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ELECTROCHEMICAL BEHAVIOURS OF SUBSTITUTED THIOPHENES

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ELECTROCHEMICAL BEHAVIOURS OF SUBSTITUTED THIOPHENES

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BY

Abebaw Adgo

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DEDICATION

TO MY BROTHERS

ACKNOWLEDGMENT

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ABSTRACT

The electrochemical oxidation of 3-methylthiophene, thiophene and 2',5'- dibtyloxy-3-phenylthiophene have been studied using platinium, glassy carbon and gold electrodes in acetonitrile. Lithium perchlorate served as supporting electrolyte in all experiments.

The oxidation of 3-methyl thiophene at different concentration was carried out on Pt, GC and Au electrodes using dc cyclic voltammetry. As the concentration increases, a preadsorption peak was noted in all electrodes. It was seen that the Pt electrode is more sensitive to the adsorption of the product (radicals). The oxidation of 3-methylthiophene was also performed under potentiostatic conditions. It was observed that the current response decays with time at a rotating electrode. This shows that diffusion is not a rate determining step in the oxidation of 3-methylthiophene.

The limiting charge passed on stationary and rotating Pt electrode was evaluated on the primary oxidation of 4.2 mmol L^{-1} 3-methylthiophene on Pt electrode. Attempts were made to compare the charge passed with the theoretically charge expected from the monolayer coverage of the electrode surface.

The diffusion coefficient of ferrocene was determined on stationary Pt electrode. This value was compared with that of 3-methylthiophene and thiophene. The higher value of the diffusion coefficient of thiophene and 3-methylthiophene was due to a smaller molecular radius.

In the electrochemical oxidation of 2',5'-dibutyloxy-3-phenylthiophene at least three anodic oxidation peaks were observed in both DC and AC cyclic voltammetry. The first peak potential occurred around 1.05 V, the second at 1.47 V and the third around 1.91 V.

1. INTRODUCTION

The electrochemical oxidation of aromatic heterocyclic, benzenoid, or nonbenzenoid molecules frequently leads to the formation of an electrically conducting organic polymer film at the electrode surface [1]. In the last two decades conducting polymers have been the subject of intense research because of their potential application in electronics, batteries, or as modified electrodes [2]. In particular the polymers obtained from thiophene and substituted thiophene have been the subject of several studies. The interesting aspect of these polymers is their remarkable stability in both air and moisture. The properties of the polymers can be easily varied by changing the substituents on the monomers. In addition, some derivatives of thiophene with the alkyl group being butyl or larger, and soluble in organic solvents have also been reported [3].

New substituted thiophenes with oligo oxyethylene, oxybutyl and oxyheptyl chains have been prepared recently [4, 5]. From these groups of monomers, corresponding polymers have been synthesized [4-8] which have various applications such as in electrochemical light emitting cells.

Substituted thiophene monomers can be polymerized by a number of routes. The two broad methods that are used to synthesize these polymers are electrochemical and chemical. A major advantage of the electrochemical approach over the standard chemical methods includes a clean, one-step production of polymeric materials directly onto the electrode surface from which a continuous film can be peeled off. More interestingly the polymers, directly doped with the anions of the supporting electrolytes,

can be produced and facile changes of their properties with the dopant anions are possible [9].

The electropolymerization of thiophene and its derivatives has been carried out in organic media, in the presence of various supporting electrolytes and commonly using platinum, gold, graphite and indium-tin oxide (ITO) working electrodes [9-12]. Recently there has also been a report that thiophene electroplymerizes on oxidizable metals (Fe, Al and Zn) from the solution in different media [13].

The electrochemical properties of polythiophene and substituted polythiophene films have been studied widely [2, 10-16]. However, the nucleation and the initial growth mechanism during the anodic electropolymerization of these polymers are not fully recognized. Schrebler *et al.* [18] state that although the potential step experiments may be used conveniently to monitor and elucidate the kinetics of deposition, studies concerning the initiation and growth mechanism of these polymers can hardly be found in the literature.

Two models have been put forward to describe the initiation and growth of polymer films prepared electrochemically [19]. The anodic polymerization process has been described either as adsorption of monomers on the electrode surface followed by the gradual addition of monomers to the surface bound species [18, 19], or as oligomer formation in solution which at a given stage "precipitates" on the electrode surface [20,21].

The primary step of polymer formation is the anodic oxidation of the monomers. Unfortunately this step has not been extensively investigated. Therefore, it is the aim of this project to study the electrochemical oxidation of thiophenes before polymer formation.

2. LITERATURE

2.1. Electrochemical polymerization

Electrochemical polymerization has been used to synthesize polythiophenes from their monomers. The main requirement in the electropolymerization of the monomer is that the monomer has an oxidation potential which is accessible through a suitable solvent. In addition to this, the monomer should produce a radical cation which reacts more quickly with other monomers to form the polymer than it will react with other nucleophiles in the electrolyte solution. The electrochemical polymerization is easily carried out with a classical three electrodes cell arrangement. The monomer is simply dissolved in a suitable solvent and anodically polymerized on the electrode surface from the solution containing the monomer and the supporting electrolyte.

The electrochemical synthesis of polythiophenes was first reported in 1981 [12] using tetraethylammonium tetrafluoroborate supporting electrolyte in acetonitrile under galvanostatic conditions, in a method similar to that employed for the polymerization of polypyrolle. The conductivity of the product was found to be in the range of 10^{-3} to 10^{-1} Scm^{-1}. Ever since then, other workers have polymerized thiophene onto platinum-

coated glass electrode to produce thin film using acetonitrile solution containing small amounts of water and a variety of supporting electrolytes [10, 11, 22]. Similar results were achieved by Kaneto *et al.* [15] using monomer solutions in oxygen-free anhydrous solvents (acetonitrile and benzonitrile) and ITO-glass substrates.

Aeiyach *et al.* [13] studied the polymerization of thiophene on oxidizable metals (Fe, Al and Zn) in acidic, neutral or basic media. They found out from several salts, PF_6^- alone could hinder the anodic dissolution of iron and allow the galvanostatic electropolymerization of thiophene on this metal [13] in a propylene carbonate. Propylene carbonate is considered as a good neutral solvent for the electroplymerization of thiophene on noble metals. In a basic solution, such as tetrahydrofuran, electroplymerization of polythiophene could not be achieved, due to passivation of the metal making the electrode surface highly insulating. The best result was obtained in dichloromethane, which allowed the deposition of homogeneous polythiophene films on Fe and Al in both potentiostatic and galvanostatic conditions. On Zn the best film was obtained in the galvanostatic mode only. This is because Zn is believed to dissolve even at a low potential [13].

It is supposed that the electropolmerization of thiophene involves coupling of a monomer radical cation through (α, α') position [9, 22]. The coupling occurs at the carbon atoms which are known to be the most reactive toward addition and substitution reactions. The general reaction steps are as shown in Fig. 1 for the thiophene polymerization. The first step in the polymerization is assumed to be the irreversible electrochemical oxidation of the neutral monomer [24] to form radical cations (1 to 3 in

Fig. 1a). In the next stage, two radical cations combine to form a dimer. The other possibility is that the radical cation could react like an electrophile and add to a neutral monomer (Fig. 1b). This reaction is expected to occur since there is a repulsion between two like charges when they come closer. The dimer loses two protons to become electrically neutral. This dimer which is more easily oxidized to a radical cation can react with other radical cations or monomers. Chain growth proceeds between the radical cation of the monomer and those of continuously forming oligomers. In order to sustain film growth at the electrode interface, the electrode potential has to be maintained at the oxidation potential of the monomer. The electrochemical reaction proceeds through successive electrochemical and chemical steps, until the oligomer becomes insoluble in the electrolyte medium and precipitates onto the electrode surface [25].

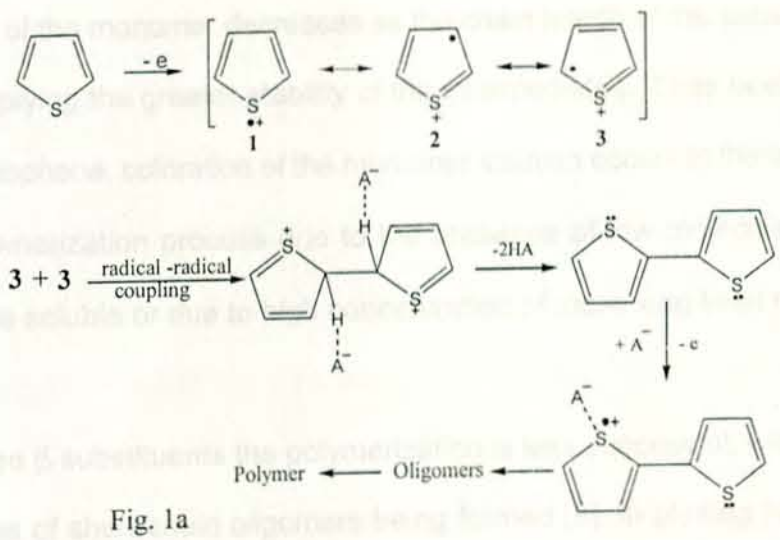


Fig. 1a

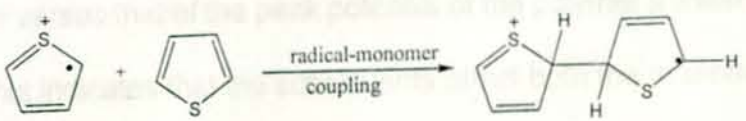


Fig. 1b

Fig. 1. Possible polymerization mechanisms for thiophene monomers [18, 24].

Since the polymerization reaction proceeds only when the potential is sufficiently high to oxidize the monomer, the coupling reaction must involve the coupling of two radicals. This is because at this potential, the concentration of thiophene is zero on the electrode surface and negligible in the region of the electrode [26].

Adding substituents to thiophene affects the oxidation potential by either increasing or decreasing the electron density in the thiophene ring. Increasing the electrophilic character of the substituent, such as $CN^{\cdot}$ and NO_2 shifts the oxidation potential to more positive value, whilst the presence of electron donating groups such as CH_3 have an opposite effect, shifting the peak potential of the monomer in a cathodic direction to the unsubstituted material [27]. On the other hand, the substitution effect on the oxidation potential was explained through the radical cation intermediates [1]. The oxidation potential of the monomer decreases as the chain length of the substituent is increased again implying the greater stability of the intermediates. It has been noted that with 3-methylthiophene, coloration of the monomer solution occurs in the anodic region during the polymerization process due to the presence of low molecular weight oligomers which are soluble or due to high concentration of more long lived radicals [28].

With large β-substituents the polymerization is less successful, with evidence of large quantities of short-chain oligomers being formed [9]. In plotting peak potential of the monomer *versus* that of the peak potential of the polymer a linear relationship has been found. This indicates that the substituents affect both the monomer and the polymer in similar ways, although to a greater extent for the latter [27].

The use of lower current densities during the polymerization results in higher quality film than when high current densities are employed. The use of oxygen and water-free conditions give films with higher conductivities. Kobel *et al.* [28] found that the use of propylene carbonate as the solvent for the monomer gave the highest quality films of poly(3-methylthiophene). The polymerization of 3-methylthiophene has also been achieved in aqueous media, although significant quantities of the solvent was incorporated into the polymer during the polymerization process.

2.2. Mechanisms of the deposition of the polymer on the electrode surface

Initially, Downward and Pletcher [29] studied the oxidation of 10 mM thiophene and bithiophene in 0.1 M tetrabuthylammoniumtetrafloroborate as supporting electrolyte in acetonitrile using Pt disk electrode. They found that the deposition of polythiohene occurs via a nucleation growth mechanism (NGM) similar to the deposition of a metal onto a foreign substrate. These authors reported a linear I *vs* $t^{1/2}$ relationship for the early portion of the current transient response to a potential step. This is almost consistent with an instantaneous nucleation/ three-dimensional growth mechanism.

Hillman and Mallen [14] have carried out a more detailed potentiostatic study on the deposition of polythiophene on Au. These authors proposed a model for the nucleation growth mechanism (NGM) of polythiophene films and estimated some of the kinetic parameters as a function of polymerization potential, indicating that the formation of a bulk film occurs by an instantaneous nucleation/three dimensional growth mechanism.

Later the same authors carried out studies using potential step and time resolved spectroscopic measurements [30] on the deposition of polythiophene on Au. As a result of this they found different stages in the polymerization process. At short times, small quantities of intermediates were observed. It has been suggested that they may be short chain oligomers consisting of 5 to 7 monomeric units. At slightly longer times, where the current-time transient shows the expansion of growing sites, the optical absorbance shifted to longer wavelengths which was attributed to the formation of longer oligomeric chains (15 to 17 monomeric units), a situation that occurs together with the predominance of metallic character of the polymer. However, Hamett and Hillman [31], through ellipsometric studies, indicated that the previous analysis of current-time data is more complex, suggesting three dimensional growth process. As they suggest the standard nucleation and growth theory does not explain the thickness *versus* the square of time (t^2) relationship found by ellipsometry data.

Liand Abert [reference cited in 18] investigated the kinetics and mechanisms of electrochemical deposition of polythiophene-3-acetic acid. The experiments were done on solutions containing 0.2 to 0.6 mol L^{-1} thiophene-3-acetic acid and 0.1 mol L^{-1} $LiClO_4$ in CH_3CN on Pt disk electrodes. They found contradictory results with a 3D growth mechanism. They prove the deposition undergo in prevailed 2D layer-to-layer growing mechanisms in polymer formation.

Schrebler *et al.* [18] described the effect of potential, monomer concentration and nature of the electrolyte on the NGM of polythiophene on a Pt electrode in dichloromethane. The current-time transient obtained were fitted using a mathematical

equation (1) [18]. This equation contains three contributions. Two dimensional (2D) and three-dimensional (3D) instantaneous nucleation both of which are charge transfer controlled and 3D progressive nucleation which is diffusion controlled. The weight of each contribution was dependent on time. They found that at any condition the principal contribution is the 3D instantaneous nucleation. The contribution of 2D instantaneous nucleation is important in the first stage of the nucleation process. The contribution of 3D progressive nucleation appears at longer times and it is favoured with increasing monomer concentration.

$$j=at[\exp(-bt^2)]+c[1-\exp(-dt^2)]+et^{-0.5}[1-\exp(-ft^2)] \qquad (1)$$

The first two terms in equation 1 correspond to 2D and 3D dimensional instantaneous growing, respectively. The last term corresponds to progressive nucleation and 3D growth mechanisms. The constants a, b, c, d, e and f are described through the following equations (equations 2-5).

$$a=2\pi nMhFN_{2D}K_2^2 \qquad b=\frac{\pi N_2 DM^2K_2^2}{\rho^2} \qquad (2)$$

$$c=NFK_3' \qquad d=\frac{\pi M^2K_3^2N_3D}{\rho^2} \qquad (3)$$

$$e=\frac{\pi FD^{1/2}C^b}{\rho^{1/2}} \qquad f=\frac{A'K\pi D}{2} \qquad (4)$$

$$A'=AN_{Dif} \qquad K=\frac{4}{3}\left(\frac{8\pi C^bM}{\rho}\right)^{1/2} \qquad (5)$$

Where n is the number of electrons transferred, F is Faraday's constant, ρ is density of the monomer, M is molecular mass of the molecules on the surface of the electrode, h is the height of nuclei, K_2 is the growth rate of the 2D nuclei, N_{2D} and N_{3D} are the instantaneous nuclei number formed at t = 0 in 2D and 3D form, K_3 and K_3' are the rate constants of the 3D nucleus for the growth parallel and perpendicular to the surface, D and C^b are diffusion coefficients and bulk concentrations of the monomer, A' is the rate constant of a nucleus formation and N_{dif} is the number of nuclei formed at t= o under diffusion control.

They also estimated the film thickness using equation (6)

$$h = \frac{K_3' V_m c d t^2}{k} \qquad (6)$$

Where

$$k = a\exp(-bt^2) + cdt + eft^{1/2}$$

V_m = the molar volume of polythiophene that is deposited

3. Experimental

3-Methylthiophene (Aldrich), thiophene (Aldrich) and the supporting electrolyte lithium perchlorate (Ventrone GMBH) were used as received. 2',5'-dibutyloxy-3-phenylthiophene was supplied by Dr. Wendimagegn Mammo of the Department of Chemistry. Acetonitrile (Riedel-deHaen) was distilled over phosphorus pentoxide (BDH) and stored over molecular sieve (3A) to ensure a minimum content of water. All electrochemical measurements were performed by using the Electrochemical Analyzer BAS 100B, in one compartment cell with three electrodes. The electrochemical cell used in the investigation is shown in Fig. 2.

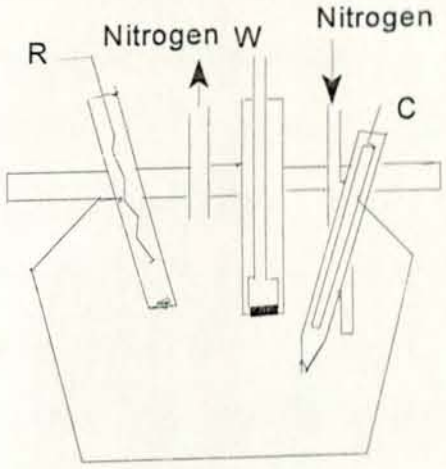


Fig. 2. Electrochemical cell arrangement. R, W and C refer to reference, working and counter electrodes, respectively.

The working electrodes employed were stationary or rotating platinum (geometrical area 0.07 cm^2), gold (0.07 cm^2) and glassy carbon (0.07 cm^2). The rotating electrode

(Metrohm) consisted of a rotation speed control unit and interchangeable tips (Pt, GC and Au). A platinum wire was used as counter electrode. A silver/silver chloride quasi-reference electrode was housed in a glass compartment containing 0.1 mol L^{-1} $LiClO_4$ in acetonitrile and separated from the solution which contains the monomer by a VYcor plug.

Before each experiment the working electrode was polished mechanically with alumina to remove contaminants and a polymer formed from the previous experiments. Solutions were purged with nitrogen prior to all experiments and N_2 was allowed to flow over the solution during the experiment to exclude oxygen. 3-Methylthiophene and thiophene were added, in the required amounts to the base electrolyte (0.1 mol L^{-1} $LiClO_4$ + CH_3CN) by a micropipet. Measurements were made at laboratory temperature (20 ± 4)° C.

4. Results and Discussion

4.1 Electrochemical oxidation of 3-metylthiophene at platinum, glassy carbon and gold electrodes

The oxidation of 3-methylthiophene (3-MeT) in acetonitrile at platinum (Pt), glassy carbon (GC) and gold (Au) electrodes have been studied by cyclic voltammetry. The experiments were performed at low concentration of the monomer. Prior to each experiment, the potential of the working electrode was cycled within a given range to determine the working potential range of the supporting electrolyte and the solvent used. The oxidation potentials of the monomer on the electrode surface were determined by cycling the potential within this range. The potentials reported here are measured *versus* quasi-reference Ag/AgCl electrode.

Figure 3 shows the cyclic voltammograms of 5.2 mmol L^{-1} 3-metylthiophene in 0.1 mol L^{-1} LiClO4 + CH_3CN obtained at Pt, GC and Au electrodes together with voltammogram of the supporting electrolyte. The anodic peak due to the oxidation of 3-MeT was found to be at 1.81 V on Pt, at 1.74 V on GC and at 1.82 V on Au electrodes. From this it is shown that the peak potential of 3-MeT is dependent on the electrode material used. At platiniun and gold elecreodes it has a comparable value. But on a glassy carbon electrode the oxidation potential was found to be less anodic compared to Pt and Au. Waltman *et al.* [1] found that the peak potential of the oxidation of 3-MeT (8.9-23 mmol L^{-1} in teteraethylammonium tetrafloroborate in acetonitrile) at Pt electrode was 1.86 V *versus* saturated potassium chloride calomel electrode. On the recorded cycle

a small reduction peak was observed at a potential of about -0.18 V on Pt electrode. No effort has been made to study the nature of this peak.

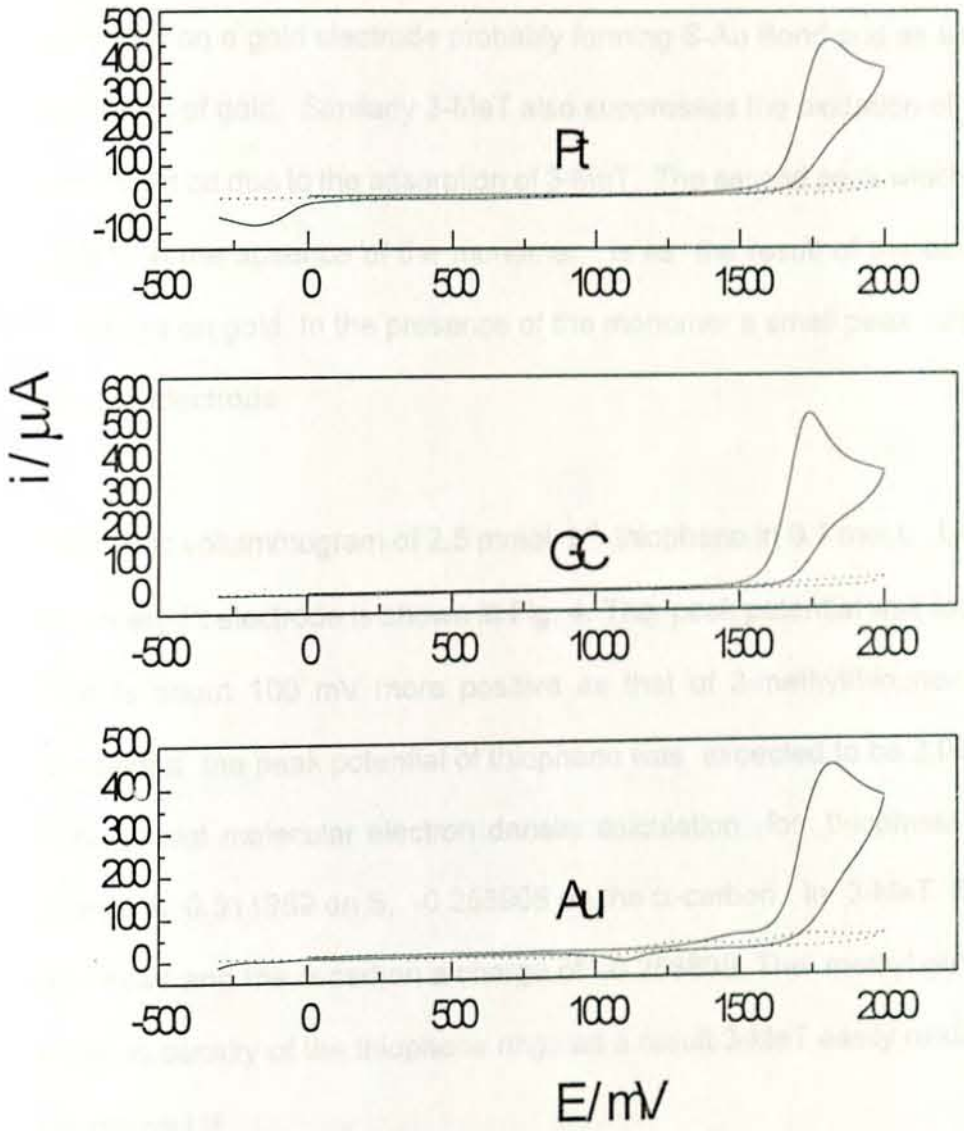


Fig. 3. Cyclic voltammograms of 5.2 mmol L^{-1} 3-methylthiophene in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN at a stationary platinum, glassy carbon and gold electrodes. At a Scan rate of 100 mV/s.

One of the problems working with a gold electrode is the dissolution of gold at potentials where 3-MeT oxidation occurs [14, 30]. The peak observed at 1.3 V in the absence of the monomer is due to the oxidation of the gold electrode. This peak is suppressed in the presence of the monomer. Hillman [30] suggested thiophene is adsorbed on a gold electrode probably forming S-Au Bond and as a result reduce the oxidation of gold. Similarly 3-MeT also suppresses the oxidation of gold in this case. This might be due to the adsorption of 3-MeT. The second peak which occurred around 1.76 V in the absence of the monomer is as the result of the oxidation of oxygen coverage on gold. In the presence of the monomer a small peak appeared at 1.47 V on gold electrode.

The cyclic voltammogram of 2.5 mmol L^{-1} thiophene in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN at stationary Pt electrode is shown in Fig. 4. The peak potential was found to be 1.91 V. This is about 100 mV more positive as that of 3-methylthiophene. Under similar conditions the peak potential of thiophene was expected to be 2.06 V (vs SCE) [9]. The indirect molecular electron density calculation for thiophene shows that the charge is 0.311982 on S, -0.255908 on the α-carbon. In 3-MeT S has a charge of 0.314944 and the α-carbon a charge of -0.258898. The methyl group increases the electron density of the thiophene ring; as a result 3-MeT easily oxidizes compared to thiophene [1].

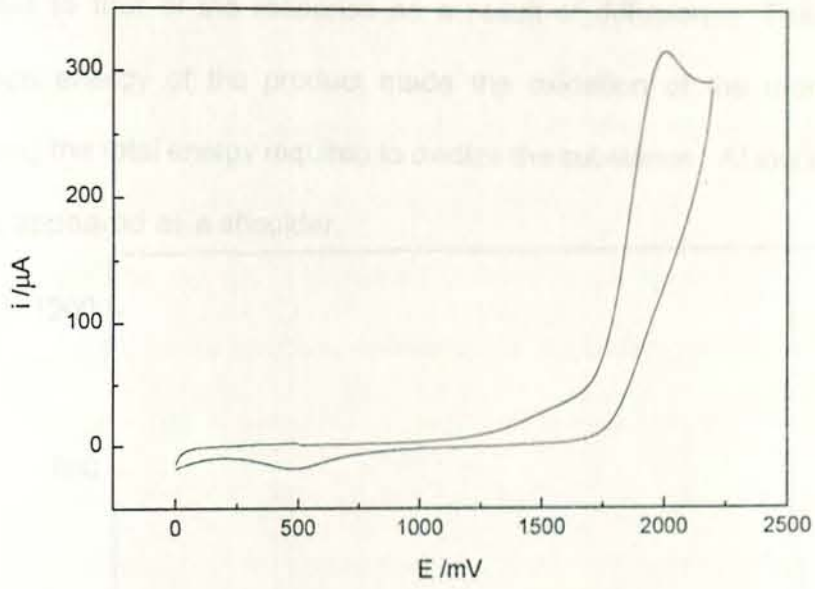


Fig. 4. The cyclic voltammogram of 2.5 mmol L^{-1} thiophene on a stationary Pt electrode. And a Scan rate of 100 mV/s (electrolyte: 0.1 mol L^{-1} LiClO4 + CH_3CN).

4.2 The concentration dependance of the electrochemical oxidation of 3-methylthiophene

The effect of the monomer concentration on the electrochemical oxidation of 3-MeT at Pt, GC and Au electrodes was studied. Cyclic voltammograms at different concentrations of 3-MeT obtained at a Pt electrode are shown in Fig. 5. As we increase the concentration of 3-MeT from 5.2 mmol L^{-1} to 0.01 mol L^{-1} a product adsorption peak was observed. It is a product adsorption peak because it appeared at less anodic potential compared with that of the single peak obtained at low concentration.

Wopschall [32] stated that product adsorption peak occurred at less anodic potential compared to that of the response as a result of diffusion. This is because the adsorption energy of the product made the oxidation of the monomer easier by decreasing the total energy required to oxidize the substance. At low concentration the prepeak appeared as a shoulder.

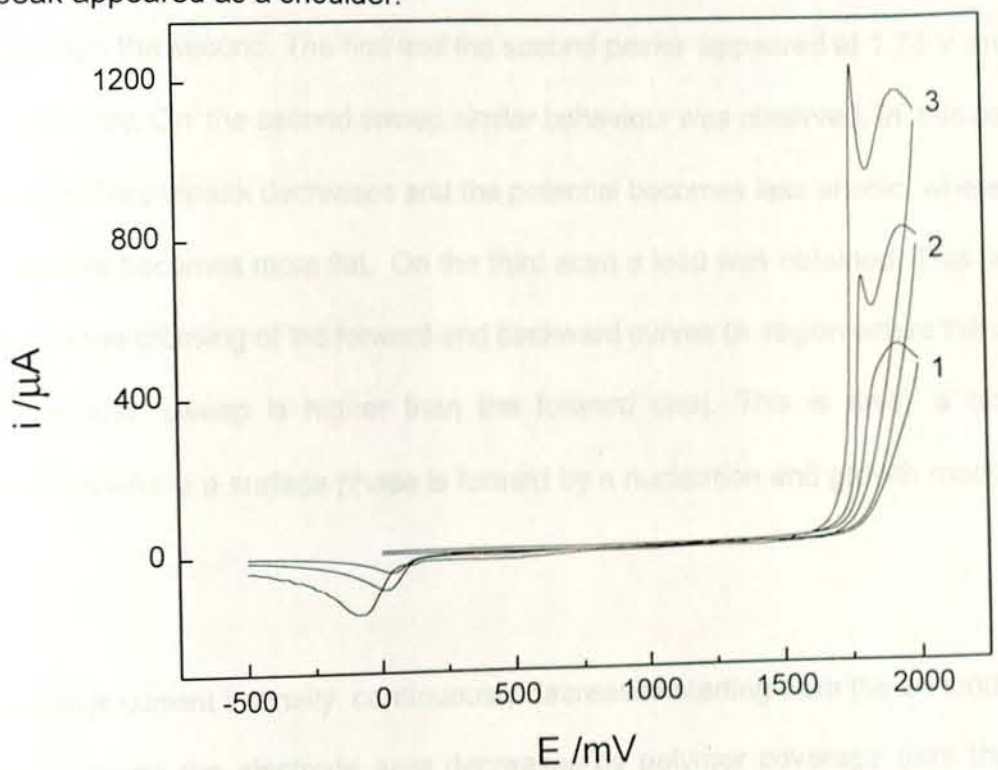


Fig. 5. Cyclic voltammograms of (1) 5.2 mmol L^{-1} M, (2) 0.01 mol L^{-1} and (3) 0.02 mol L^{-1} 3-MeT in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN on a stationary Pt electrode at a scan rate of 100 mV/s.

Similar behaviour was obtained at a GC electrode. The prepeak at a GC electrode appeared at higher concentration of the monomer than at the Pt electrode. The response of the adsorption peak earlier on Pt electrode may be due to the structure of the Pt metal. A similar trend was observed at a gold electrode. But on a gold electrode there is a report that a thiophene monomer is adsorbed [30]. From this observation it

seems that the radicals initially produced in the oxidation of 3-MeT are adsorbed on the electrode surface.

Figure 6 shows cyclic voltammograms of 0.02 mol L^{-1} of 3-methylthiophene with the three successive cycles at a stationary Pt electrode. On the first cycle the prepeak is sharper than the second. The first and the second peaks appeared at 1.78 V and 2.07 V, respectively. On the second sweep similar behaviour was observed. In this case the intensity of the prepeak decreases and the potential becomes less anodic, whereas the second peak becomes more flat. On the third scan a loop was obtained. This loop is a result of the crossing of the forward and backward curves (a region where the current in the reverse sweep is higher than the forward one). This is also a common observation where a surface phase is formed by a nucleation and growth mechanism [33].

The prepeak current intensity continuously decreases starting from the second cycle. This is because the electrode area decreases by polymer coverage from the first preceding cycles. As a result adsorption becomes difficult and consequently the intensity of the current decreases.

On the other hand cyclic voltammetric curves obtained on a rotating Pt electrode (Fig. 7) show also two anodic peaks similar to that on the stationary electrode. Even though deposition is disturbed upon rotating, the occurrences of the peaks in these case also shows these peaks are a result of strongly adsorbed species which undergo a surface reaction. In this case the intensity of both peaks in the first cycle increases

approximately by 1.5 mA compared to that obtained at the stationary case even though the first peak is not diffusion controlled. The adsorption peak current intensity decreases quickly in the second and third cycles compared with the stationary case. This may be due to the faster coverage of the electrode by polymer as a result of stirring. A current loop is seen in this case starting from the second cycle. This loop is a sign of the formation of a polymer layer on the electrode. The appreance of the loop also shows that polymerization occurs in solution and instantaneously precipitation occurs on the electrode surface.

In addition to this a small reduction peak, which appeared on a stationary Pt electrode disappeared at a rotating electrode. From this observation we concluded that this peak was a result of soluble products on the electrode.

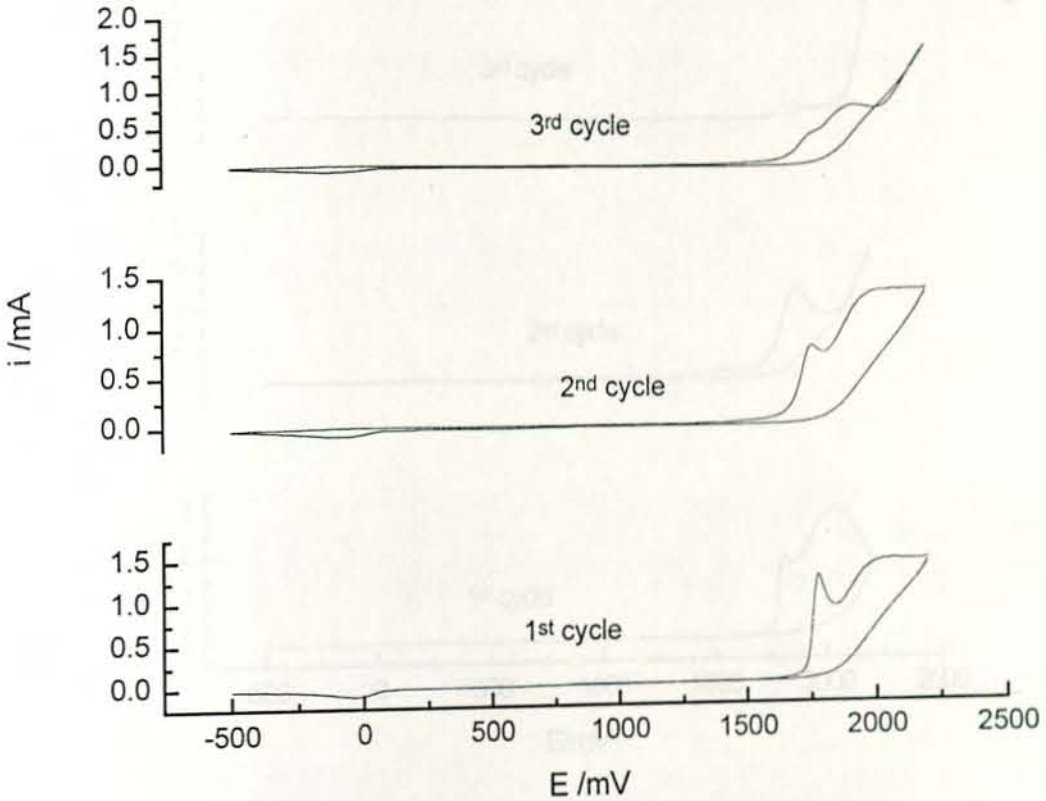


Fig. 6. Cyclic voltammograms of the first three cycles of 0.02 mol L^{-1} 3-MeT in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN on a stationary Pt electrode at a scan rate of 100 mV/s.

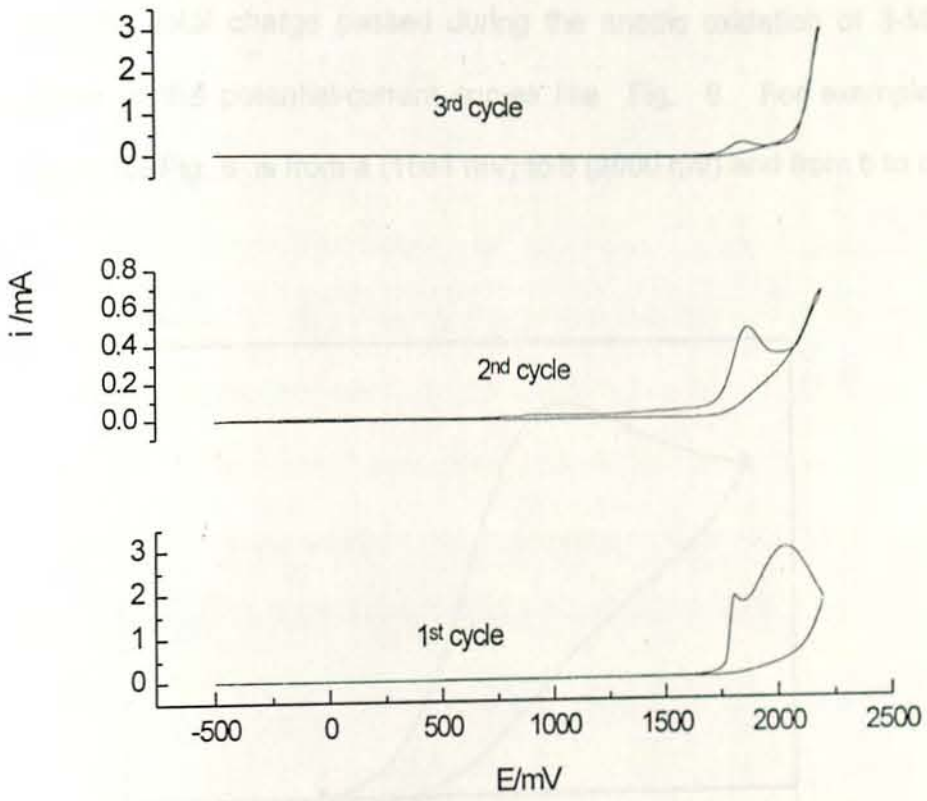


Fig. 7. Cyclic voltammograms of the first three cycles of 0.02 mol L^{-1} of 3-MeT in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN on a rotating Pt electrode (3000 rev/min) at a scan rate of 100 mV/s.

In order to find a relation between the degree of oxidation with a sweep rate, we evaluate the total charge passed during the anodic oxidation of 3-MeT from the integration of the potential-current curves like Fig. 8. For example the limit of integration for Fig. 8 is from a (1561 mV) to b (2000 mV) and from b to c (1647 V).

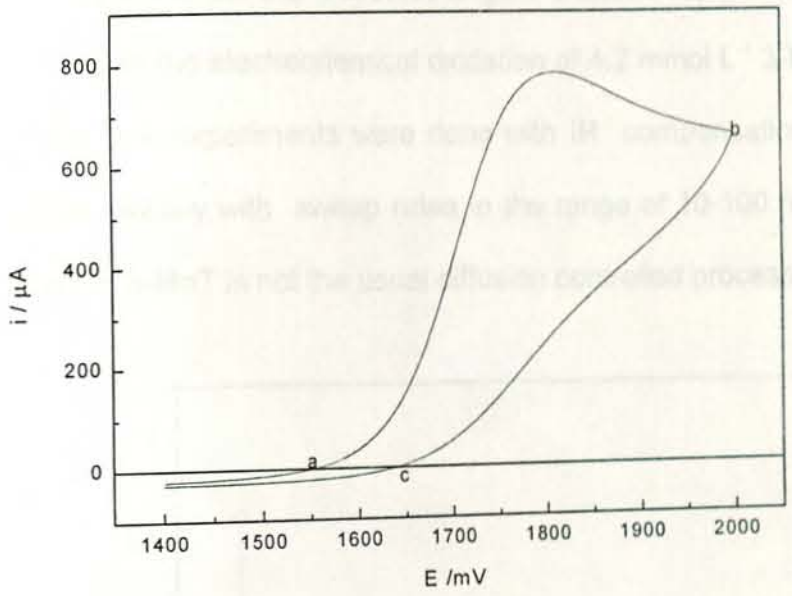


Fig. 8. The cyclic voltammogram of 4.2 mmol L^{-1} in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN at a stationary Pt electrode (scan rate of 100 mV/s).

The charge can be calculated from the area using equation (7) [34].

$$Q = \frac{A}{v} \qquad (7)$$

Where Q is the total charge passed, v is the sweep rate and A is the area of the cyclic voltammogram under the I-E curve. Figure 9 shows the plot of the charge Q against sweep rate in the electrochemical oxidation of 4.2 mmol L^{-1} 3-MeT at a stationary Pt electrode. The experiments were done with IR compensation. The charge passed decreases quickly with sweep rates in the range of 10-100 mV/s. This shows the oxidation of 3-MeT is not the usual diffusion controlled process type.

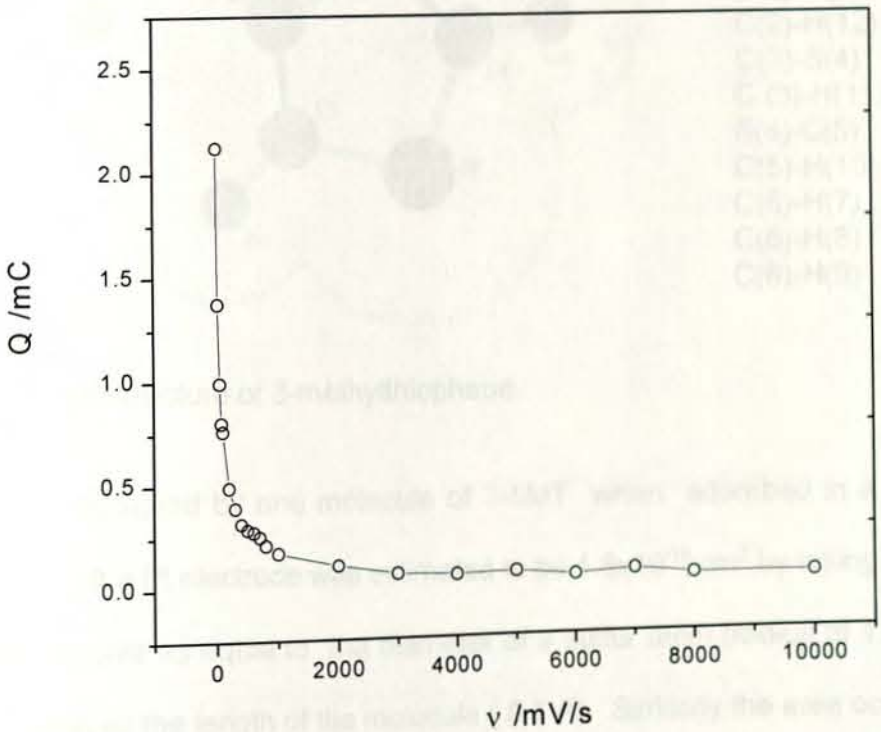
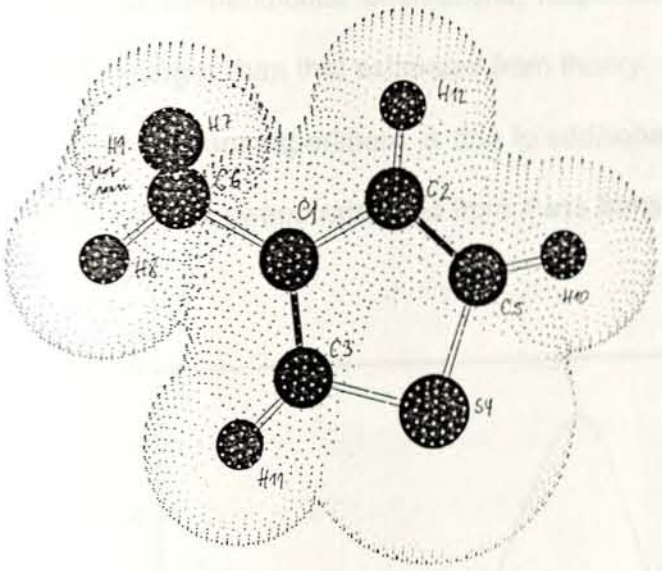


Fig. 9. The dependance of the charge passed on sweep rates during the anodic oxidation of 4.2 mmol L^{-1} 3-MeT in 0.1 mol L^{-1} $LiClO_4$ +CH_3CN on stationary Pt electrode.

In a diffusion controlled reaction the charge passed slowly decrease with a sweep rate. That means in this process there is adsorption of the substance that makes the charge passed immediately fall with sweep rates. At higher sweep rates the charge passed attained a limiting value. At larger sweep rates the charge passed mostly through the oxidation of the adsorbed molecules. Because the time scale is so fast that contribution from the oxidation of the monomer coming by diffusion is low. The final limiting charge attained was found to be 0.13 mC (Fig. 9).



Atoms	Bond length(A)
C(1)-C(2)	1.461
C(1)-C(3)	1.381
C(1)-C(6)	1.494
C(2)-C(5)	1.373
C(2)-H(12)	1.082
C(3)-S(4)	1.677
C (3)-H(11)	1.082
S(4)-C(5)	1.677
C(5)-H(10)	1.081
C(6)-H(7)	1.110
C(6)-H(8)	1.109
C(6)-H(9)	1.111

Fig. 10. The structure of 3-methylthiophene.

The area occupied by one molecule of 3-MeT when adsorbed in a perpendicular orientation at a Pt electrode was estimated to be 1.8×10^{-15} cm^2 by taking the thickness of the molecule as equal to the diameter of a sulfur atom (radius of 1.02 A) and the longest side as the length of the molecule (8.7 A). Similarly the area occupied by one molecule when it is adsorbed in a parallel orientation was calculated. In this case the thickness (2.01 A) and the length (9.1 A) was estimated from the structure of 3-MeT

(Fig. 10). Using these values the area occupied by one molecule was calculated to be $1.8x10^{-16}$ cm^2.

From the area of the electrode (0.07 cm^2) the maximum number of molecules that can be on the surface of the electrode was calculated to be ($3.9x10^{13}$ and $3.8x10^{13}$). Multiplying this numbers by the charge of an electron, the limiting charges passed were estimated to be $6.309x10^{-6}$ C and $6.15x10^{-6}$ C, when the 3-MeT units are adsorbed in parallel and perpendicular orientations, respectively. The result obtained in the experiment is larger than that estimated from theory. The higher value of the charge passed obtained from experiment is due to additional contribution from double layer charging at highest sweep rates and from mass transport of 3-MeT by diffusion.

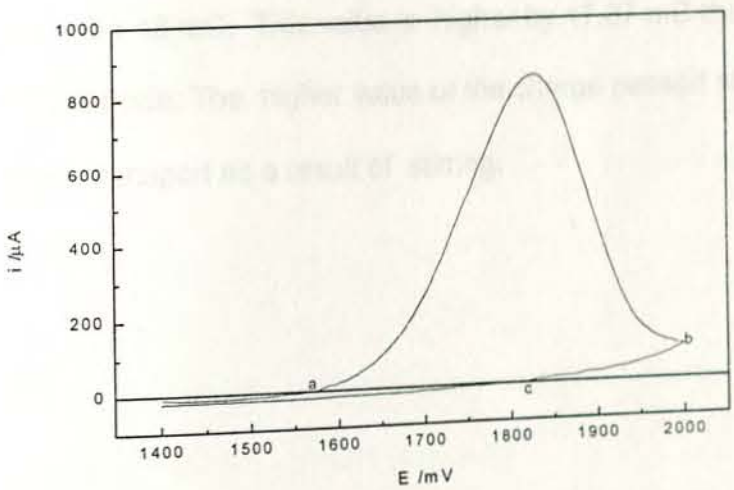


Fig. 11. The cyclic voltammogram of 4.2 mmol L^{-1} in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN at a rotating electrode (3000 rev/min) and at a scan rate of 10 mV/s.

Figure 11 shows the cyclic voltammogram of 4.2 mmol L^{-1} 3-MeT obtained at a rotating Pt electrode. In a rotating electrode the diffusion layer thickness is independent of time and results in a limiting current for a diffusion controlled process. In our case we obtained a peak rather than a limiting current (Fig. 11). This indicates that the reaction is not controlled by diffusion. The charge passed calculated by integrating the curve Fig. 11 the same as in the stationary case.

The charge passed in a stirred solution is shown in Fig. 12 as a function of the square root of angular frequency. It is observed that the charge passed during the anodic oxidation of 4.2 mmol L^{-1} 3-MeT is independent of the rotational speed of the electrode (for $\omega^{1/2}$ = 10.33, 12.53 and 14.49 $rps^{1/2}$). This shows that diffusion is not a rate determining step. The average charge passed in the range of 5-25 mV/s sweep rates was found to be 18 mC. This value is higher by 17.87 mC than that obtained on the stationary electrode. The higher value of the charge passed at a rotating electrode is due to mass transport as a result of stirring.

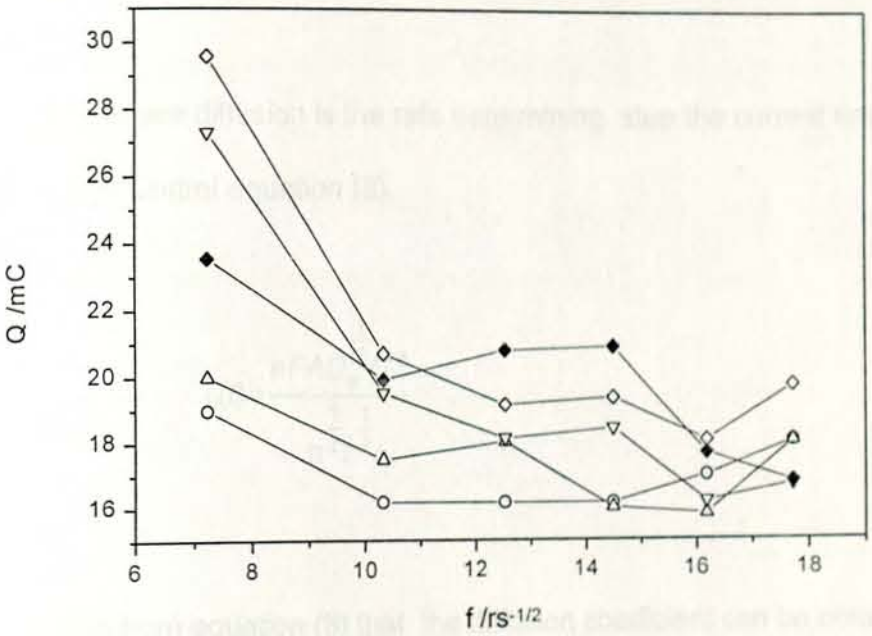


Fig. 12. The dependance of the charge passed during the anodic oxidation of 4.2 mmol L^{-1} 3-MeT in 0.1 mol L^{-1} $LiClO_4$ +CH_3CN on rotating Pt electrode (at a scan rate of (○) 5 mv/s, (△) 10 mV/s, (▽)15 mV/s, (◇) 20 mV/s and(♦) 25 mV/s).

4.3. **Chronoamperometric, potentiostatic experiment on the electropolymerization of 3-methylthiophene at Pt electrode**

In chronoamperometry, the potential is stepped from an initial value where no oxidation takes place to a potential within the limiting current region. The resulting current is recorded as a function of time. If the potential is stepped back to the initial value after

a certain time, the technique is termed double potential chronoamperometry. In our experiment we employed the double potential step.

In a process where diffusion is the rate determining step the current time relationship is given by the Cottrel equation (8).

$$i_l(t) = \frac{nFAD_o^{\frac{1}{2}} C^b}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}} \qquad (8)$$

It can be seen from equation (8) that the diffusion coefficient can be obtained from the slope of i_l *versus* $t^{-1/2}$. Only if the potential is stepped to a value within the limiting current region is the Cottrel equation applicable. The potential of 2 V is only 200 mV more positive than the peak potential of 3-MeT (1.81 V). The diffusion coefficient of 3-MeT obtained with chronoamperometric experiment at 2 V is found to be 5.14 $x10^{-5}$ cm^2s^{-1}, a value which is comparable with that found from voltammetry (8.67$x10^{-5}$ cm^2s^{-1}).

The current response on rotating Pt electrode at potential of 1.8 V is shown in Fig. 13. The current continuously falls down at short times independent of the angular frequency. In a rotating electrode the diffusion layer thickness remains constant. It is expected that the current remains constant if the process were diffusion controlled. This shows diffusion is not a rate determining step in the oxidation of 3-MeT.

The effect of the applied potential on the oxidation of 3-MeT with a rotational speed of (3000 rev/min) is shown in Fig. 14. As the potential is made more anodic (1.9 to 2.2 V) two distinct processes occur as shown in the Fig. 14 b-d. First the current decreases sharply as a result of charging the double layer . Then for 5 seconds the current decrease slowly, proportional to the square root of time. This means that for a very short period of time the process is most likely diffusion controlled.

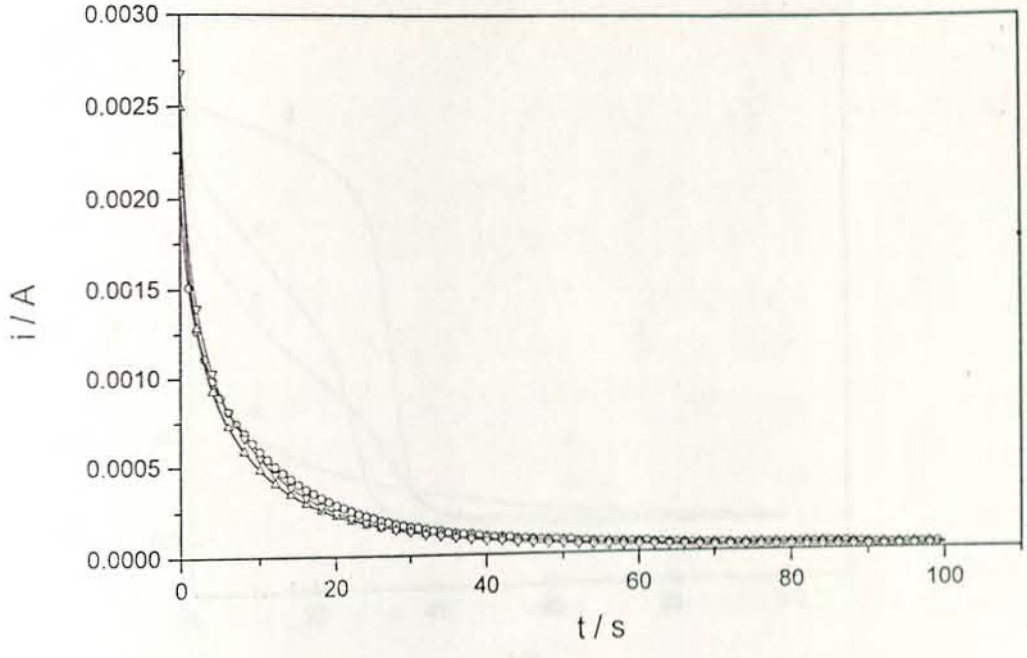


Fig. 13. The response of current as a function of time at constant potential with different rotating speed of a Pt electrode (○) 1000 rev/min, (△) 2000 rev/min and (▽) 3000 rev/min electrolyte 4.2 mmol L^{-1} 3-MeT in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN.

At a later time, the current decreases sharply. At this point the mechanism of the reaction changes, because no more diffusion controlled. At longer times, the current

decreases continuously and approaches zero with high applied potential. In all cases a blue deposit was observed which poorly adhered to the electrode. The potentiostatic experiment generally indicates there is a reaction product that blocks the electrode at time passes and diffusion is not a rate determining step.

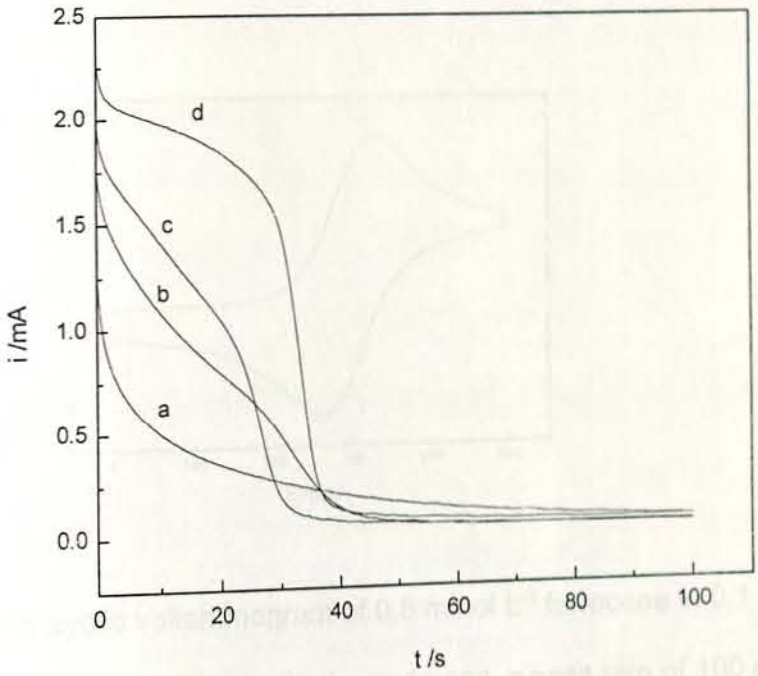


Fig. 14. The response of current with time at different applied potentials on the electrochemical oxidation of 4.2 mmol L^{-1} 3-MeT in 0.1 mol L^{-1} $LiClO_4$ in acetonitrile at a rotational speed of 3000 rev/min. (a) 1.8 V, (b) 1.9 V, (C) 2.0 V, and (d) 2.2 V.

4.4. Comparison of the diffusion coefficients of ferrocene, 3-methylthiophene and thiophene

To compare the diffusion coefficient of ferrocene, which is a well known standard, reversible one electron transfer reaction, with 3-MeT and thiophene, 0.5 mmol L^{-1} feroccene was oxidized under similar conditions as 3-MeT in acetonitrile. The oxidation peak potential was found to be 0.33 V (Fig. 15).

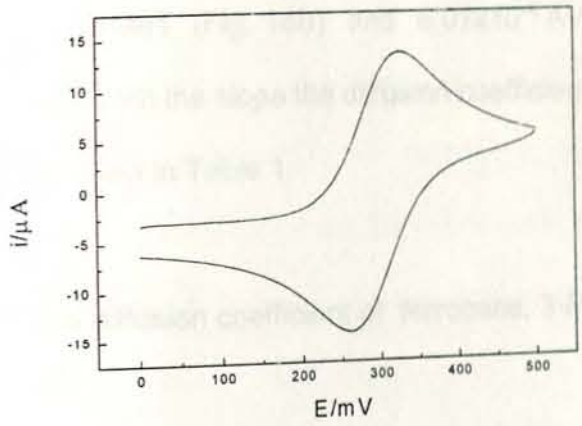


Fig. 15. The cyclic voltammogram of 0.5 mmol L^{-1} ferrocene in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN at stationary Pt electrode and a scan rate of 100 mV/s.

The peak current increases against with sweep rates while the peak potential remains constant which are the characteristics of reversible electrochemical oxidation reactions. From the plot of peak current with the square root of sweep rates, it is possible to determine the diffusion coefficient of ferrocene from the slope using Randles-Sevcik equation (9).

$$i=2.69x10^5 n^{\frac{3}{2}} D^{\frac{1}{2}} v^{\frac{1}{2}} C \qquad (9)$$

Where i is the anodic peak current, n is the number of electrons involved, D is the diffusion coefficient of the electroactive species, C is the concentration and v is the sweep rate. Fig. 16A shows the dependance of peak current with the square root of the sweep rate in the electrochemical oxidation of ferrocene and a good fit was obtained with a slope of $4.80x10^{-5}$ A $V^{1/2}S^{-1/2}$. Similarly the slope obtained was $9.17x\ 10^{-4}$ A $V^{1/2}S^{-1/2}$ for 3-MeT (Fig. 16B) and $6.07x10^{-4}$ $AV^{1/2}S^{-1/2}$ for thiophene (Fig. 16C), respectively. From the slope the diffusion coefficient was calculated using equation (9) and this is shown in Table 1.

Table 1. The diffusion coefficient of ferrocene, 3-MeT and thiophene

	Diffusion coefficient	
Molecule	Experimental /$cm^2\ s^{-1}$	Theoretical / cm^2s^{-1}
Ferrocene	$2.60x10^{-5}$	$9.78x10^{-6}$
3-Methylthiophene	$8.77x10^{-5}$	$2.07x10^{-5}$
Thiophene	$1.66x10^{-4}$	$3.06x10^{-5}$

The larger value of the diffusion coefficient of 3-MeT and thiophene compared with ferrocene is due to the smaller molecular size of the molecules. According to the Einstein-Stokes equation (10) the larger the molecular size the lower the diffusion coefficient [35]. The hydrodynamic radii of ferrocene, 3-MeT and thiophene, estimated

from the bond lengths were found to be 6.05 A, 2.86 A and 2.0 A respectively. The larger the molecular radius the smaller the diffusion coefficient.

$$D = \frac{kT}{6\pi\eta r} \qquad (10)$$

Where D is the diffusion coefficient, η is the viscosity of the solvent (acetonitrile = 0.369 centipoise), r is the hydrodynamic molecular radius, k is the Boltzmann constant and T is the temperature.

The ratio of the diffusion coefficient of 3-MeT to that of ferrocene obtained experimentally was 3.37 while that estimated theoretically is 2.12. The ratio for thiophene to ferrocene obtained experimentally was 6.38 while that estimated theoretically was 3.13. It is seen that no agreement was found between the values obtained experimentally and theoretically. The reason may be because the hydrodynamic radius estimated from the bond length is not the actual value of the diffusing species.

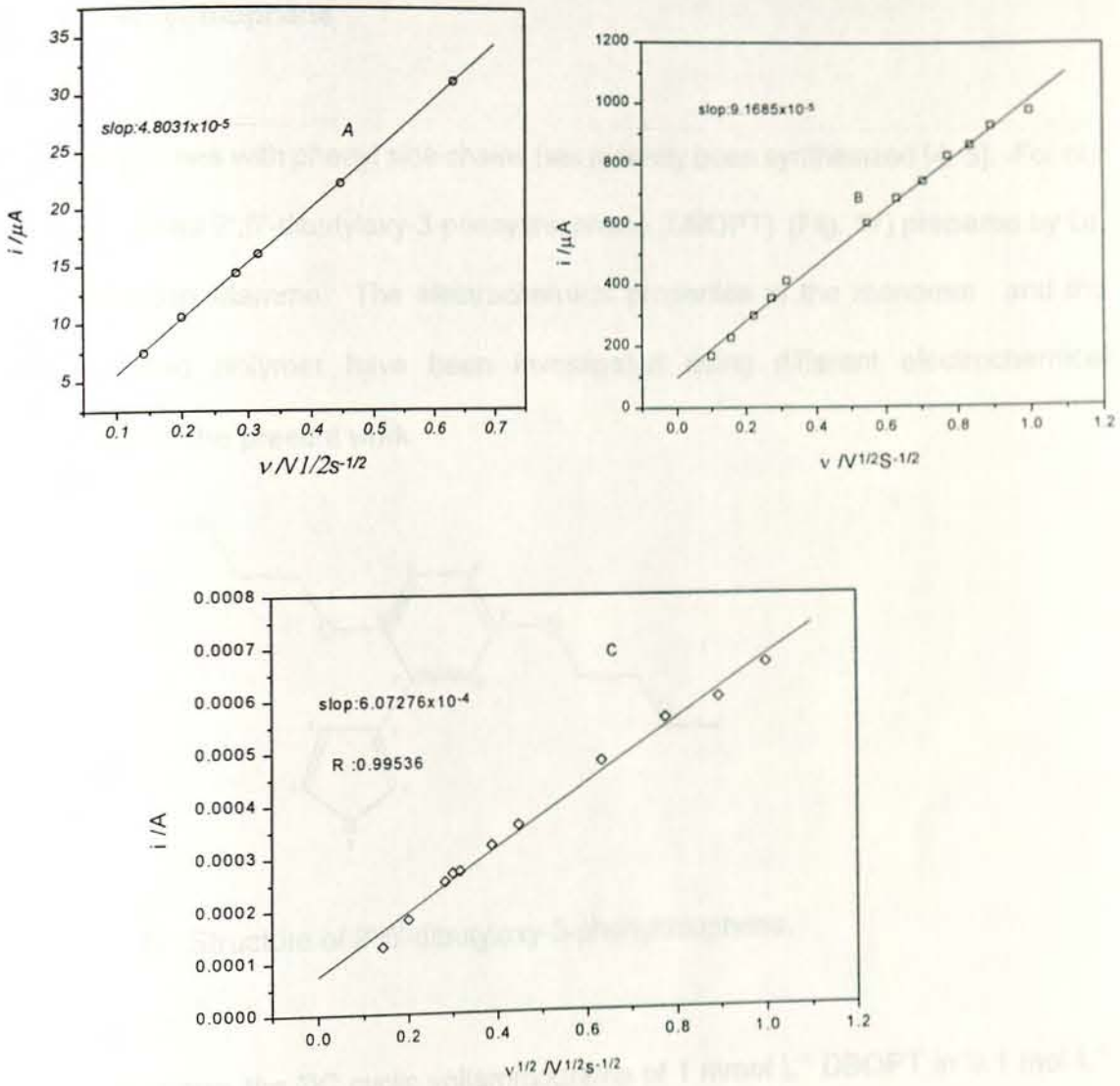


Fig. 16. The plot of the dependence of Peak current *versus* the square root of scan rates (A) 0.5 mmol L^{-1} ferrocene, (B) 5.2 mmol L^{-1} 3-MeT and (C) 2.5 mmol L^{-1} thiophene on a stationary Pt electrode.

4.5 Electrochemical oxidation and polymerization of 2',5'-dibutyloxy-3-phenylthiophene

New thiophenes with phenyl side chains has recently been synthesized [4, 5]. For our study we select 2',5'-dibutyloxy-3-phenylthiophene (DBOPT) (Fig. 17) prepared by Dr. Wendimagegn Mammo. The electrochemical properties of the monomer and the corresponding polymer have been investigated using different electrochemical techniques in the present work.

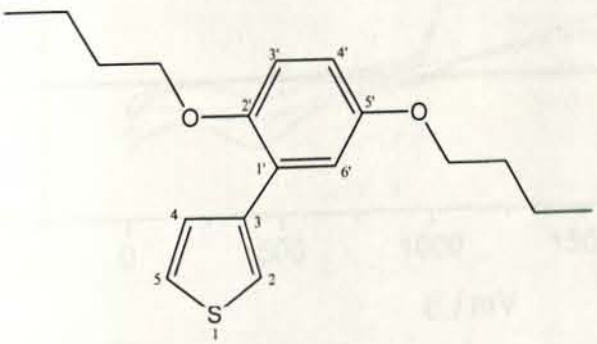


Fig. 17. Structure of 2',5'-dibutyloxy-3-phenylthiophene.

Figure 18 shows the DC cyclic voltammograms of 1 mmol L^{-1} DBOPT in 0.1 mol L^{-1} $LiClO_4$ in acetonitrile on a stationary Pt electrode. The cyclic voltammogram revealed three anodic oxidation peaks. The first peak potential was found at 1.15 V, the second at 1.45 V and third peak occurred around 1.91 V *versus* Ag/AgCl quasi- reference electrode. In addition to this, a reduction peak was observed at 0.42 V. The first peak is due to the oxidation of thiophene which is believed to have highest electron density at carbon atom four. The second and the third anodic peaks are most probably the result of the oxidation of the lone pairs of the oxygen atoms in the molecule.

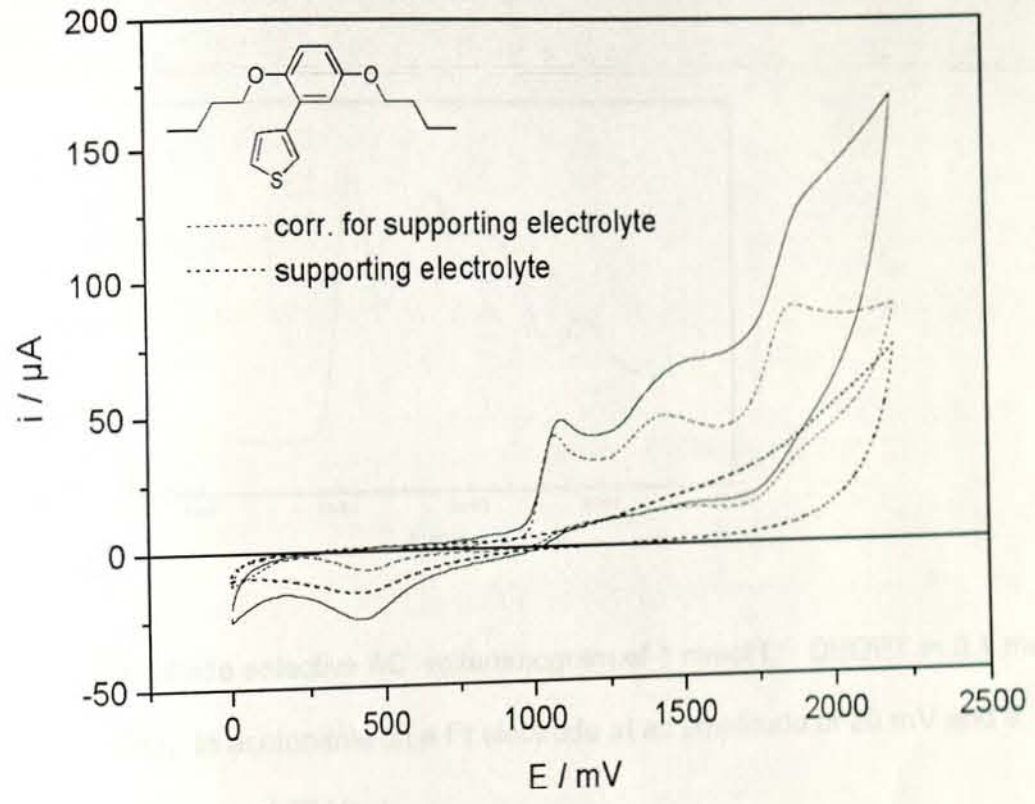


Fig. 18. Cyclic voltammograms of 1 mmol L^{-1} DBOPT in 0.1 mol L^{-1} $LiClO_4$ + CH_3CN on a stationary Pt electrode at a scan rate of 100 mV/s.

The AC voltammogram of 1 mmol L^{-1} DBOPT on a Pt electrode is shown in Fig. 19. AC voltammetry is a technique in which AC voltage of small- amplitude is superimposed on a linear voltage ramp. The AC signal thus causes a perturbation in the surface concentration, around the concentration maintained by the DC potential. The resulting AC current is displayed *versus* the potential in Fig. 19. Phase selective AC voltammetry is preferable for quantitative information. This is because phase selective

AC voltammetry discriminates the charging current and gives only the faradaic response.

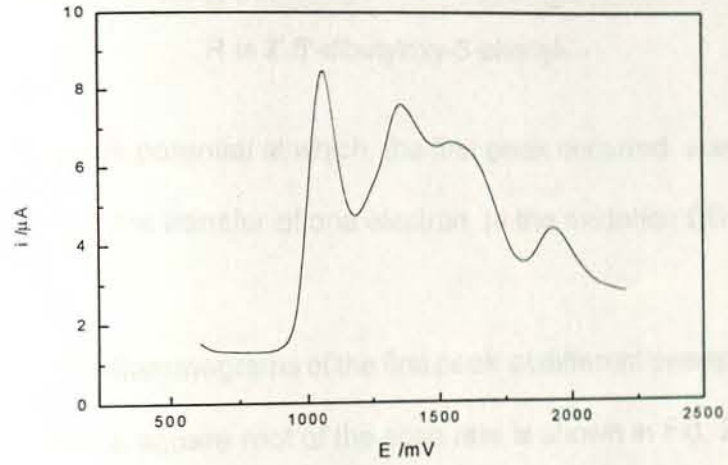
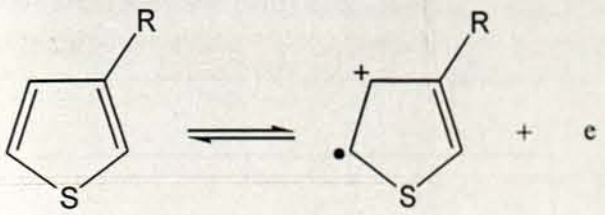


Fig. 19. The phase selective AC voltammogram of 1 mmol L^{-1} DBOPT in 0.1 mol L^{-1} $LiClO_4$ in acetonitrile on a Pt electrode at ac amplitude of 20 mV and a frequency of 35 Hz.

Diffusion controlled process is shown in AC-experiment by peak widths of 90/n mV regardless of scan rates [36]. The three peaks observed in the DC voltammogram are observed at less anodic peak potential in the ac voltammogram (Fig. 19). The AC voltammogram shows reversible electron transfer reaction. The reaction is shown below. There is no peak separation for the forward and the reverse scans in Fig. 19. The time scale of the ac experiment allows the radical to have enough time to reduce back and give a peak if the process were irreversible.



R is 2',5'-dibutyloxy-3-phenyl-

The half peak potential at which the first peak occurred was found to be 50 mV. This attributes to the transfer of one electron in the oxidation DBOPT at this position.

The cyclic voltammograms of the first peak at different sweep rates and the plot of peak current with a square root of the scan rate is shown in Fig. 20. It is observed that the peak potential does not vary significantly with scan rates as was observed in the case of 3-MeT. This also shows the reversibility of the process. From the slope of peak current versus the square root of scan rates (1.4589×10^{-4} $AV^{1/2}s^{-1/2}$) the diffusion coefficient was found to be 6.0×10^{-5} cm^2/s.

Comparing the diffusion coefficient of DBOPT obtained with that of 3-MeT (8.67 cm^2s^{-1}) it is observed that they are in the same range of magnitude, although there is a bulky substituent on the thiophene ring in DBOPT. From this it is possible to say that the size the molecule is not the only determining factor that makes the diffusion coefficient large or small.

Potentiostatic oxidation of DBOPT by applying a potential at which the first peak appeared (1.2 V) gave polymer film. At this potential DBOPT starts to polymerize.

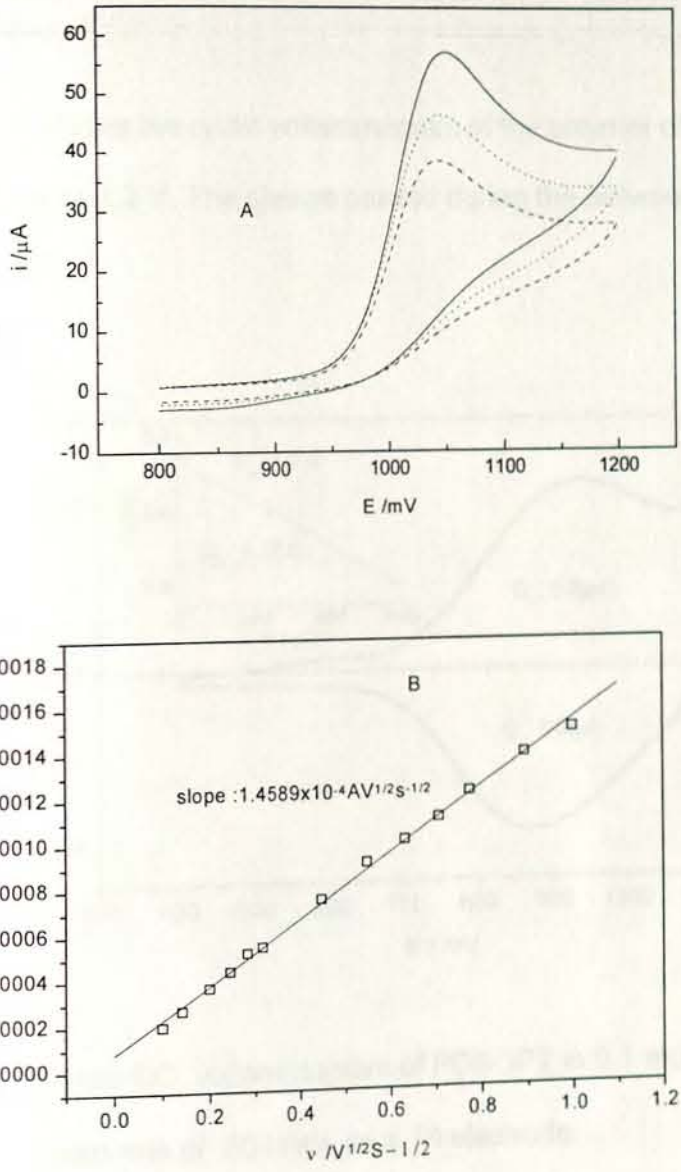


Fig. 20. (A) The cyclic voltammograms of 1 mmol L^{-1} at different scan rates (-) 100 mv/s, (.....) 60 mv/s (---) 40 mv/s, (B) the plot of peak current versus the square root of the scan rate.

The first peak corresponds to the oxidation of the thiophene which has a high electron density according to indirect molecular electron density calculations at the C_4 (carbon four)position. It is also observed that the polymer covered the electrode.

Figure 21 shows the cyclic voltammogram of the polymer of DBOPT grown by applying a potential of 1.2 V. The charge passed during the polymer growth was 0.37 C.

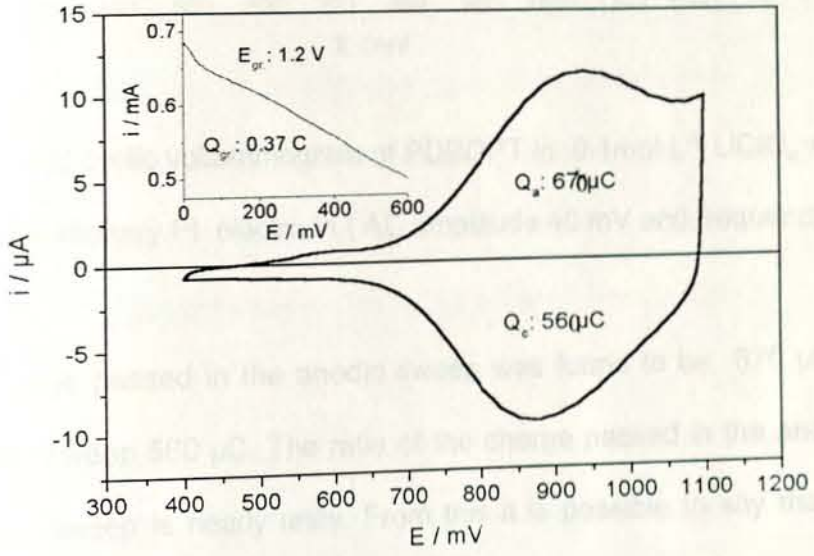


Fig. 21. Cyclic DC voltammogram of PDBOPT in 0.1 mol L^{-1} M $LiClO_4$ + CH_3CN at a scan rate of 50 mV/s on a Pt electrode.

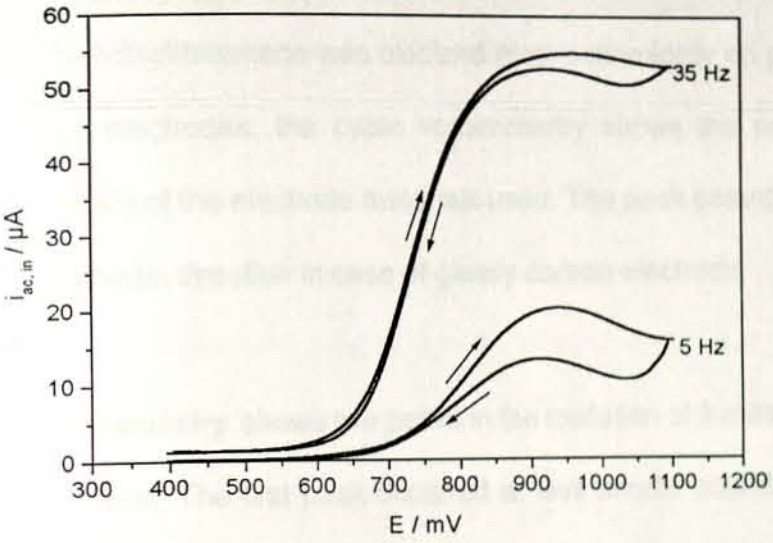


Fig. 22. AC cyclic voltammogram of PDBOPT in 0.1mol L^{-1} $LiClO_4$ + CH_3CN at a stationary Pt electrode (AC amplitude 40 mV and frequency of 5 and 35 Hz).

The charge passed in the anodic sweep was found to be 670 µC whereas in the cathodic sweep 560 µC. The ratio of the charge passed in the anodic sweep to the cathodic sweep is nearly unity. From this it is possible to say that the doping and dedoping of PDBOPT is nearly reversible.

The AC voltammogram of the same polymer is shown in Fig. 22 at different frequency. It was found that the process is AC reversible in this case also and the peak current increases as the frequency increased. The peak potential of the forward and the reverse scan also have the same value at the frequency of 5 Hz compare with that of 35 HZ.

5. **Conclusion**

When 3-methylthiophene was oxidized electrochemically on platinium, glassy carbon and gold electrodes, the cyclic voltammertry shows the peak potential is almost independent of the electrode materials used. The peak potential is only slightly shifted in the cathodic direction in case of glassy carbon electrode.

Cyclic voltammetry shows two peaks in the oxidation of 3-methylthiophene at a higher concentration. The first peak occurred at less anodic potential relative to that of the single peak observed at low concentration. This indicates that the first peak is as a result of product adsorption. The observed prepeak appeared on all electrodes. The preadsorption peak response was particularly pronounced at a platinium electrode. This has not been reported earlier. This may be due to the structure of the platinium metal.

From this adsorption process, it seems that the initial stage of polymerization took place on the electrode surface. Adsorption and diffusion contribute to the formation of the polymer. The former is the dominant contribution at high concentration of the monomer.

In the oxidation of 3-metylthiophene, a current loop was observed in the subsequent cycle. This has been reported to be a sign of the instantaneous precipitation of the oligomers which are formed in the solution on the electrode surface [10].

The decrease of current continuously with time during the oxidation of 3-methylthiophene on a rotating Pt electrode under potentiostatic conditions indicates

diffusion is not a rate determining step in the oxidation of 3-MeT. The effect of applied potential was also noted. As the potential was made more positive, two distinct processes were observed.

The limiting charge obtained from the sweep rate dependance on stationary Pt electrode was also comparable with that calculated from the monolayer coverage of the electrode in a perpendicular or parallel orientation. The higher value of the limiting charge obtained on a rotating platinium electrode compared with a stationary one shows also the contribution of mass transport in the oxidation process.

The larger value of the diffusion coefficient of 3-methylthiophene and thiophene compared with ferrocene is because of the smaller molecular size of 3-methylthiophene and thiophene. That is as theoretically expected.

The oxidation of 2', 5'-dibutyloxy-3-phenylthiophene shows at least three anodic peaks. The first corresponds to the oxidation of the thiophene ring, which is believed to have highest electron density. This also confirms that the polymerization starts at this potential. The other peaks may be as a result of oxidation of the lone pairs of the oxygen atom. AC voltammetry shows reversible oxidation of 2',5'-dibutyloxy-3-phenylthiophene. The polymer of this compound also behaves reversibility in both DC and AC voltammetry.

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DECLARATION

I the undersigned, declare that this thesis is my original work and has not been presented for a degree in any other university.

Signature

Name : Abebaw Adgo _____

This thesis has been submitted for examination with our approval as University Advisors.

Name	Signature
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