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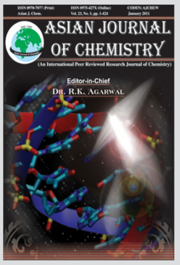

Electrochemical Investigation of Thiophene on Glassy Carbon Electrode and Quantitative Determination of it in Simulated Oil Solution by Differential Pulse Voltammetry and Amperometry Techniques

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In this study, the electrooxidation of thiophene was investigated by cyclic voltammetry in acetonitrile solution on glassy carbon electrode (GCE). It was been observed that electrooxidation of thiophene in acetonitrile is completely irreversible on glassy carbon electrode surface. For thiophene, a sharp oxidation peak at 2.06 V is obtained at glassy carbon electrode in acetonitrile media with 1 mM of $TBAPF_6$ as support. The diffusion constant was also calculated by chronoamperometry. Differential pulse voltammetry and amperometry were used for the determination of thiophene in acetonitrile media. Quantitative determination of thiophene was done by using calibration curve of anodic peak current of differential pulse voltammetry and amperometry *versus* concentration in concentrative range 2.0×10^{-7} to 1.0×10^{-6} and RSD < 3.0 %. This method is also used for determination of thiophene in simulated solution including thiophene, dibenzothiophene, thiophenol and some mercaptanes in octane media.

Key Words: Thiophene, Electrooxidation, Differential pulse voltammetry, Cyclic voltammetry.

INTRODUCTION

The aim of this project is to investigate the electrochemical behaviour of thiophene and determination of it in simulated oil solution. Due to presence of thiophene and its derivatives in petroleum compounds and using of thiophene in electropolymerization and conductivity of it, this investigation was carried out. Because of the electrical conductivity of polythiophene, some of recent researches were focused on electropolymerization of it[1-7]. Among conducting polymers, polythiophene have been the most studied due to its stability to both moisture and oxygen[1-5]. Most conductive polythiophene and poly(3-methylthiophene) films were prepared by electrochemical polymerization on noble metals (Pt, Au) in nonaqueous solvents[6,7]. Small oligomers such as oligothiophenes are well-structured molecules, which allow the rationalization of structural effects on electronic properties of their parent polymers and are interesting materials for applications in electrochemistry, electronics, modification of electrodes and optoelectronics[8-13]. A large amount of work has been dedicated to the electrooxidation of thiophene and oligothiophenes for which the properties can easily been modified using chemical substituents, pointing out the large potential offered by these modifications[12-17]. Extensive research on *p*-conjugated organic polymers, such as polythiophene, polypyrrole, polyaniline and other cyclic species, as well as derivatives of these materials, has been carried out owing to the desirable properties that these substances possess, such as non-linear optical behaviour, electronic conductivity and luminescence[13,18]. In this project, first, electrochemical properties of thiophene were studied and then thiophene was determined in simulated oil solution.

EXPERIMENTAL

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with an AUTOLAB PGSTAT30 electrochemical workstation (made by Echo chemie, Netherland). The working electrode was a glassy carbon electrode (GCE). The auxiliary electrode is platinum wire and reference electrode was silver wire.

All other reagents were of analytical grade and purchased from Merck. Water was double distilled. Thiophene solution in acetonitrile was prepared freshly. All experiments were carried out at room temperature (18 ± 2 ºC). Alumina powder with 0.5 µm diameter was used for cleaning of electrode surface.

RESULTS AND DISCUSSION

Cyclic voltammetry (CV) of thiophene on the glassy carbon electrode: Fig. 1 show 4 consecutive cycles for thiophene cyclic voltammetry in 1×10^{-5} M acetonitrile solution. As observed, the current is reduced during the second to forth cycles and the electrode surface is covered with sticky thiophene oxide products which decrease the current due to its lack of electrical conductivity and these products, which cover the surface of glassy carbon electrode. Peak potential shifts to more positive value after contaminating the electrode surface.

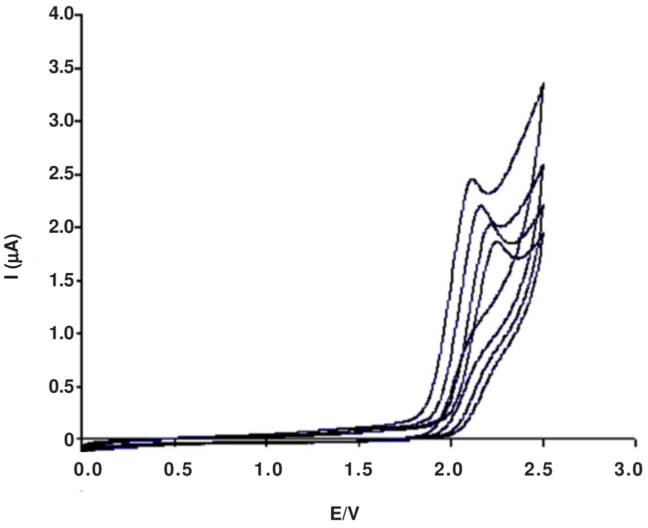
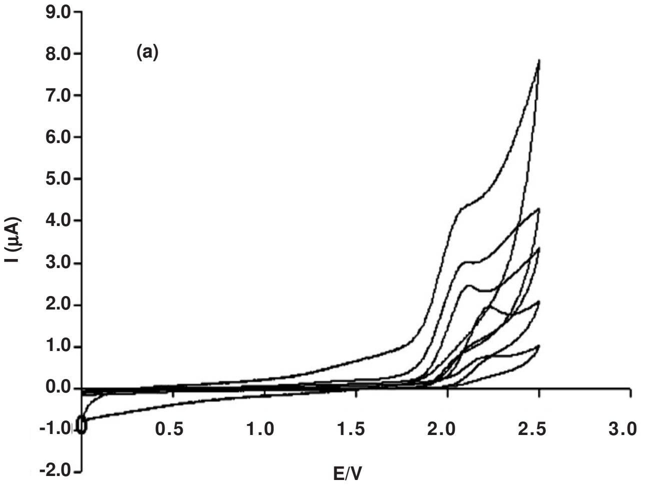


Fig. 1. Cyclic voltammograms of 4 consecutive cycles in 1×10^{-5} M thiophene and 1×10^{-3} M $TBABF_4$ in acetonitrile. Scan rate is 100 m V/s on surface of glassy carbon electrode with 2 mm diameter and in room temperature

Concentration effect: Fig. 2 shows the cyclic voltammetry for glassy carbon electrode in different concentrations. It is observed that the anodic current increases when concentration increases. After drawing the calibration curve, it is realized that after increasing concentration the current peak height is increased and there is a linear correlation between them.



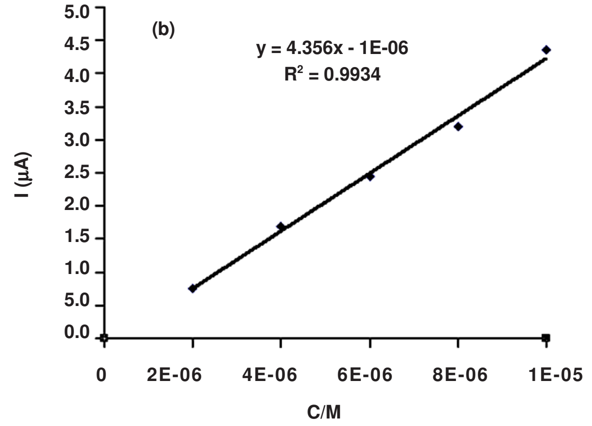


Fig. 2. a) Cyclic voltammograms in 2.0×10^{-6}, 4.0×10^{-6}, 6.0×10^{-6}, 8.0×10^{-6}, 1.0×10^{-5} M thiophene and 1×10^{-3} M $TBABF_4$ in acetonitrile. Scan rate is 100 m V/s on surface of glassy carbon electrode with 2 mm diameter and in room temperature. b) Calibration curve of cyclic voltammetry

Scan rate effect: Examination on the effect of scan rate on anodic peak current ($I_{p,a}$) showed that anodic peak potential shifts to more positive potentials after an increase in scan rate. After analyzing two ranges of 20-100 and 100-800 mV/s, it was observed that there is a linear correlation between peak current (I_p) and scan rate (ν) within the range of 20-100 mV/s. Also, within the range of 100 to 800 mV, there is a linear correlation between peak current (I_p) and square of scan rate ($\nu^{1/2}$) (Fig. 3). This point demonstrates that in higher rates a quicker change transfer occurs.

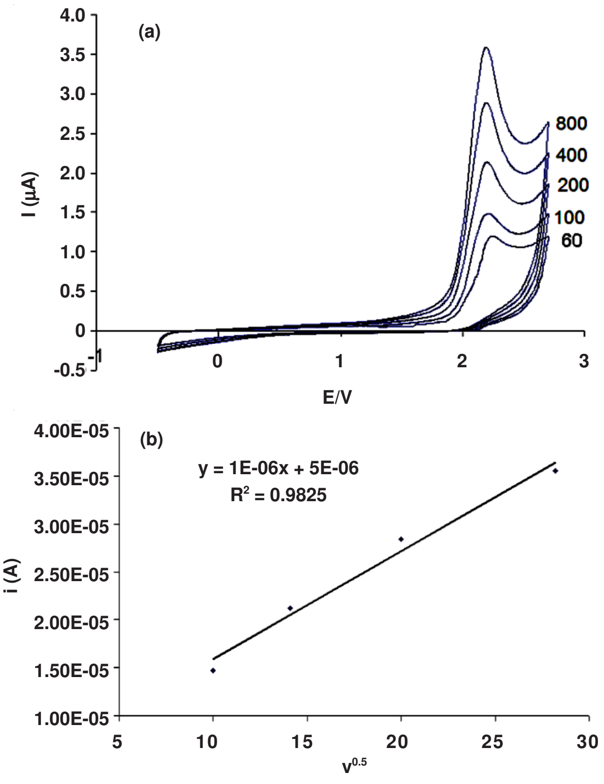


Fig. 3. a) Investigation of scan rate effect on oxidation peak current of thiophene in 2.0×10^{-5} M thiophene and 1×10^{-3} M $TBABF_4$ in acetonitrile on surface of glassy carbon electrode. Scan rate is 100 mV/s on surface of glassy carbon electrode with 2 mm diameter and in room temperature. b) Calibration curve of cyclic voltammetry in different scan rate

Peak current (I_p) obtained from randles-sevik formula, is the second of the current from diffusion process ($I_{p,diff}$) and the current from absorption ($I_{p,abs}$)

$$I_p = I_{p.diff} + I_{p.ads} = 0.446\frac{n^{3/2}F^{3/2}}{R^{1/2}T^{1/2}}AD^{1/2}\nu^{1/2}C + \frac{n^2F^2}{4RT}\nu A\Gamma$$

In above formula, A is the electrode surface, D, the diffusion control, ν the scan rate, C the analyte concentration, Γ the amount of surface absorption analyte and n, R, F and T have their common definitions.

The first phase in this formula defines the diffusion controlled process on the electrode which is in direct correlation with $\nu^{1/2}$. Drawing the current according to $\nu^{1/2}$ for thiophene, it is observed that the oxidation reaction is controlled by diffusion process. Therefore no preconcentration happens before electrochemical reaction.

Investigation of thiophene oxidation on glassy carbon electrode using chronoamperometry: Chronoamperometry obtained from staircase potential in 2.06 on glassy carbon electrode in thiophene solution in different concentrations. The diffusion coefficient for thiophene was detected using chronoamperometric studies. According to cottrel formula, we can define the diffusion current obtained from an electroactive compound with the diffusion coefficient of D, as follows:

$$I = n\,FAC_{ox}\,D_{ox}^{1/2}/(\pi t)^{1/2}$$

In this formula, D is the diffusion coefficient (cm^2/s) and C is the concentration for that sample. If the reaction mechanism undergoes the diffusion, the diagram for I Shifts according to $t^{-1/2}$ will be linear and we can get D using its slope. Fig. 4 shows the chronoamperometry curve of thiophene and Fig. 5 shows the I-$t^{1/2}$ shifts for different concentration of thiophene. We found thiophene diffusion coefficient of 7.0×10^{-6} cm^2/s in acetonitrile solution by using slope diagram.

Measuring the value of thiophene

Amperometry: Amperometry technique is used to determine the thiophene amount in acetonitrile using glassy carbon electrode. In Fig. 6 shows the glassy carbon electrode amperometry according to staircase changes for thiophene concentration applying the potential of 2.06 V. As the thiophene concentration increases, the current increases and comes to a constant rate. The calibration curve for these measurements was drawn, ranging from 1.0×10^{-7} to 6.0×10^{-7}. The detection limit, defined as 3 s, was 7.0×10^{-8} for thiophene. Relative standard deviation for 10 measurements for 1.0×10^{-7} concentration was 3.4 %. Thiophene makes some noises on the amperometry staircase because of its sulphur absorption on the electrode; thus detecting the peak current becomes difficult. The current decreases after the thiophene amount is increased.

Differential pulse voltammetry (DPV): To detect the amount of thiophene, differential pulse voltammetry is also used with potential of +1.7 to +2.1 V. As observed in Fig. 7, a clear peak was observed in the potential of +2.06 according to the Ag wire electrode which was related to the differential pulse voltammetry of thiophene compound. The calibration curve for these measurements were drawn ranging from 2.0×10^{-7} to 1.0×10^{-6} M. Theoretical detection limit, defined as s, was 9.0×10^{-8} for thiophene. The relative standard deviation was 2.25 % for 10 measurements in 1.0×10^{-7} M concentration.

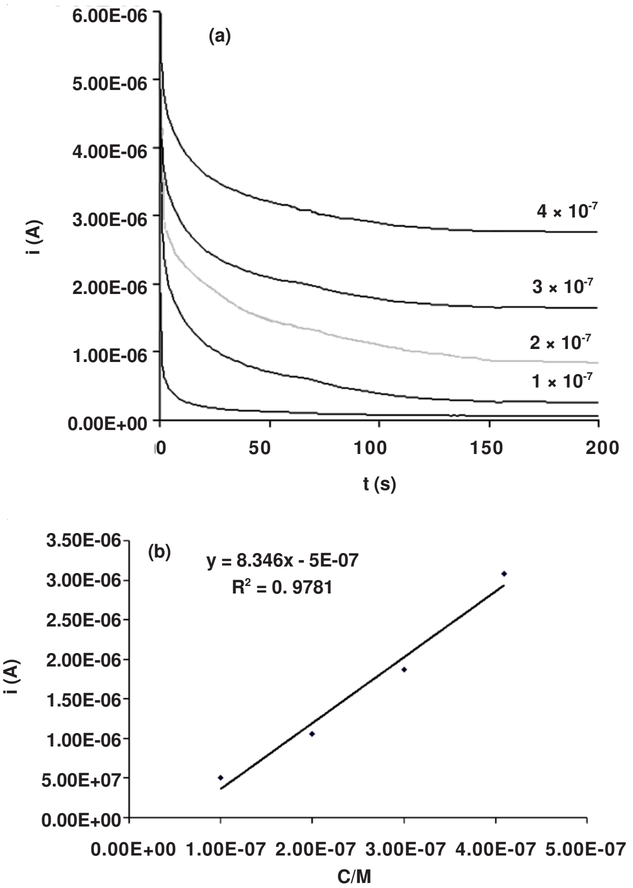


Fig 4. Single staircase chronoamperometric curve of thiophene in 1.0×10^{-7}, 2.0×10^{-7}, 3.0×10^{-7} and 4.0×10^{-7} M thiophene and 1×10^{-3} M $TBABF_4$ in acetonitrile in +2.06 V on surface of glassy carbon electrode with 2 mm diameter and in room temperature. Second curve is about peak current curve *versus* concentration in t = 100

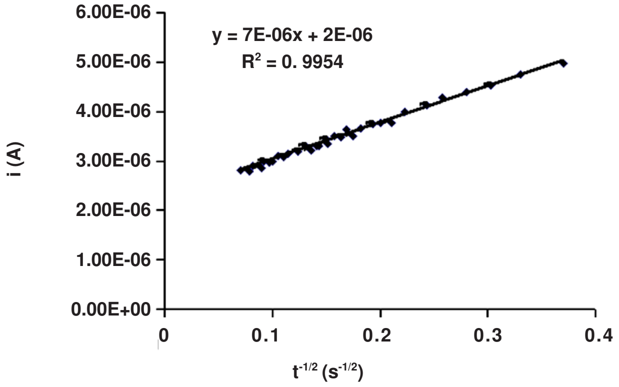
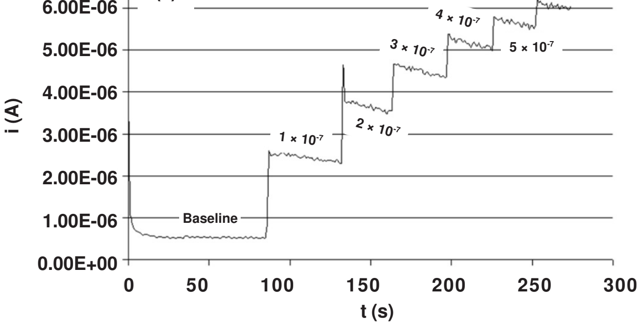


Fig. 5. I-$t^{-1/2}$ curve in 4.0×10^{-7} M thiophene on glassy carbon electrode with 2 mm diameter and in room temperature



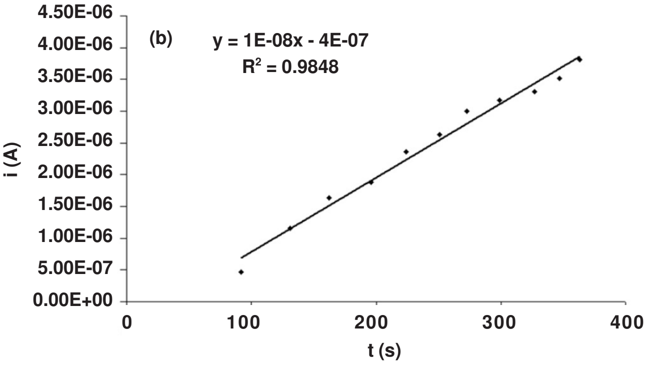


Fig. 6. a) Staircase amperometric curve of thiophene and calibration curve in 1.0×10^{-7} - 6.0×10^{-7} M thiophene and 1×10^{-3} M TBABF$_4$ in acetonitrile on surface of glassy carbon electrode with 2 mm diameter and in room temperature. b) Calibration curve of cyclic voltammetry in different concentration

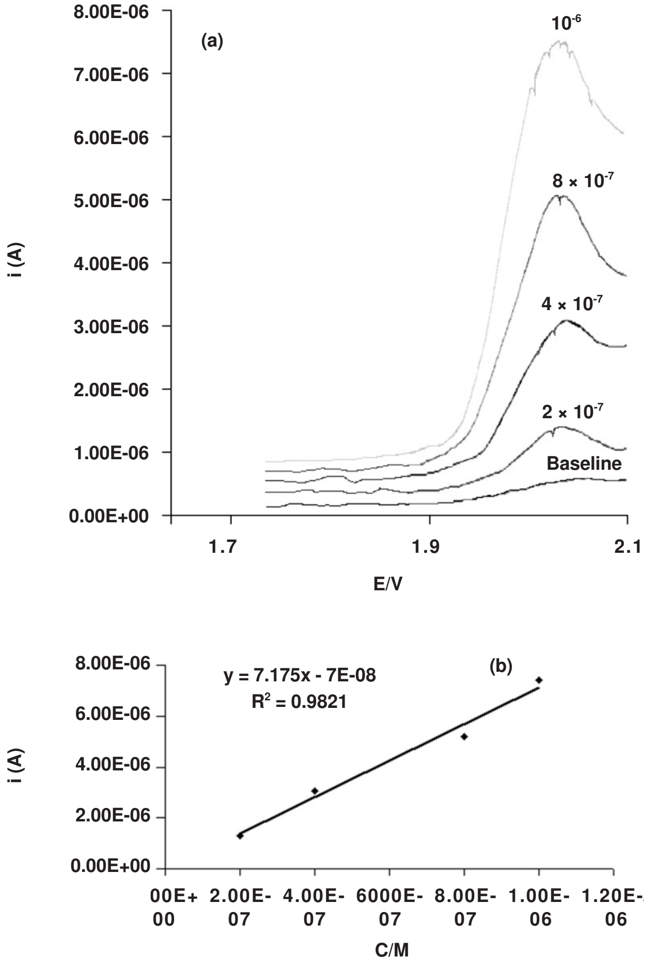


Fig. 7. a) DPV curve of thiophene in 2.0×10^{-7} - 1.0×10^{-6} M thiophene and 1×10^{-3} M TBABF$_4$ in acetonitrile in +2.06 V on surface of glassy carbon electrode with 2mm diameter and in room temperature. b) Calibration curve of cyclic voltammetry in different concentration

Drawing thiophene calibration curve in octane: To stimulate oil compounds containing thiophene, we used a non-polar solvent such as octane. In this method, stock solution of thiophene was prepared inside the octane solution. Then six solutions of 1, 2, 5, 6, 8 and 10 ppm concentration, were prepared from this stock solution as a semi-oil compound inside acetonitrile. Next, supporting electrolyte for TBAPF$_6$ was added and DPV measurement was done on it. The obtained calibration curve is shown in Fig. 8.

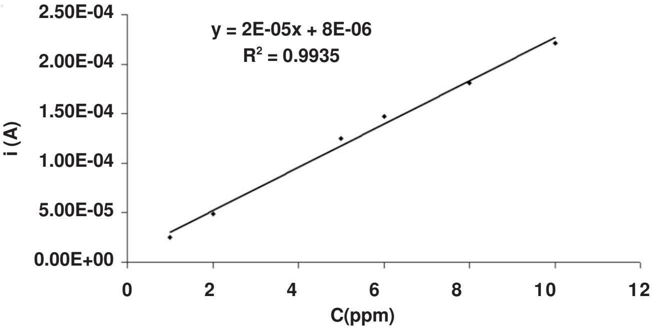


Fig. 8. Calibration curve of octane in ranging 1-10 ppm by using DPV technique

In next section, 10 mM of thiophene, dibenzothiophene, thiophenol, butane thiol and methyl-ethyl thioether was solved in octane and after adding of support, diluting was done to 10 μM and standard addition measuring was carried out by DPV (Table-1). Because of abutting of oxidation peaks of thiophene and dibenzothiophene together and presenting of sulfur contaminant on surface of electrode, thiophene was measured is more than real value.

TABLE-1
MEASUREMENT OF THIOPHENE IN PRESENCE OF DIBENZOTHIOPHENE, THIOPHENOL, BUTANETHIOL AND METHYL-ETHYL THIOETHER BY DPV

Detected (μM)	Added (μM)	Found (μM)	Recovery (%)
10 (± 1.1)	30.0	43.1 (± 2.1)	107.7

Conclusion

By using electrochemical techniques, thiophene is determined in the presence of some sulfur compounds. Some important data about electrochemical behaviour of thiophene is also obtained.

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