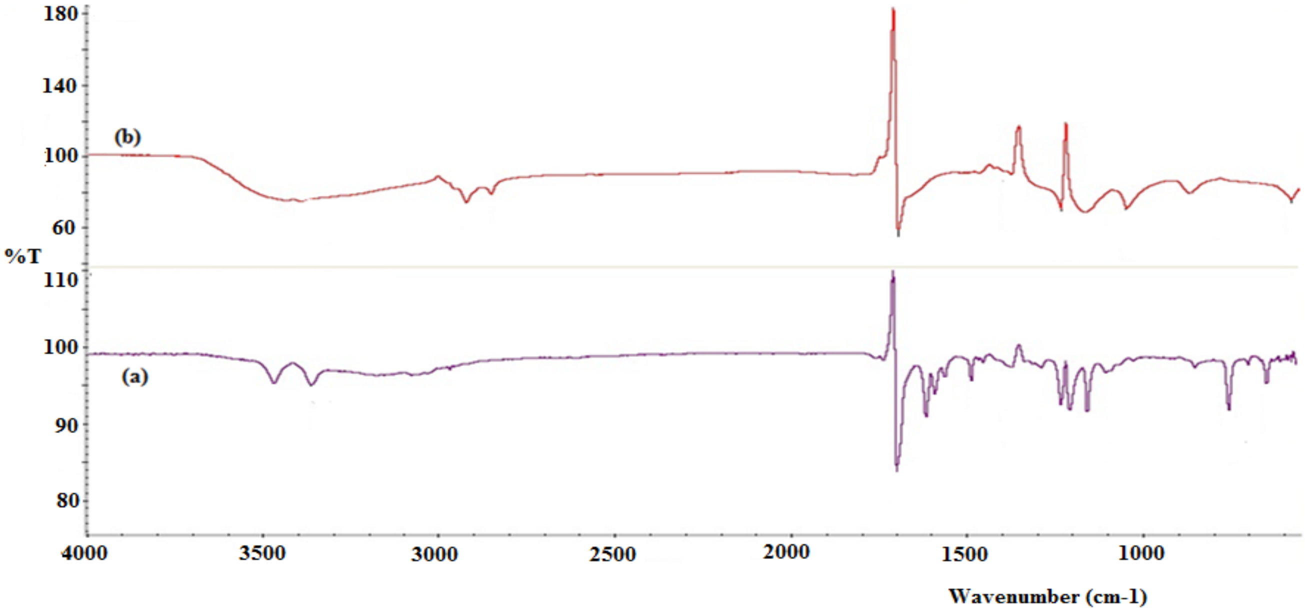


Figure 2. FTIR spectrum of (a) o-toluidine monomer and (b) its polymer

Data obtained from the UV-visible spectra of the monomer and the as-deposited polymer film clearly shows that, in case of monomer, one absorption band observed at λ_{max} = 273 nm while showing a bathochromic shift at λ_{max} = 331 nm in case of the polymer due to the high conjugation of the aromatic polymeric chains.

3.2. Electrocatalytic activity of modified platinum electrode:

Poly (o-toluidine) modified platinum electrode is investigated as an electrocatalyst towards benzyl alcohol oxidation in acidic medium using a cyclic voltammetry technique.

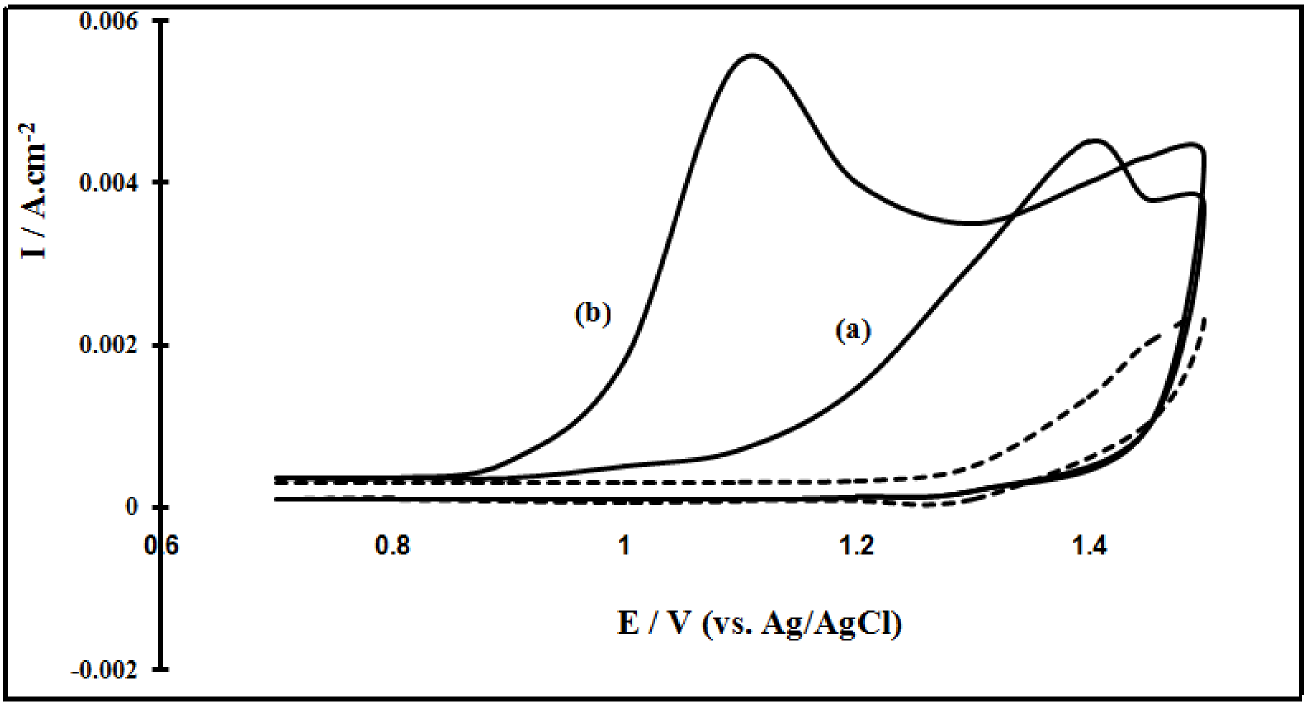


Figure 3. Cyclic voltammograms of aqueous solution (5 : 95 v/v $CHCl_3$: H_2O) containing 0.5 M sulphuric acid and 0.3 M benzyl alcohol at (a) Pt and (b) Pt/o-CH_3 modified electrodes at 25 ^{o}C with scan rate of 100 mV.s^{-1}

Figure (3) represents the cyclic voltammograms of aqueous solutions (5 : 95 v/v $CHCl_3$ / H_2O) containing 0.3 M benzyl alcohol and 0.5 M H_2SO_4 at 25 ^{o}C with scan rate of 100 mVs^{-1} at platinum (Pt) electrode (Fig.3a) and at poly(o-toluidine) modified platinum (Pt/o-CH_3) electrode (Fig.3.b) while the dashed line represents the basic curve in the absence of benzyl alcohol at Pt and modified electrodes. Data shows that the onset oxidation potentials for benzyl alcohol are 1400 and 1100 mV (vs. Ag/ AgCl) at Pt and at Pt/o-CH_3 electrodes respectively as well as the anodic peak current density (I*pa*) at Pt/o-CH_3 electrode is higher than that at Pt electrode. From the above data, we can conclude that, the oxidation potential of benzyl alcohol at Pt/o-CH_3 electrode is shifted about 300 mV in the negative direction comparing with at Pt electrode, this behavior confirms the electrocatalytic activity of Pt/o-CH_3 electrode as a result of the synergistic effects of the presence of poly(o-toluidine) film coated platinum surface that can enhance the adsorption of benzyl alcohol on the catalytic site [28].

3.3. Factors affecting on the electrocatalytic activity of Pt/o-CH_3 electrode:

3.3.1. Effect of o-toluidine monomer concentrations:

Effect of o-toluidine monomer concentrations on the electrodeposition of poly (o-toluidine) films on the platinum electrode surface during its modification and consequently on the electrocatalytic activity of the Pt/o-CH_3 electrode towards benzyl alcohol oxidation is studied from aqueous solution (5 : 95 v/v Methanol: H_2O) containing 0.5 M sulphuric acid in the presence of o-toluidine monomer concentrations ranged from 0.01 to 0.1 M using cyclic voltammetry technique with scan rate of 100 mVs^{-1} at 25 ^{o}C and the data are graphically represented in Figure (4).

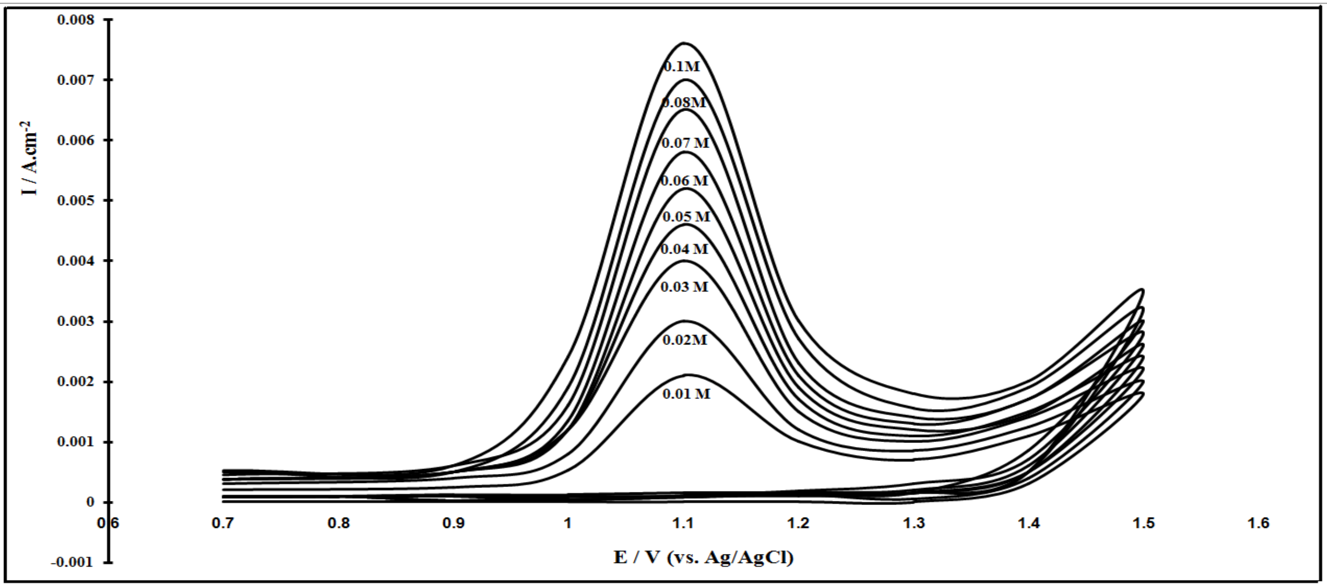


Figure 4. Cyclic voltammograms of aqueous solution (5 : 95 v/v Methanol : H_2O) containing 0.5 M sulphuric and *x* M o-toluidine monomer at 25^{o} C with scan rate of 100 mV.s^{-1}

The obtained results show that, increasing the monomer concentrations increases the anodic current density of the electropolymerization process as a result of increasing the rate of the polymerization and consequently the amount of polymer deposit on a platinum surface, but the adherence of the electrodeposited polymer films on platinum electrodes starts to decrease in the concentration higher than 0.07 M and the polymer films come down in the solution.

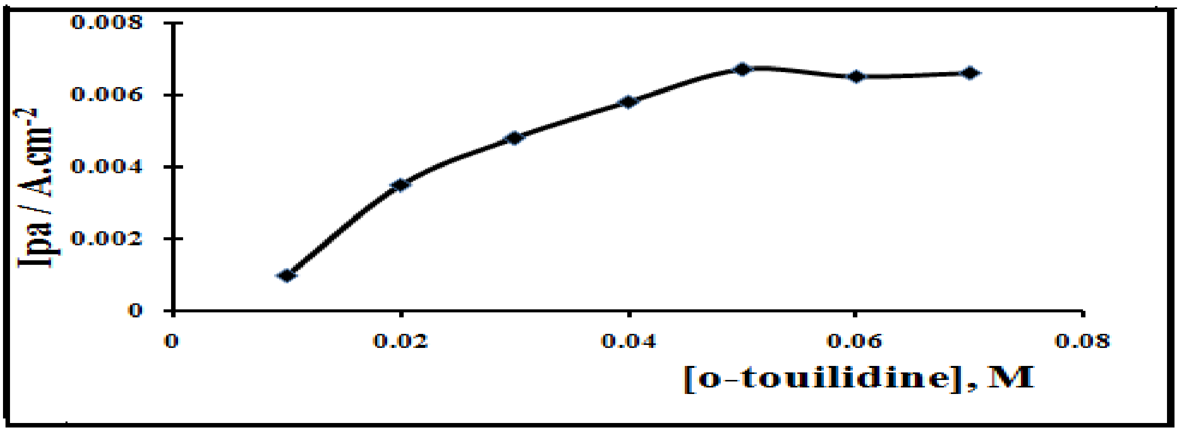


Figure 5. Anodic peak current densities (I*pa*) of benzyl alcohol oxidation versus monomer concentrations

The Electrocatalytic activity of Pt/o-CH_3 electrode modified by using monomer concentrations from 0.01 – 0.07 M towards benzyl alcohol oxidation in acidic medium is evaluated in aqueous solutions (5 : 95 v/v $CHCl_3$ / H_2O) containing 0.3 M benzyl alcohol and 0.5 M H_2SO_4 at 25 ^{o}C using cyclic voltammetry technique in the potential range between 700 – 1500 mV (vs. Ag/AgCl) with a scan rate of 100 mVs^{-1}. Data shows that, the anodic peak current densities (I*pa*) of the benzyl alcohol oxidation increase with increasing the monomer concentration up to 0.05 M and nearly constant as shown in Figure (5). The electrocatalytic activity of Pt/o-CH_3 electrode is explained as a result of the increasing the surface area and the adsorption sites in the polymer film coated platinum electrode but the nearly constant in the anodic peak current densities after 0.05 M monomer can be illustrated due to the constant active surface area in polymer film. From the obtained data, we can conclude that, 0.05 M monomer is chosen as an optimum concentration during the modification of the electrode.

3.3.2. Effect of repetitive potential scan:

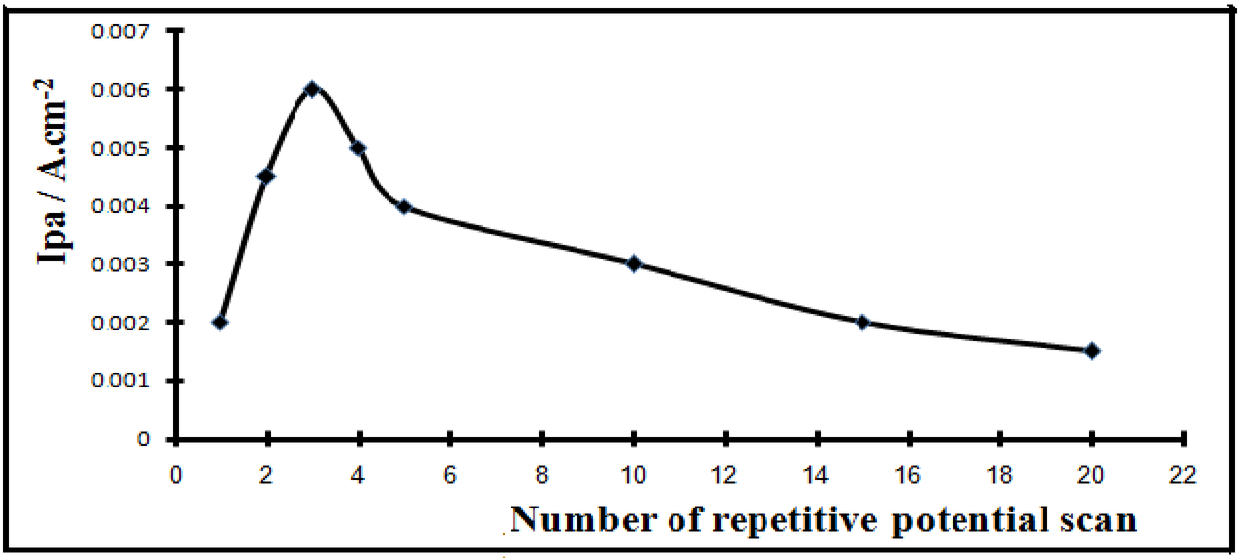


Figure 6. Anodic peak current densities (I*pa*) of benzyl alcohol oxidation versus number of repetitive potential scan

Figure (6) shows the relation between the anodic peak current densities (I*pa*) of benzyl alcohol oxidation as a function of the number of repetitive potential scan during the modification of a platinum electrode. Data shows that, I*pa* increases up to third cycle and start to decrease, this behavior is assigned to the deposition of a thick, nonporous and highly adherent polymer film on the electrode surface during its modification that causes a decrease in the active adsorption sites available for alcohol oxidation reaction, also a thick film leads to difficulties in electron transfer and diffusion of benzyl alcohol through the film itself.

3.3.3. Effect of scan rate

The effect of the scan rate (ν) on the benzyl alcohol electrooxidation at Pt/o-CH_3 electrode from aqueous solutions (5 : 95 v/v $CHCl_3$ / H_2O) containing 0.3 M benzyl alcohol and 0.5 M H_2SO_4 at 25 °C is investigated and the data are represented in Figure (7).

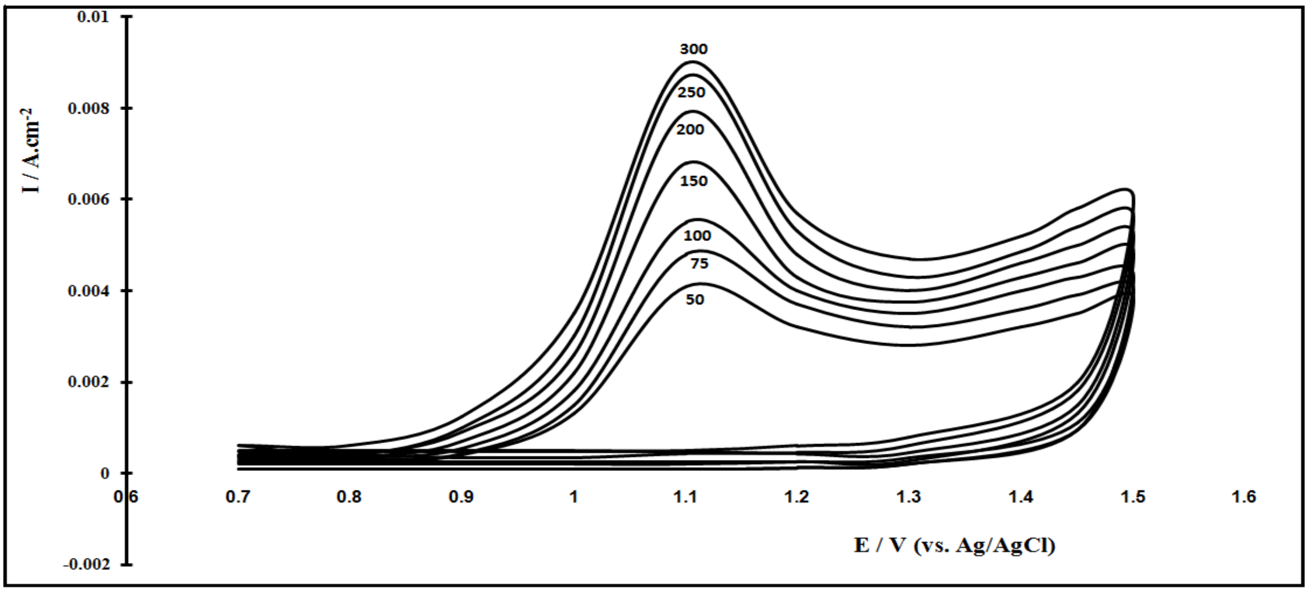


Figure 7. Cyclic voltammograms of aqueous solution (5 : 95 v/v $CHCl_3$: H_2O) containing 0.5 M sulphuric acid and 0.3 M benzyl alcohol Pt/o-CH_3 electrode at 25 °C with different scan rate

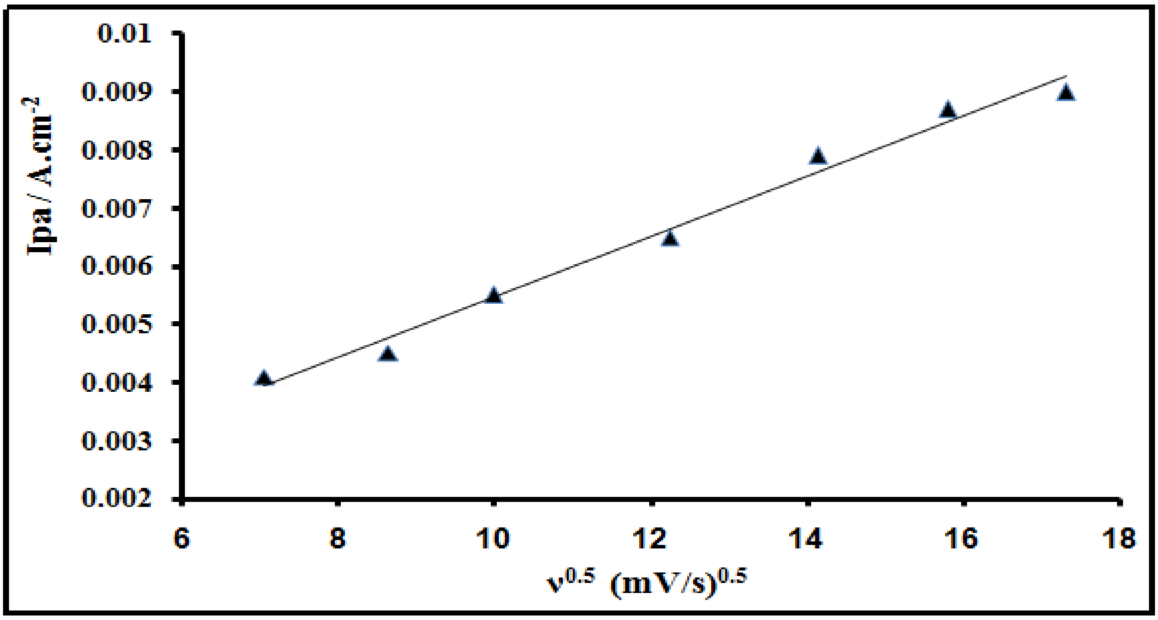


Figure 8. Relation between $\nu^{0.5}$ and Ipa

From the Figure, the anodic peak current densities (I*pa*) increase with increasing the scan rate (Figure 7) and there is a linear dependence (Figure 8) between the I*pa* and $\nu^{0.5}$ (Randless [29] and

Sevick [30] equations) indicating that the electrocatalytic oxidation of benzyl alcohol at Pt/o-CH_3 electrode is described partially by a diffusion-controlled process.

3.3.4. Effect of alcohol concentrations :

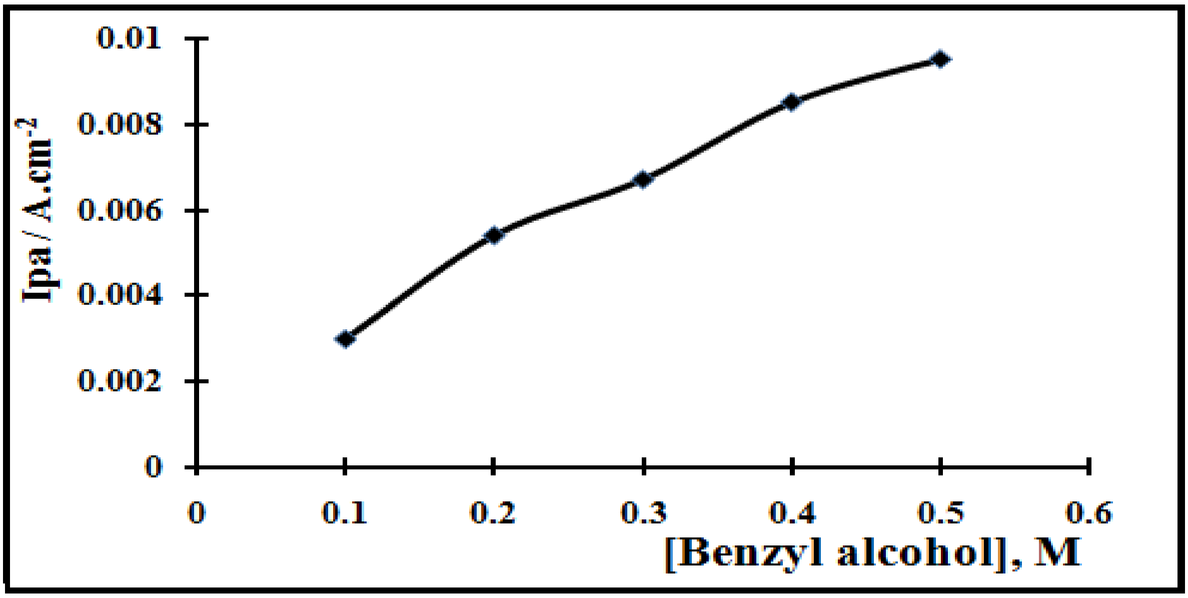


Figure 9. Anodic peak current densities (I*pa*) of benzyl alcohol oxidation versus alcohol concentrations

The effect of of benzyl alcohol concentrations from 0.1 to 0.5 M (> 0.05 M alcohol is immiscible in the aqueous tested solution) on the anodic peak current densities (I*pa*) of the electrocatalytic oxidation from aqueous solutions (5 : 95 v/v $CHCl_3$ / H_2O) containing 0.5 M H_2SO_4 at 25 °C is studied. Figure (9) illustrates the increasing of I*pa* with increasing the alcohol concentrations as a result of increasing the amount of adsorbed alcohol on the active surface area.

4. CONCLUSION

- Electrodeposition of poly (o-toluidine) on platinum electrode is carried out using cyclic voltammetry under different experimental conditions as monomer concentrations and repetitive potential scan.
- FTIR and UV-Visible spectroscopic analysis confirm the suggested structure of the as-deposited brown and good adherent poly (o-toluidine) polymer film coated platinum electrode.
- Poly (o-toluidine) modified platinum electrode shows high electrocatalytic activity towards benzyl alcohol oxidation in acidic medium compared with platinum electrode under the same conditions.

- The oxidation potential of benzyl alcohol is shifted from 1400 mV (vs. Ag/AgCl) at the platinum electrode to 1100 mV (vs. Ag/AgCl) at poly(o-toluidine) modified platinum electrode.
- Electrooxidation of benzyl alcohol at poly(o-toluidine) modified platinum electrode shows partially-diffusion controlled.

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