Karaelmas Science and Engineering Journal
Journal home page: http://fbd.beun.edu.tr
DOI: 10.7212/zkufbd.v9i2.1416

Research Article
Received / Geliş tarihi : 24.12.2018
Accepted / Kabul tarihi : 10.02.2019

Determination of Water Content in Aprotic Solvent by Anthraquinone-Modified Multi-Walled Carbon Nanotubes

Antrakinonla Modifiye Edilmiş Karbon Nanotüpler ile Aprotik Çözücüler İçerisindeki Su İçeriğinin Tayin Edilmesi

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Abstract

The attachment of etylenediamine bearing tert-butyloxycarbonyl (BOC) by electrochemical oxidation of corresponding diamine linker was achieved onto multi-walled carbon nanotube immobilized at glassy carbon surfaces. Subsequent to removal of BOC protecting group, the coupling of anthraquinone-2-carboxylic acid to amine-terminated surfaces was carried out using solid-phase synthesis methodology. It was demonstrated that anthraquinone exhibits electrochemically two sequential single-electron reductions in aprotic solutions through cyclic voltammetry technique. Peak separation potential between first and second electron transfer step was found to be decreased with the addition of water as a proton source. When the water concentration reaches up to 1 M, only one electrochemical process is observed, which is due to formation of hydrogen bonding between reduced form of anthraquinone and aprotic solvent (acetonitrile). Determination of water content in the aprotic solutions was shown to be quite possible using linear relationship between water concentration and peak separation potential. Limit of detection was also calculated to be around 1.1x10^{-7} M.

Keywords: Anthraquinone, Aprotic solvent, Carbon nanotubes, Electrode modification, Water

Öz

Camsı karbon elektrot üzerine immobilize edilmiş çok katmanlı karbon nanotüp yüzeyine (MWCNT), yapısında BOC (tert-bütiloksikarbonil) koruyucu grup bulunan etilen diamin elektrokimyasal oksidasyon işlemi vasıtasıyla kovalent olarak bağlanmıştır. BOC koruyucu grubunun uzaklaştırılmasına müteakiben elektrot yüzeyindeki amin gruplarına antrakinon-2-karboksilli asitin bağlanması sağlanmıştır. Antrakinon aprotik çözücülerde elektrokimyasal olarak ard arda gelen 2 tane tersinir 1 tek elektron indirgenme prosesine maruz kaldığı döngüsel voltametri tekniği vasıtasıyla gösterilmiştir. İlk ve ikinci elektron transfer adımları arasındaki potansiyel ayrım bir proton kaynağı olarak artan su miktatının ilavesiyle gittikçe azaldığı tespit edilmiştir. İlave edilen su miktarı belli bir seviyeye çıktığında (~1 M) sadece bir tane elektrokimyasal proses gözlemlenmiştir ki, bu durumun temel nedeninin ise antrakinonun indirgenmiş hali ile aprotik çözücü arasında meydana gelen hidrojen bağından kaynaklandığı düşünülmektedir. Su konsantrasyonu ile pik ayrım potansiyeli arasındaki doğrusal ilişki kullanılarak aprotik çözücülerdeki su miktarının tespit edilebileceğinin mümkün olacağı gösterilmiştir. Tayin sınırıda ayrıca 1.1x10^{-7} M olarak hesaplanmıştır.

Anahtar Kelimeler: Antrakinon, Aprotik çözücü, Karbon nanotüpler, Elektrot modifikasyonu, Su içeriği

1. Introduction

The modification of carbon materials (glassy carbon (GC), highly ordered pyrolytic graphite (HOPG) electrodes, carbon nanotube and graphene) has attracted substantial attention over the last two decades owing to the fact that this method is quite manageable, indicating that carbon electrode can be modified in a desirable way in many implementation areas such as from sensors to bioelectronics (Mattiuzzi et al. 2012, Allongue et al. 1997, Celiktas et al. 2012, Gooding et al. 2008, Chehimi 2012, Belanger et al. 2011, Pinson and Pedvorica 2005, McCreery 2008).

Quinone derivatives undergo two consecutive one electron reduction process in non-aqueous solutions. Subsequent to quinone is electrochemically reduced to an anion radical ($Q^{-\bullet}$), further one electron reduction of quinone to the dianion

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(Q^{2-}) takes place at more negative reduction potential compared to first step. It is well established that reduction potential of quinone derivatives is not independent of water content of aprotic media, thus it gives rise to complication in determination formal potential of quinones. Therefore, a great deal of effort has been devoted to investigate how water concentration in aprotic solvent has an influence on the reduction potential of quinones (Hui et al 2010, Tessensohn et al 2017, Hui et al 2009). It was found that as the water concentration increases reduction potential belonging to anion radical (Q$^{-\bullet}$) and dianion (Q^{2-}) shift to more positive potential without any lost in the electrochemical reversibility. When the water content reaches up to certain level, two reversible electrochemical processes merge into single 2-electron reduction.

In our work, multiwalled carbon nanotube (MWCNT) was placed onto glassy carbon electrode by pipetting MWCNT solution in ethanol. Once modification of multiwalled carbon electrode was achieved by electrochemical modification of ethylene diamine bearing BOC (tert-butyloxycarbonyl) protecting group, the BOC was removed in the solution of 4M HCl in dioxane. Anthraquinone-2-carboxylic acid was coupled to resulting amine terminated surface. Electrochemical properties of AQ-modified MWCNT in aprotic solvents were investigated and the effect of addition of proton source such as water was studied to see how the electrochemistry and voltammogram of AQ-modified surface altered with the increase of water concentration. To best of our knowledge, this is the first study focusing on AQ-modified MWCNT electrodes can be utilized as a sensor to detect the water content in the non-aqueous solvents.

2. Materials and Methods

All chemicals were used as received and without any further purification. All aqueous solutions used throughout this study were made with reagent-grade water (18 MΩ cm) from a Whatman RO80 system coupled to a Whatman Still Plus, 1,4-Dioxane and Dichloromethane were obtained from Fisher Scientific. Ethanol, Hydrochloric acid, N-Boc-ethylenediamine (EDA), DMF, Tetrabutylammonium tetrafluoroborate (TBATFB) and N,N- Diisopropylethylamine were purchased from Sigma Aldrich. Acetonitrile and Anthraquinone-2- carboxylic acid were also obtained from Rathburn Chemicals and TCI Chemicals, respectively.

Electrochemical experiments were carried out with an SP-50 model Biologic Science Instruments Potentiostat/Galvanostat and controlled using EC-Lab software, a conventional three-electrode system which is made up of GC as a working electrode, a platinum wire and a Ag/AgCl were used as a counter electrode and a reference electrode, respectively. All potentials are reported vs. the Ag/AgCl in aqueous solution. Argon gas was passed through the electrochemical cell for 15 min before electrochemical measurement.

Electrografting of mono-Boc-protected amine linker, Boc-EDA, onto MWCNT immobilized GC electrodes was performed by electrochemical oxidation from the corresponding solutions containing 10 mM Boc-EDA and 0.1 M TBATFB in acetonitrile. The modification of electrodes was performed by cycling the electrode potential from 0.7 to 2.2 V versus Ag/AgCl for Boc-protected diamine linker,

The modified electrode was suspended in a solution of 4 M HCl in dioxane at room temperature for 1 h. The electrode was then washed by DMF, deionized water and absolute ethanol prior to electrochemical characterization

Anthraquinone-2-carboxylic acid (252 mg, 1.0 mmol), HBTU (450 mg, 1.2 mmol) and DIEA (4.2 mmol) were dissolved in DMF. The mixture was heated to 60 °C for 15 min. Modified MWCNT electrodes were then placed in this solution, stirred for 16 h. The electrode was then washed with DMF and absolute ethanol before electrochemical characterization.

Immobilization of MWCNT to GC electrodes were carried out as follows, Initially, 20 mg of MWCNT was put into the absolute ethanol. This suspension was then sonicated for 30 minutes to obtain homogeneous dispersion. 5 μL of this suspension was eventually pipetted onto GC electrode and allowed to be dried at the room temperature.

3. Results and Discussion

The electrochemical grafting of the Boc-protected etylenediamine onto the MWCNT immobilized GC was achieved by the electrochemical oxidation of the relevant linker in ACN and in the presence of supporting electrolyte, TBATFB. Figure 3.1 illustrates the first and fifth CVs recorded at the scan rate of 50 mV s^{-1} after holding the electrode in the second scan at 1.4 V for 20 minutes.

As clearly seen in Figure 1, there is a rather broad irreversible peak appearing at peak potential of 1.6 V, which might be attributed to the creation of the amine radical that attaches to the surface of carbon electrode. On the other hand, subsequent to holding the potential at the 1.5 V, this peak disappears, which suggests that electrode surface is passivated by the diamine. This finding is quite in good agreement with literature (Ghanem et al 2013, Chretien et al 2008).

In order to determine whether the surface of MWCNT electrode was completely covered by corresponding Boc-protected EDA linker, cyclic voltammetry experiment was carried out in the presence of a redox probe, $K_4[Fe(CN)_6]$. As can clearly be noticed in Figure 2, voltammogram of redox probe exhibits reversible behavior with redox potential of 1.80 V at the unmodified MWCNT electrode, however, in the case of functionalized MWCNT electrode through EDA linker, regarding voltammogram is greatly suppressed within scanned potential range. This obviously refers to the existence of the Boc-protected linker on the surface.

As previously mentioned, in aqueous solutions (neutral pH values), quinone derivatives undergo reversible 2 protons and 2 electron reduction process, depending on the pH of the solutions. For instance, as seen Figure 3. as the pH increases the mid-peak potential (E_{mp}) shifts to more negative potential. This is because, electrochemical reduction of quinones occurs via 2 successive 2 protons 2 electron reduction in acidic media, whereas in alkali media, as there is no proton source, 2 electron reduction mechanism takes place and it follows 1 proton-2 electron or only 2 electron reduction process under the neutral circumstances (Ghanem et al. 2008, Shamsipur et al. 1993).

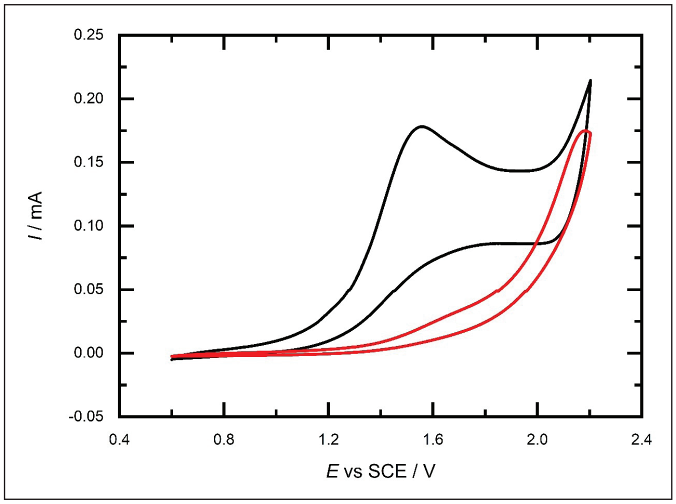

Figure 1. Cyclic voltammetry for MWCNT immobilized on glassy carbon electrode in 5 mM of EDA-Boc in 0.1 M TBATFB in acetonitrile, scan rate 50 mV s^{-1}. Black and red solid lines represent first and fifth voltammogram, respectively.

However, the EC reduction of quinones in aprotic solvent exhibit significantly different behavior in comparison to aqueous solutions since it occurs through the 2 successive 1 electron reduction, which generates semiquinone anion radical ($Q^{\bullet-}$) and quinone dianion (Q^{2-}) (Tessensohn et al 2013, Staley et al 2015, Tessensohn and Webster 2016). In such situation, 2 cathodic and 2 anodic peaks are obtained. First EC voltammogram indicates reversible process, whereas second process follows quasireversible electrochemical process. As seen from our experimental findings depicted in Figure 4, EC reduction of AQ-modified MWCNT electrode follows 2 successive 1 proton-1 electron reduction

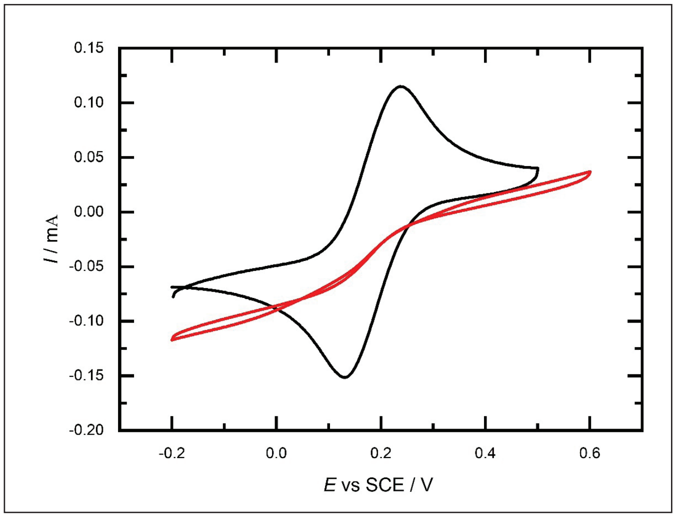

Figure 2. CV recorded at 50 mV s^{-1} for unmodified MWCNT (black line) and modified MWCNT through EDA linker in the presence of $K_4Fe(CN)_6$.

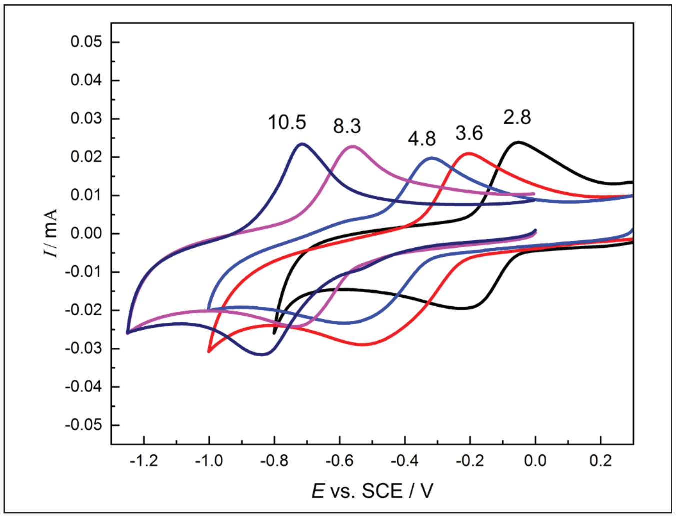

Figure 3. The effect of pH on CVs of AQ-modified MWCNT through EDA linker. pH values vary from 2.8 to 10.5.

mechanism. First reversible voltammogram ($E_{1/2}$= 95 mV and 145 mV for ACN and DCM, respectively) indicates the formation of semiquinone and anodic-cathodic peak separation potentials are found to be as 198 mV and 298 mV in ACN and DCM, respectively. The following 2 electrons quasi reversible reduction process points out the generation of quinone-dianion ($E_{1/2}$= 100 mV and 175 mV for ACN and DCM, respectively). CV measurements were also recorded at the different scan rate, ranging from 5 mV to 500 mV and cathodic and anodic peak current were found to increase linearly, referring to the fact that the coupling of AQ to the surface of modified MWCNT was successfully accomplished.

Figure 5 and 6 show the how the voltammogram of the AQ-modified MWCNT electrodes changes with the increasing the concentration of a proton source (water) in the ACN. ıt was found that as the concentration of water increases, the voltammogram belonging to second electrochemical reduction process shifts towards more positive potential, whereas peak potential of the first electrochemical reduction process slightly moves to more negative potential. This such an interesting behavior is thought to stem from formation of a rather stable structure formed via hydrogen bonding between product of mono and dianion generated during the EC reduction of anthraquinone (Tessensohn et al 2015). However, it is noteworthy the reduction potential of dianion for the second process shifts to more positive value compared to reduction potential of first process ($\Delta E2 > \Delta E1$). According to attained experimental findings, both mono and dianion form hydrogen bonding with water and hydrogen bonding formed with dianion are more durable with respect to monoanion owing to the fact that positive shift in the second process is larger. The reason of this finding can be attributed to the higher electronegativity of the oxygen atom in the dianion in comparison to oxygen atom in the monoanion interacts strongly with water molecules. On the basis of obtained experimental results, it could be concluded that this method can be utilized as a sensor for the determination trace amount of water in the aprotic solvent through positive shift in the peak potential upon the addition of a proton source.

It is well established that one of the highly requested features of a biosensor is that it should be able to maintain its potential against changing circumstances. Therefore, in order to test the stability of the electrode, redox potential of the electrode was measured against increasing water concertation in both aprotic solvents. Figure 7 shows standard potential of the electrode belonging to first and second reduction mechanism versus water concentration in ACN and DCM. It is quite noticeable that even though there are some fluctuations in the standard potential of the electrode in ACN or DCM, it could be said that the potential of the developed biosensor is not significantly changed. It can therefore be deduced that AQ-modified MWCNT electrode can be used for the determination of the trace amount of water in the aprotic media (Dağdevren et al. 2015).

As demonstrated in this work, there is a positive shift in the peak potential of first and second reduction process as increasing water content in the aprotic solvent. We then thought that it would be worthy to investigate whether our

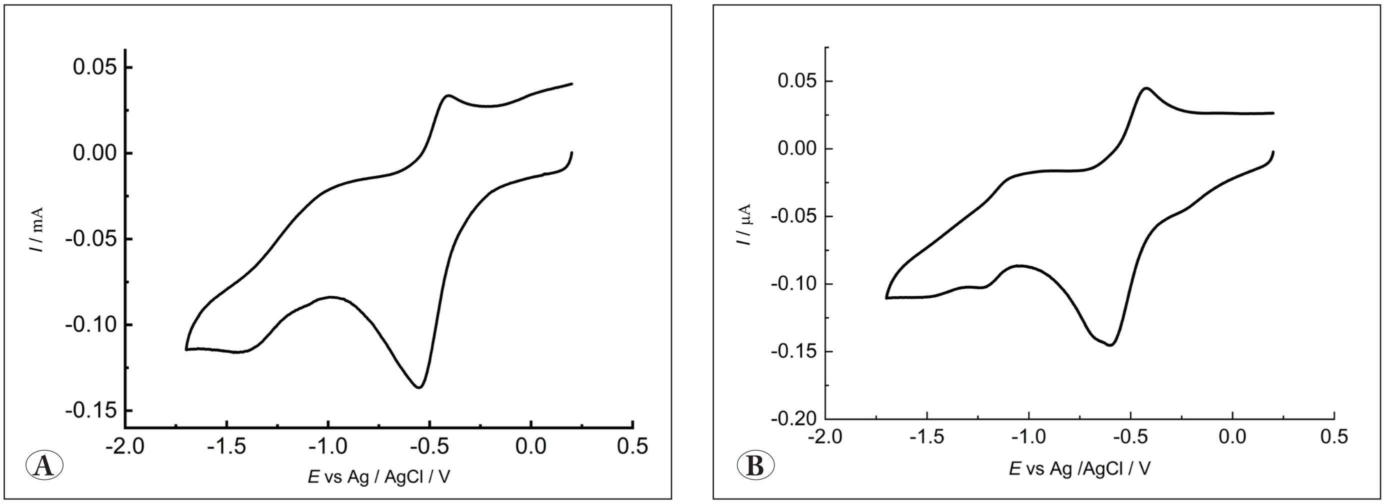

Figure 4. Cyclic voltammogram (CV) of anthraquinone modified MWCNT immobilized onto glassy carbon surface in ACN **(A)** and DCM **(B)** at the scan rate of 50 mV s^{-1}.

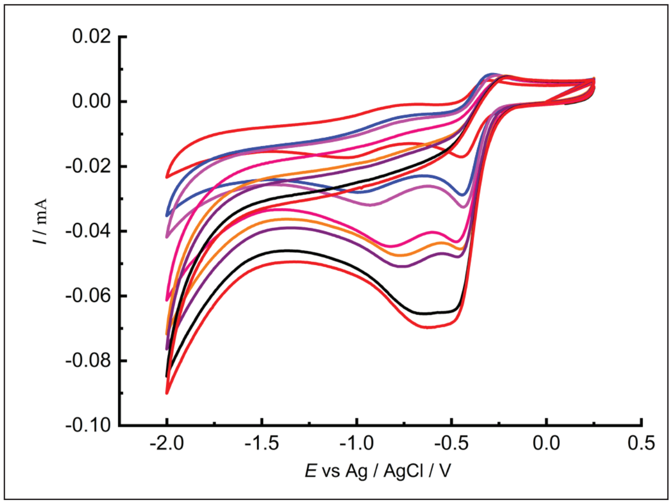

Figure 5. CV obtained during the electrochemical reduction of anthraquinone coupled to the MWCNT through EDA linker containing varying amounts of water and 0.1 M TBATFB in ACN at the scan rate of 50 mVs-1.

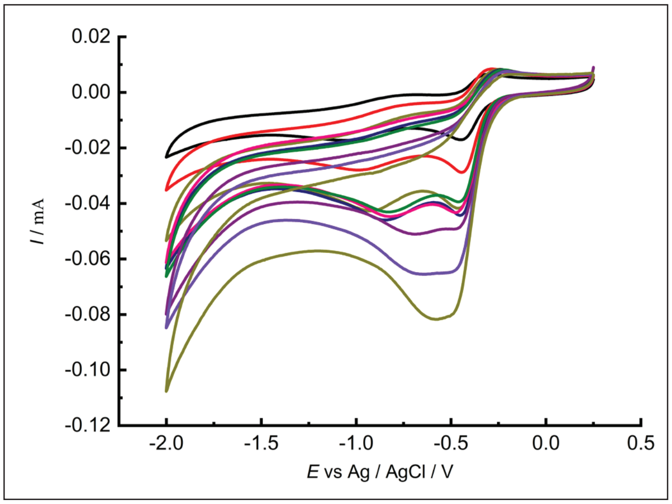

Figure 6. CV obtained during the electrochemical reduction of anthraquinone coupled to the MWCNT through EDA linker containing varying amounts of water and 0.1 M TBATFB in DCM at the scan rate of 50 mVs^{-1}.

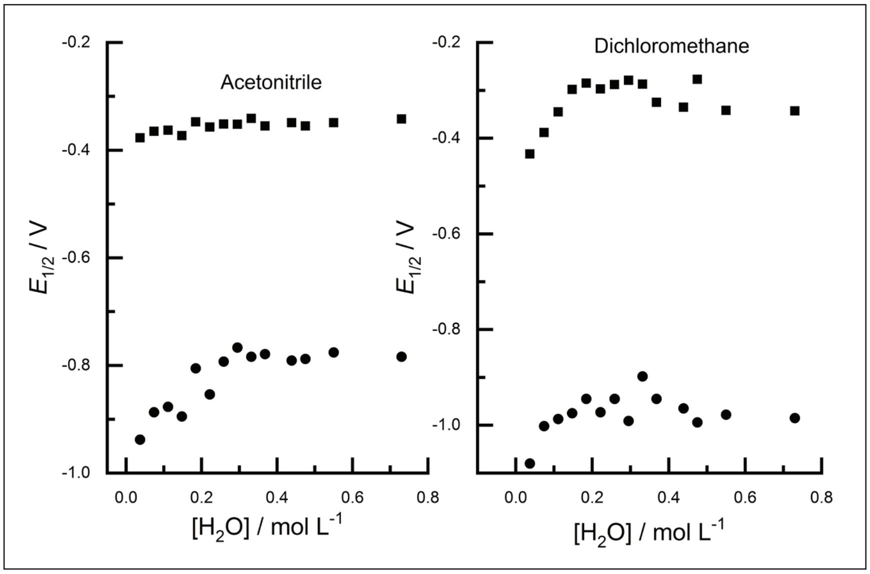

Figure 7. shows $E_{1/2}$ of the first reduction (square), the second reduction peak potential (circle) of AQ-modified MWCNT vs water content of the solvent during the CV measurements in ACN (on the left) and DCM (on the right) containing 0.1 M TBATFB.

AQ-modified MWCNT electrode can be employed as a sensor for the detection of water by evaluating relationship between potential separation between first and second process versus water concentration in ACN or DCM. Figure 8 shows plots of the first and second process versus water content in aprotic solvent. The calibration curves are linear, which makes straight lines possible to be fitted. LOD can be calculated from the slope and LOD is found to be as $1.1x10^{-7}$ mole L^{-1} using 3σ, where σ is standard deviation of blank solution with 15 parallel measurements.

4. Conclusion

Anthraquinone is attached to MWCNT surfaces through by the electrochemical oxidation of Boc-protected EDA linker. Subsequent to deprotection of BOC group, coupling of the AQ-2- carboxylic acid to amine terminated surface was successfully carried out. This study has illustrated that very small amount of proton source, for instance water, can have a significant influence on the reduction of quinone derivatives, which pursues sequential 1 electron 1 proton reduction in aprotic solvents. It was experimentally proved that as the concentration of water increases peak potential belonging to 1st and 2nd reduction process shifts towards

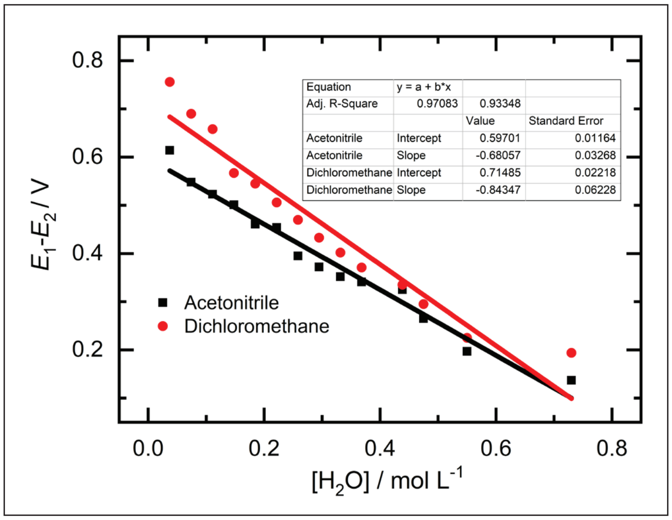

Figure 8. Plots of $|E_1 - E_2|$ measured by CV during the reduction of AQ-modified MWCNT versus the water content of the solvent, ACN and DCM containing 0.1M TBATFB.

more positive potential. However, water content in the aprotic media reaches up to 1 M, two reduction peaks merges and the second process merges with the first one, indicating the reversible transfer of two electrons per molecule. It was also found that developed sensor for water detection has exhibited rather good stability since standard reduction potential of the electrode almost remained constant upon the increasing water concentration. The calibration curve demonstrated linear relationship between reduction peak potential difference between first and second process against water content in ACN or DCM. LOD value was calculated as $1x10^{-7}$ mole/L. It is also noteworthy that we have developed a novel sensor for the electrochemical detection of H_2O. Because the best of our knowledge, there is no paper in the literature that describes the electrochemical water determination at the modified electrode and this constructed sensor allows us to the direct detection of trace amount of water content in aprotic medium.

5. Acknowledgments

The author thanks Bulent Ecevit University Scientific Research Project Coordination Unit for financial support, Project Number 201572118496-09.

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