Fen Bilimleri Dergisi Sayı: 12 2011

REDUCTION OF SOME DITHIOPHOSPHONATES IN APROTIC MEDIA ON FRESHLY COPPER PLATED GLASSY CARBON ELECTRODE

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Abstract

Dithiophosphonates are reduced electrochemically with two electron transfer in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) at a freshly copper plated GC electrode. The peaks for all of the dithiophosphonate derivatives were observed at about –1.5 V (vs. Ag/Ag^+) at copper plated GC electrode. Data revealed that the reduction process on copper electrode was irreversible and followed by EC mechanism. The diffusion coefficients and numbers of electrons transferred were found by UME electrode using Baranski method. The adsorption tests were applied to examine the adsorption characteristics of the derivatives under investigation. Simulation CV voltammograms of dithiophosphonates were acquired by DigiSim® 3.03 version and compared with the experimental voltammograms to calculate the chemical and electrochemical constants.

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Key words: Dithiophosphonates, electrochemical reduction, cyclic voltammetry, digital simulation, chronoamperometry, adsorption, ultramicro electrode.

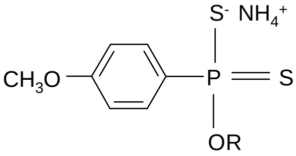
Introduction

Dithiophosphonates are important class of compounds which have found some applications in medical and agricultural areas. Considerable studies concerning this important group of compounds have been encountered in literature in recent years. They have found an application in the chemotherapy to combat following diseases; adenocarcinoma of breast, adenocarcinoma of the ovary, intracavitary affisions, bladder cancer, lymphoma [1, 2]. Dithiophosphonates are effective therapeutic agents for the treatment of acquired immune deficiency syndrome (AIDS) and reverse transcriptase [3]. They are known to possess biologically important properties [4] and may also inhibit hydrocarbon oxidation [5]. Some dithiophosphonates have been used as insecticides [6] and nematocides [7], and their salts are useful as antioxidants in lubricants and plastics [8]. Despite these applications the use of dithiophosphonates and their complexes have been poorly investigated. Thiophosphorous ligands represent an important class of S-donor ligands. Members of this class include dithiophosphates, dithiophosphinates and dithiophosphonates. Generally this molecules can be synthesized as ammonium salts by reacting Lawesson's reagent, $[S_2P(p\text{-}C_6H_4OMe)_2]$, appropriate type of alcohol in benzene by bubbling $NH_3(g)$ through the solution [9]. Dithiophosphonates and dithiophosphinates and related compounds have been reviewed by Haiduc [10].

Electrochemical behaviour of dithiophosphonates and related -P=S- containing compounds are important from the point of view of determination in various samples and uses in medical purposes. Electrochemical studies that have been carried out about the dithiophosphonates and related compounds bearing -P=S- group are summarized as follows:

Marin et al. have used electrochemical methods to study the hydrolysis of thiotepa (TT), which possesses a P=S bond, at pH 4.2 and thiotepa interactions with DNA. It has been shown that the anticancer activity of TT, which is also a well-known mutagen, is connected with the formation of covalent bond to DNA. It has been shown that in DC polarography the TT is inactive but, the hydrolysis product TT-SH produces a diffusion controlled anodic wave [11]. Schischkov et al. studied the electrochemical behavior of bis(diphenyldithi-phosphine)disulphide (RSSR) and mercuric diphenyldithiophosphinate [$(RS)_2Hg$] in ethanol-lithium perchlorate and ethanol-sulphuric acid media by the methods of classical polarography and electrolysis at controlled-potential at a rotating disc platinum electrode. The data obtained show that RSSR is not reduced directly on the dropping mercury electrode but is adsorbed to form $(RS)_2Hg$. The electrolysis at controlled potential proves that $(RS)_2Hg$ undergoes a two-electron reduction [12]. Nikitin et al. investigated the electrochemistry of phosphorylation of alkenes that produced –P=O- group that might show similar electrochemical behaviour with –P=S group. They were found that anodically generated radical-cations of trialkyl phosphites, dialkyl trimethylsilyl phosphites, mono and diamidophosphites were added to olefin molecules to give unsaturated alkenephosphonates [13]. Blankespoor examined the electrochemical oxidation of zinc bis(O,O-di-Et-phosphorodithioate-S,S') and zinc bis(O,O-(bis(1-methylethyl)-phosphorodithioate-S,S') at glassy carbon electrode. This study provides a basis for using electrochemical techniques in the quantitative analysis of former compound in hydrocarbon samples. They observed irreversible waves with peak potentials of +1.5 V by using cyclic voltammetry [14]. Cheng et al. studied electroanalytical application of Tosflex, a perfluoro-anion exchange membrane, is demonstrated using diethyldithiophosphoric acid (DEDTP). They reported that DEDTP undergone dimerization upon electrochemical oxidation at a glassy carbon electrode (GCE) in pH 5.5 solution [15]. Nabaoi et al. found that the cationic Nb(V) species were an effective catalyst for the electrochemical oxidation of triphenylphosphine. Indirect anodic oxidation in the presence of water gives triphenylphosphine oxide in good yields [16]. Zeng et al. studied electrocatalytic oxidation of hypophosphite on a nickel electrode by cyclic voltammetry and used UV spectroscopy to obtain information about the oxidation mechanism [17]. Vagina et al. investigated the electrochemical reduction of boryl phosphinoethene in nonaqueous medium. The electrolysis of boryl phosphinoethene was carried out at constant potential. Formed products were isolated and identified. The P-C bond cleavage was observed during the reduction of this molecule in an aprotic medium [18]. Mueller et al. examined relation between the electrosorption of homologous dialkylphosphine and trialkylphosphine oxides and their inhibitive effect on the rate of electrode reactions [19]. Hicyilmaz et al. determined the response of the surface of pyrite to copper activation in the presence and absence of sodium diisobutyl dithiophosphinates (DTPI) under electrochemically controlled conditions. The mechanism of interactions between the concerned reagents and pyrite was investigated using cyclic voltammetry in solutions of different pH [20].

In the present work, we studied electroreduction of some dithiophosphonates, namely ammonium-*o*-alkyl(4-methoxyphenyl)dithiophosphonates where alkyl groups (R) are -methyl (*MDTP)*, -ethyl (*EDTP), -n*-propyl (*PDTP), -iso*propyl (*IPDTP), -n*-butyl (*BDTP)* and ammonium-*o*-phenyl(4-methoxyphenyl)dithiophosphonate (*PhDTP)* on freshly copper plated glassy carbon electrode in nonaqueous media by cyclic voltammetry (CV), chronoamperometry (CA) and square wave voltammetry (SWV). The electrochemical behaviour was discussed and the mechanism of the reduction and kinetic parameters was evaluated.



The molecular structures of the dithiophosphonates (R is –methyl, -ethyl, -*n*-propyl, -*iso*propyl, -*n*-butyl and -*o*-phenyl).

Experimental

Tetrabutylammoniumtetrafluoroborate (TBATFB) (Merck), Lawesson reagent and aliphatic alcohols (Merck), activated carbon (Aldrich) and acetonitrile (Aldrich) were used as received. Ultra pure water was obtained from Human Power I+ water purification system and output resistance was 18.3 MΩ·cm. The voltammetric measurements were carried out with a BAS100B Model Electrochemical Analyzer equipped with a BAS C-2 Cell Stand and these systems were connected to a computer and the data was processed with the software of the instrument. All experiments were carried out in a three electrode cell with a working electrode of Cu plated GC electrode, a platinum wire auxiliary electrode and a reference electrode of $Ag|Ag^+$ with an inner solution of 0.01 M $AgNO_3$ dissolved in acetonitrile containing 0.1 M TBATFB. GC ultramicroelectrode (UME, 10 μm BAS Model MF 2007) was used to calculate the number of electrons by Baranski method [21]. All measurements were performed at room temperature (25 ± 1 ^oC) and all solutions were deaerated with pure argon gas for at least 10 min. before executing the voltammetric experiments. GC electrodes were polished successively in 1 μm, 0.3 μm, and 0.05 μm alumina slurries prepared from dry Buehler alumina powder and Ultra Pure water (18.3 MΩ·cm) on Buehler polishing microcloth. Polished GC electrodes were sonicated in Ultra Pure water and then in a mixture of 50:50 (v/v) 2-propanol/acetonitrile treated with an equal volume of Norit A activated carbon.

Dithiophosphonates were synthesized by the addition reaction between 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiodiphosphetane-2,4-disulfide (Lawesson reagent) and alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol and phenyl alcohol and then treated with dry ammonia, as described in our previous paper [22].

Results and discussion

Plating of GC electrode with copper

GC electrode was plated with copper under 1, 3, 4, and 10 CV cycles to test the completeness of the copper coverage of GC electrode. As Figure 1 shows, plating of the surface is almost complete after 2 CV cycles. But to be sure about the Cu electrode, plating was achieved in 4 cycles. The voltammogram was taken at 200 mV s^{-1} scan rate and from -0.1 V to -0.97 V. In either case the irreversible peak current decreases with the number of potential cycles and reaches a steady state condition after a few cycles.

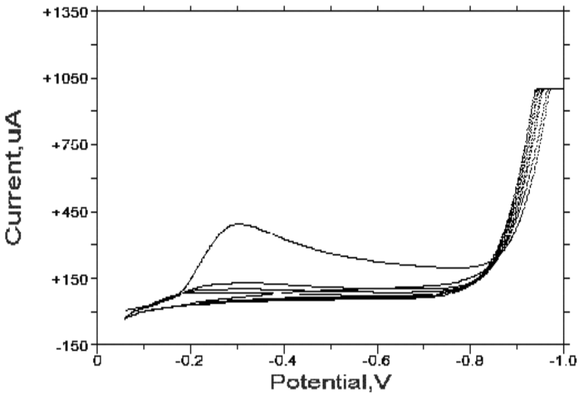


Fig. 1. Plating of copper (as $CuSO_4$) by multi sweep cyclic voltammetry on GC electrode (v= 0.2 V/s) (vs. Ag/Ag^+ electrode).

The completeness of Cu coverage of the GC surface was tested in acetonitrile (0.1 M TBATFB) solution containing BDTP dithiophosphonate derivative. Figure 2 shows the voltammograms of BDTP on the different number of plating cycles. This figure shows that BDTP reduced giving the same peak current and peak potential for different number of plating cycles. Although the GC surface was covered in 1 cycle plating, we decided 4 cycles coverage to be sure about the Cu electrode. This electrode will be designated as Cu-GC from now on.

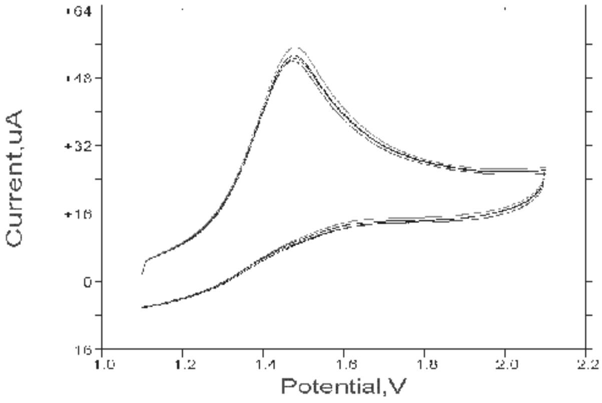


Fig. 2. Reduction of BDTP after plating of GC electrode with copper with 1, 3, 4, and 10 CV cycles by cyclic voltammetry, v = 0.1 V/s (vs. Ag/Ag^+ electrode).

Cyclic voltammetry of dithiophosphonates on Cu-GC electrode

The voltammograms of 1 mM dithiophosphonates in solutions containing acetonitrile and 0.1 M TBATFB on copper plated GC electrode is shown in Fig. 3. As can be seen from this figure, the reduction potentials of these molecules were observed around -1.5 V at 100 mV/s. No anodic peak was observed for each molecule. Reduction peaks for each compound correspond to the 2-electron irreversible wave on Cu-GC electrode. When the scan rate was changed from10 mV/s to50000 mV/s, reduction peak potentials were shifted towards the negative values. The peaks are very sensitive to the amount of oxygen dissolved in the medium. When the solution was not deaerated the peak of the molecule was merged into the large oxygen peak. Thus it is important to emphasize that the removal of the dissolved oxygen is crucial for the voltammetric studies of the dithiophosphonates.

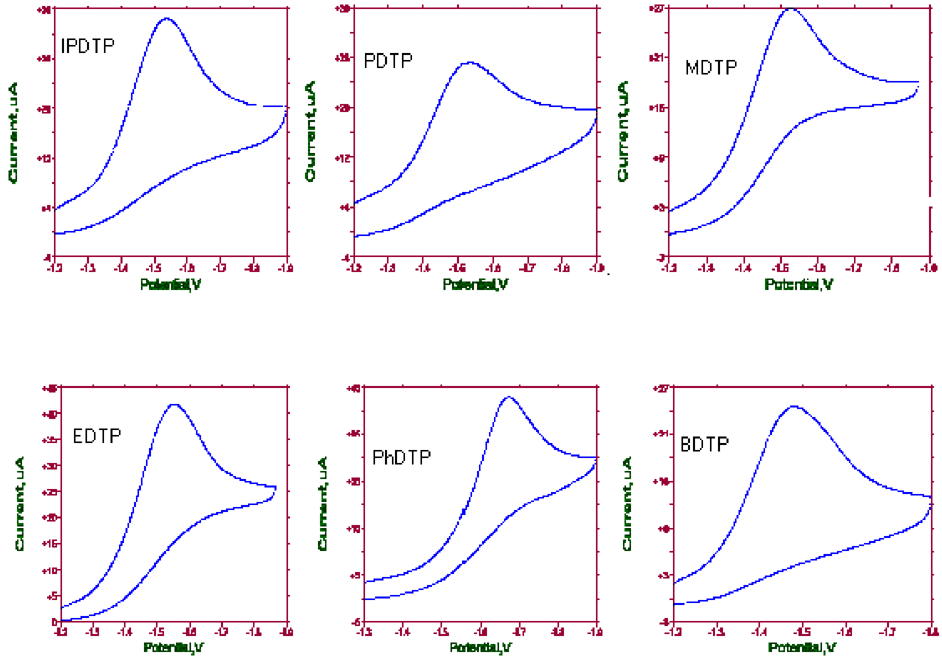


Fig. 3. Cyclic voltammograms of 1 mM dithiophosphonates in acetonitrile (0.1 M TBATFB) on Cu-GC electrode at a scan rate of 0.1 V s^{-1}.(vs. Ag/Ag^{+} electrode).

Determination of diffusion coefficients and the number of electrons transferred

The number of electrons transferred (n) and diffusion coefficient (D) for the dithiophosphonates were determined at the ultramicroelectrode using Baranski method [21]. Cottrell slope was acquired by chronoamperometric measurements at the normal size Cu-GC electrodes. Steady state currents were acquired by CV experiments at a ultramicroelectrode for 1 mM dithiophosphonate and 1 mM ferrocene solutions. n and D were calculated according to the equations given below.

$$n = \frac{n_S S^2 i_S C_S}{S_S^2 i C}, \qquad D = \frac{D_S S_S^2 i^2}{S^2 i_S^2}$$

where i is the steady-state current (Fig. 4), C is the concentration, S is the slope of Cottrell curve and n is the electron transferred for dithiophosphonate molecules. On the other hand i_s, C_s, S_s and n_s (which is equal to 1 for ferrocene) are the same terms for ferrocene molecule used as a standard system.

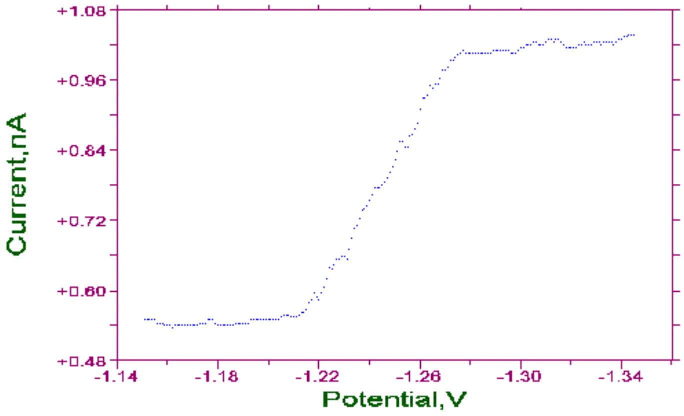


Fig. 4. Linear sweep voltammogram of 1 mM MDTP and in acetonitrile (0.1 M TBATFB) on the ultramicroelectrode at a scan rate of 0.01 V s^{-1} (vs. Ag/Ag^+ electrode).

Table 1. n and D values for electrode reactions of dithiophosphonates molecules in acetonitrile.

Molecules	Cottrell slope(S)	UME limiting current (i, A)	n values	Diffusion coefficient (D,cm^2/s)
PDTP	$3.38\times10^{-4} \pm 0.61\times10^{-4}$	$1.050\times10^{-9} \pm 4.271\times10^{-11}$	2,38 ±0,04	$6,94\times10^{-6} \pm 3,12\times10^{-7}$
MDTP	$3.25\times10^{-4} \pm 0.46\times10^{-4}$	$1.013\times10^{-9} \pm 3.160\times10^{-12}$	2,36 ± 0,02	$7,17\times10^{-6} \pm 6,76\times10^{-8}$
BDTP	$3.18\times10^{-4} \pm 0.86\times10^{-4}$	$1.041\times10^{-9} \pm 1.854\times10^{-11}$	2,19 ± 0,01	$7,81\times10^{-6} \pm 2,63\times10^{-8}$
IPDTP	$3.32\times10^{-4} \pm 0.71\times10^{-4}$	$1.015\times10^{-9} \pm 3.316\times10^{-12}$	2,45 ± 0,05	$6,92\times10^{-6} \pm 3,88\times10^{-8}$
PhDTP	$3.19\times10^{-4} \pm 0.76\times10^{-4}$	$1.017\times10^{-9} \pm 4.163\times10^{-12}$	2,26 ± 0,03	$7,50\times10^{-6} \pm 5,16\times10^{-7}$
EDTP	$3.09\times10^{-4} \pm 0.37\times10^{-4}$	$1.016\times10^{-9} \pm 2.142\times10^{-12}$	2,13± 0,02	$8,00\times10^{-6} \pm 4,32\times10^{-8}$
Ferrocene	$2.19\times10^{-4} \pm 1.06\times10^{-4}$	$1.08\times10^{-9} \pm 2.126\times10^{-11}$	1	1.70×10^{-5}

a: standard deviation for 4 results

The Cottrell slopes, the steady-state currents and n and D values as well as the standard deviations for the dithiophosphonate and ferrocene molecules, obtained from the chronoamperometric and cyclic voltammetric measurements, were given in Table 1.

As shown from the Table 1, the number of electrons transferred for the reduction of dithiophosphonates was calculated as 2 for all the derivatives.

Adsorptional characteristics of dithiophosphonates on the electrode

When electroactive species are adsorbed on the electrode surface, electrode reactions are strongly affected [23]. Therefore, the presence of either strong or weak adsorption on the electrode was first checked using several criteria. The voltammograms of the dithiophosphonates do not show any pre-peak and post-peak, indicating that no strong adsorption exists on the Cu-GC electrode. The easiest and the most straightforward way of testing the weak adsorption effects is to calculate the slope of the log i_p-log v graph. If the electrode reaction is diffusion controlled, slope of this graph is equal to 0.5 to fit the Randless-Sevcik equation [23]. If the adsorption is effective on the electrode reaction the slope of this graph should be greater than 0.5 [23]. Log i_p-log *v* graph and its equation for MDTP in acetonitrile at the Cu-GC electrodes in cyclic voltammetry are shown in Figure 5. As can be seen from Figure 5, the slope is 0.44 for MDTP on Cu-GC electrode. Since the slopes of log i_p-log *v* graphs of other molecules were smaller than 0.5, these graphs for the other dithiophosphonates were not shown.

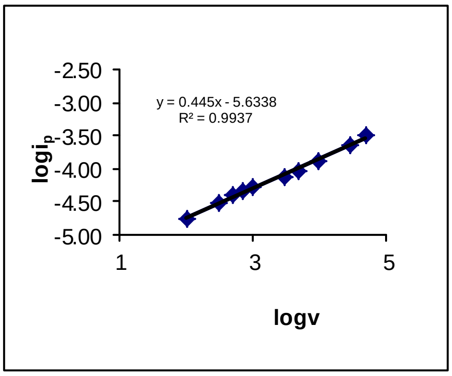


Fig. 5. Log i_p-log *v* graph of MDTP in acetonitrile (0.1 M TBATFB) on the Cu-GC electrode.

The other tests for weak adsorption, namely $i_p/Cv^{1/2}$-*v*, i_p/Cv-*v* plots, were also applied to all dithiophosphonate derivatives. If the weak adsorption is effective, while the change of $i_p/ Cv^{1/2}$ with *v* increases, the change of i_p/Cv with *v* stays constant [24, 25]. When these two criteria for the weak adsorption effects were applied for the dithiophosphonates, it was observed that weak adsorption was also effective.

Characterization of the electrode reactions of the dithiophosphonates

Because there is no anodic peak in CV voltammograms of all the dithiophosphonates, we first examined the irreversible character of the electrode reaction. The most marked feature of cyclic voltammogram of a totally irreversible system is the total absence of a reverse peak. However such a feature on its own does not necessarily imply an irreversible electron transfer process but could be due to a fast following chemical reaction [23]. Therefore other irreversibility criteria should also be tested in addition to the absence of the anodic peak. For the reversible case, E_p^c is independent of scan rate contrary to the irreversible case for which E_p^c changes with the scan rate. The shift is $30/\alpha_c n_\alpha$ (60 mV) for each decade change in v when α_c is 0.5 and n_α is 1 [23,26]. The shape factor $| E_p – E_{p/2} |$ is given by $48/(\alpha_c n_\alpha)$(96 mV) when α_c is 0.5 and n_α is 1 [23, 26]. The other test for the irreversibility of the system is the linearity of the i_p vs. $v^{1/2}$ plot [23,26]. We applied above criteria for dithiophosphonates, and found that the reduction of all the molecules appeared to be nearly irreversible. Because the anodic peak was not observed even at high scan rates of 50 V/s, the shift in E_p^c and $| E_p – E_{p/2} |$ were very close to the theoretical values, as can be seen Table 2. According to these results the electron transfer process is expected to be highly irreversible two-electron transfer [23].

Table 2. Peak widths and shift in E_p^c for the EDTP, MDTP, PDTP, IPDTP, BDTP, PhDTP at the Cu-GC electrodes.

Molecules	Shift in E_p^c (100-1000 mV)	$E_p – E_{p/2}$ (1000 mV)	k_s (cm/s)
EDTP	68 ± 9	104 ± 11	8×10^{-4}
MDTP	63 ± 11	99 ± 5	7×10^{-4}
PDTP	75 ± 6	89 ± 7	8×10^{-4}
IPDTP	84 ± 12	100 ± 8	8×10^{-4}
BDTP	75 ± 7	97 ± 6	8×10^{-4}
PhDTP	99 ± 9	92 ± 7	7×10^{-4}

As is evident on the voltammograms the anodic peak was not seen even at high scan rates; indicating that the concerned electroreductions of dithiophosphonates might proceed through the EC mechanism. The current function ($i_p/v^{1/2}$ or $i_p/Cv^{1/2}$) values were plotted against the scan rate in order to apply the EC mechanism criteria to determine the reaction mechanism. Plots of MDTP were given in Figure 6. The fact that the current function decreased a small extent towards higher scan rates was an indication that electron transfer was followed by a chemical reaction [23]. All of these points suggested that the overall reaction was irreversible and go through the EC mechanism.

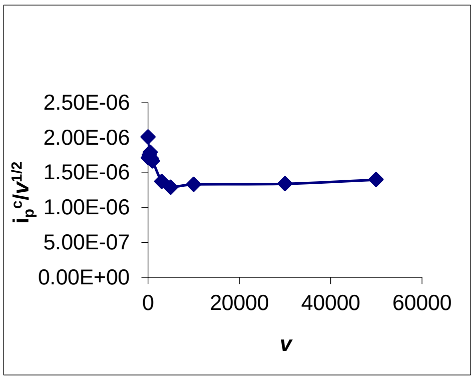


Fig. 6. Changes of $i_p^c/v^{1/2}$ with $v^{1/2}$ for MDTP in acetonitrile on Cu-GC electrodes.

The simulation curves of dithiophosphonates were plotted by DigiSim® 3.03 version to investigate the reduction mechanism and to determine of the relevant chemical and electrochemical parameters. The heterogeneous electron transfer rate constant (k_s), the homogeneous forward and backward rate constant (k_f, k_b) and equilibrium constant (K) for the following chemical reaction were calculated by direct comparison of simulation and experimental voltammograms. The superimposed theoretical and experimental voltammograms for MDTP on the Cu-GC electrode are shown in Fig. 7. At the scan rate of 0.5 V s^{-1} the following parameters were used to produce the best fit. The standard electrode potential for MDTP $E^o = -1.55$ V; the diffusion coefficient of this compound 7.1×10^{-6} cm/s; the area of the electrode 0.071 cm^2; the number of electrons in the electrochemical rate determining step n=1; double layer capacitance $C_d = 8\times10^{-6}$ Farad and transfer coefficient $\alpha = 0.5$. Simulating this situation for EC reaction mechanism gave the heterogeneous rate constant for the dithiophosphonates as in Table 2. The values of the kinetic constants for the following chemical reaction were found as $K = 1.0\times10^4$, $k_f = 100\ s^{-1}$ and $k_b = 1\times10^{-2}\ s^{-1}$. k_s values found from simulation data were given in Table 2. Simulation CV voltammograms of the other molecules showed also very good agreement with the experimental CV voltammograms.

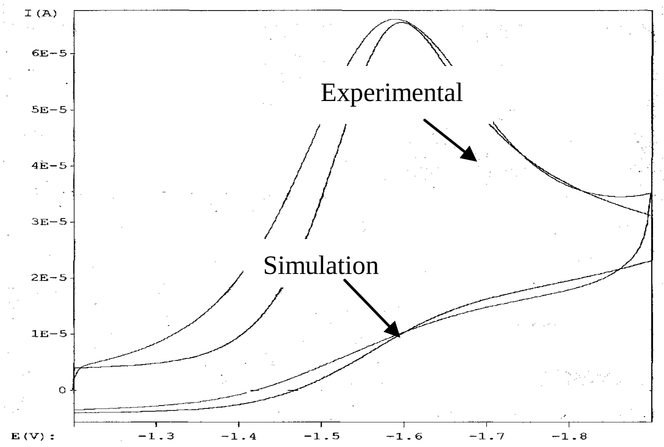


Fig. 7. The experimental and simulation voltammograms of MDTP molecules for 1 mM solution in acetonitrile containing 0.1 M TBATFB at Cu-GC electrode (Scan rate is 0.5 V s^{-1}).

Current-concentration relationship of dithiophosphonates on Cu-GC electrode

A square wave voltammetric (SWV) method has been described for the determination of dithiophosphonates at Cu-GC. The results of these experiments showed that SWV peak currents of dithiophosphonates increased linearly with concentration on Cu-GC. Figure 8 shows the calibration graph of EDTP, as a representative molecule, in acetonitrile at Cu-GC. For comparison purposes we also showed the calibration graph of EDTP at the Pt electrode in the same Figure. The statistical results of the calibration graphs were also compared for Cu-GC and Pt electrodes in Table 3. The slope of the calibration graph for Cu-GC electrode was greater than the slope of the calibration graph for Pt electrode. Therefore the analysis of dithiophosphonates of Cu-GC electrode is more sensitive than that of the Pt electrode. Dithiophosphonates can be determined quantitatively in acetonitrile using such a calibration graph.

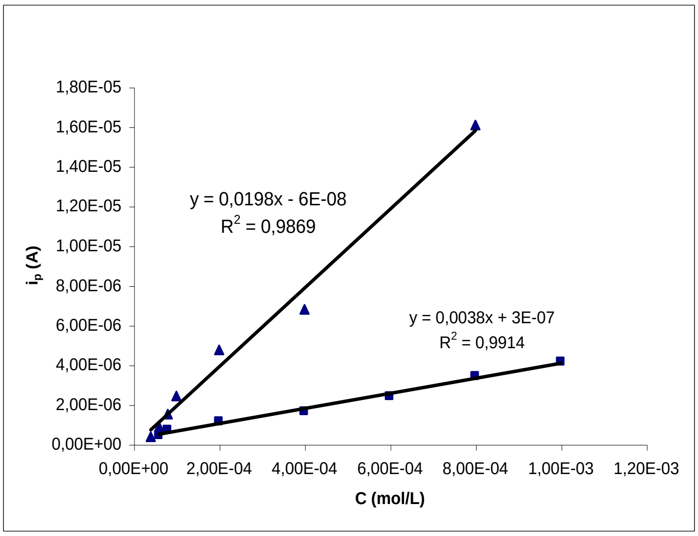


Fig. 8. Change of the current with the concentration for EDTP in a solution of acetonitrile containing 0.1 M TBATFB on Cu-GC (▲) and Pt (■)electrodes using SWV method (f_r= 15 Hz, E_{sw}=25 mV).

Table 3. Statistical results of the calibration graph for EDTP given in Figure 8.

Working range (mol/L)	Slope	Intercept	Standard deviation of the slope	Standard deviation of the intercept	Standard deviation of the method
4×10^{-5}- 8×10^{-4} (Cu-GC)	0.0198	6.0×10^{-8}	0.0088	3.09×10^{-6}	7.6×10^{-7}
8×10^{-5} - 1×10^{-3} (Pt)	0.0038	3.0×10^{-7}	0.0002	9.4×10^{-8}	1.5×10^{-7}

Acknowledgment

The authors gratefully acknowledge the financial support of the Ankara University Scientific Research Fund under Grant No: 97-25-00-02.

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