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Ion Transfer Study on a New Designed Nanocomposite Carbon Paste Electrode

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In this work, a new and sensitive carbon paste electrode (CPE), based on nanocomposite materials and Ferrocene (Fc), is introduced. Proposed electrode was designed for sensitive and accurate ion transfer investigations. Ion transfer across water/ionic liquid was studied by cyclic voltammetry and fast Fourier transform square wave voltammetry (FFT-SWV) techniques. We compared the effect of three ionic liquids including 1-Octyl-3-Methyl-Imidazolium Tetrafluoroborate, N-butylpyridinium tetrafluoroborate and 1-hexyl-3-methylimidazolium tetrafluoroborate on the voltammograms of Fc. The changes in the processes of the ion transfer was studied in the presence of NO_3^-, Cl^-, Br^-, SCN^- and ClO_4^- ions in the aqueous solution. Also, for the first time, we succeeded to obtain very stable voltammograms of Fc during ion transfer studies, by using $[OMIM]BF_4$ as a superior binder. The effect of the presence of multiwall carbon nanotube (MWCNT) in composition of CPE, on the electron transfer and ion transfer across $[OMIM]BF_4$/aqueous solution interface was also investigated. It was found that the presence of MWCNT can increase the electron transfer and the ion transfer process. A linear relationship was observed between the peak potential of FFT-SWV of Fc and standard transfer potential of the mentioned anions.

Keywords: Ion transfer, Liquid/liquid interface, Ionic liquid, Carbon paste electrode, Multiwall carbon nanotube

1. INTRODUCTION

The liquid–liquid ion transfer has received a lot of attention in recent years [1] since it is one of the most important phenomena in systems involving an interface between two immiscible liquids [2-4]. It has been proposed that ion transfer across the interface between two immiscible electrolyte solutions (ITIES) solves technical problems, inefficient energy conversion, in phase transfer catalysis and for drug or gene delivery, and furthermore this method has potential applications in extraction, liquid–liquid separation [5,6] electroanalysis, liquid state ion-selective electrodes [7]. In these systems ion transfer is driven by electrochemically generating charged species in the non-aqueous phase [8]. The redox reaction is accompanied by expulsion or insertion of ions to maintain charge neutrality in the non-eqoueous phase [9].

Redox probes used in ITIES investigations have been compared in some articles [8,10,11], which revealed that an anion transfer reaction across the liquid–liquid interface dominates only when more hydrophobic redox probes such as decamethylferrocene (DMFc) and *t*-butylferrocene (*t*BuFc) were used, because the stability of voltammograms correlates with the hydrophobicity of the redox probe. In fact, the increase in hydrophobicity is in the order of Fc < *t*BuFc < DMFc [10]. Therefore, in most articles DMFc and tBuFc [1,7,9,11-15] were used as a redox probe. Because for the most hydrophobic redox probes, such as DMFc and tBuFc multiple cyclic voltammograms are stable, but for less hydrophobic redox probes like Fc, current is significantly unstable. In such situation instability is due to partial loss of electrooxidized redox probe from nonaqueous in to the aqueous phase. The kind of binder, redox probe or counter ions may also affect the stability of the resulting voltammograms [8].

In recent years, the ion transfer processes occurring across room temperature ionic liquid (RTIL)|aqueous solution interface have attracted some attention, because liquid|liquid systems based on RTILs have potential applications in the extraction or separation technology [6,16]. Hence three ionic liquids namely (N-butylpyridinium tetrafluoroborate ([Bpy]BF_4), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF_4) and1-Octyl-3-Methyl-Imidazolium Tetrafluoroborate ([OMIM]BF_4) were studied in order to choose the best binder that can stabilize Fc in nonaqueous phase.

In this study, Fc was used as a redox probe, due to its lower cost and more availability and stabilizing in nonaqueous phase. The results showed that using [OMIM]BF_4 causes Fc to act similar to redox probes with high hydrophobic properties. It, also, improves the electrode stability compare to the electrodes prepared with DMFc and tBuFc. In addition, among the different electrode materials that have been used in the ITIES systems, CPE was employed as an electrode because of it can be, easily, modified. Moreover, ion transfer across RTIL/aqueous solution interface, in the presence of multiwall carbon nanotube (MWCNT) in CPE was investigated. Electron transfer and ion transfer reactions were monitored by cyclic voltammetry (CV) [17-25] and fast Fourier transform square wave voltammetry (FFT-SWV) techniques [26-29], which are powerful tools for studying ion transfer processes. A large number of salts with different hydrophobicities were employed to detect ion transfer across the RTIL/water interface.

2. EXPERIMENTAL

2.1. Chemicals

Fc (98%) and [OMIM]BF_4 (99%), NaF, NaBr, NaCl, NaI, NaSCN, $KClO_4$, and KNO_3 (analytical grade) were purchased from Merck. The graphite powder with a 1–2 μm particle size was obtained from Merck. The MWCNT were purchased from Research Institute of the Petroleum Industry (RIPI). All chemicals were used without further purification. Double-distilled deionized water was used throughout.

2.2. Electrode preparation

0.17 g of graphite powder was mixed with 100 μL of RTIL and 0.014 g (5% w/w) MWCNT. The resulting mixture was placed into a 20 mm deep cavity of the 0.4 mm inner diameter glass tubing filled tightly with a graphite rod. The electrode was polished with smooth paper. Next, the electrode was immersed into an electrochemical cell with aqueous electrolyte solution.

2.3. Instrumentation

CV and FFT-SWV were performed by a setup of a PC Pentium 500 MHz microcomputer, equipped with a data acquisition board (PCL-818HG, Advantech. Co.) and a custom-made potentiostat [18,19]. The corresponding programs were developed in Delphi 6 environment. CPE, Ag/AgCl/KCl (sat.) and platinum wire (diameter 0.2 mm) were used as the working, reference and counter electrode, respectively. The three electrodes were immersed into the aqueous salt solution. All experiments were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. The mechanism of the biphasic electrode process

In general, the cyclic voltammograms observed in the studied system can be attributed to the electrochemical oxidation of Fc in the RTIL phase:

$$\mathrm{Fc}_{\,(\mathrm{RTIL})}\text{-}\mathrm{e}^{-}_{\,(\mathrm{electrode})} \leftrightarrow \mathrm{Fc}^{+}_{\,(\mathrm{RTIL})} \qquad (1)$$

This reaction produces a positive charge in the RTIL phase, and is accompanied by ion transfer in order to maintain the electroneutrality. Here, two processes can be possible. The first one is leaking of Fc^+ into the aqueous phase,

$$\mathrm{Fc}^{+}_{\,(\mathrm{RTIL})} \longrightarrow \mathrm{Fc}^{+}_{\,(\mathrm{aq})} \qquad (2)$$

This process is more feasible by using the non-polar redox probes, because, in this case, transferring of Fc^+ seems to be the only way to maintain charge neutrality in the system. The second reaction is the transfer of aqueous anions from the aqueous phase into the RTIL phase.

$$\mathrm{Fc}^{+}_{\,(\mathrm{RTIL})} + \mathrm{X}^{-}_{\,(\mathrm{aq})} \Leftrightarrow \mathrm{Fc}^{+}_{\,(\mathrm{RTIL})} + \mathrm{X}^{-}_{\,(\mathrm{RTIL})} \qquad (3)$$

This process depended on the polarity of the binder and the formation of ion pairs in the nonaqueous phase [9]. For electrochemical electron transfer reactions followed by reaction (3) redox potential ($E_{\mathrm{Red}/Ox}$) can be described using a Nernstian type equation [30,31], provided that the concentration of the aqueous electrolyte is considerably larger than the concentration of Fc in the RTIL.

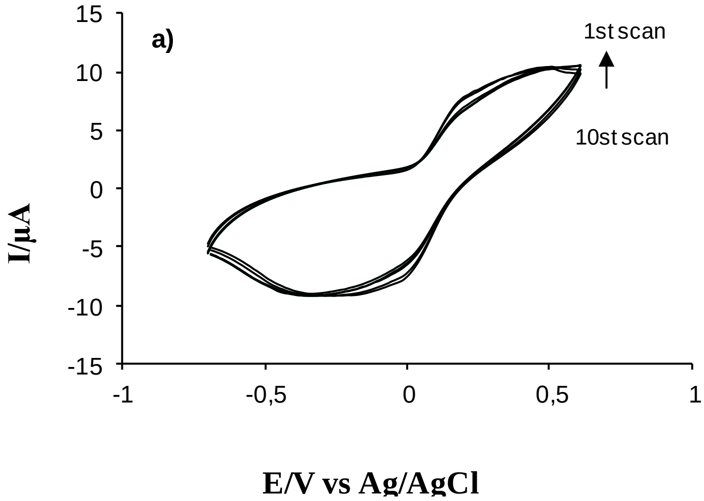
$$E_{\mathrm{Red}/Ox} = E^0_{Fc^+_{RTIL}/Fc_{RTIL}} + \Delta^{RTIL}_{aq}\varphi^0_X - \frac{RT}{F}\ln c_{X^-} + \frac{RT}{F}\ln\frac{C^*_{Fc_{RTIL}}}{2} \qquad (4)$$

Where $E^0_{Fc^+_{RTIL}/Fc_{RTIL}}$ is the standard redox potential of Fc^+/Fc couple in the RTIL phase, $\Delta^{RTIL}_{aq}\varphi^0_X$ is the standard transfer potential of X^- from water to RTIL, C_{X^-} and $C^*_{Fc_{RTIL}}$ are the initial concentrations of X^- in water and Fc in RTIL phase, respectively. The values of the standard transfer potential of anion from water to nitrobenzene (NB), $\Delta^{NB}_{aq}\varphi^0_X$ were used [32], because of the lack of data for [OMIM]Bf$_4$| water interface. If there is no contribution reaction (2), one should expect $E_{\mathrm{Red}/Ox}$ vs. $\Delta^{RTIL}_{aq}\varphi^0_X$ to have a slope of 1.

3.2. Characterization of the voltammetric responses for the biphasic oxidation of Fc

In order to find the best binder, the effect of various ionic liquid including [OMIM]BF$_4$, [Bpy]BF$_4$ and ([HMIM]BF$_4$ on the voltammograms of Fc were compared , as shown in Figure 1. In this figure, it can be noted that the voltammograms of electrode containing [OMIM]BF$_4$ was reproducible and stable (figure 1.a). Whereas no stable voltammogrames obtained in case of [Bpy]BF$_4$ and ([HMIM]BF$_4$. The changes of current in the figure 1.b were even more than figure 1.c. Anodic and cathodic peak in figure 1.a show the forward and backward components of the reaction 1.

Reduction and oxidation of Fc both occur in non-aqueous phase. Hence after oxidation of Fc a lot of positive charges are accumulated in RTIL phase. If the reaction 3 dominates, entrance of ClO_4^- in to non-aqueous phase can compensate excess charges and prevent Fc^+ ejection into the aqueous phase. As a result, the stability of voltammograms and increasing reduction currents confirm that Fc^+ remains in the RTIL phase. On the other hand, the results obtained of this study showed that the proposed electrode was even more stable, during voltammetric measurements, than previously reported electrodes using more hydrophobic redox probes [8,9,12,33].



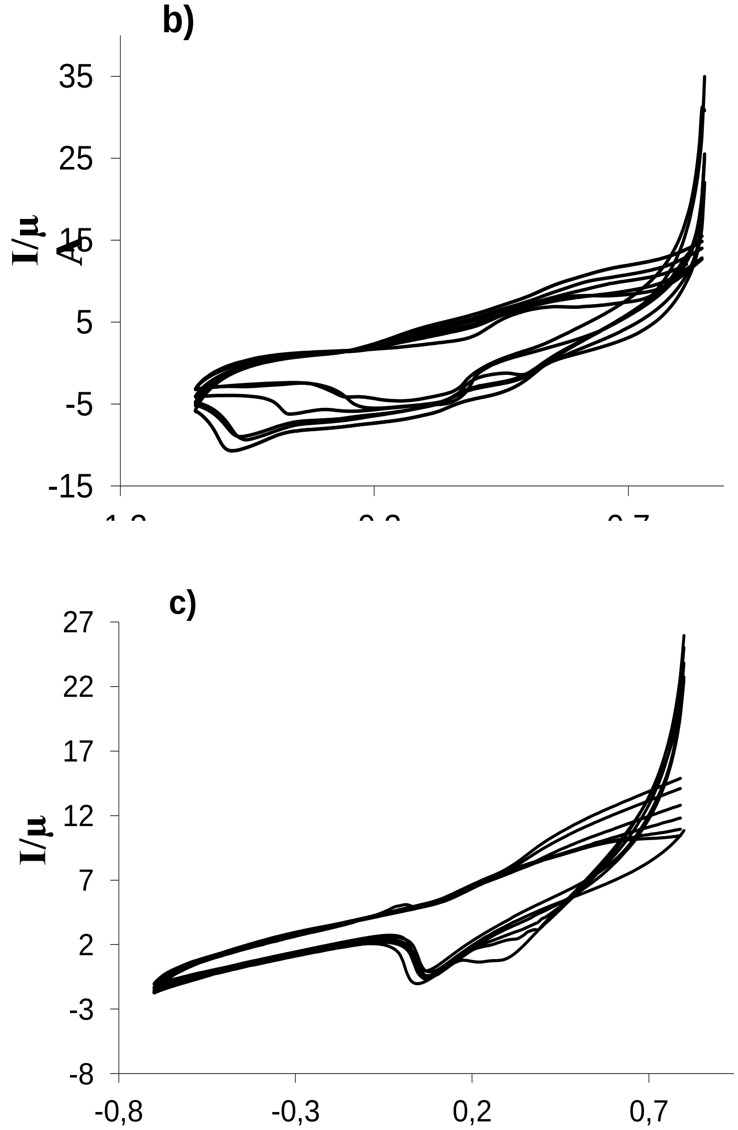


Figure 1. Voltammograms of CPE containing 0.01 mol dm^{-3} Fc solution in a) [OMIM]BF_4 b) [Bpy]BF_4 c) ([HMIM]BF_4, immersed in 0.1 mol dm^{-3} aqueous $KClO_4$. The 1st, 2nd, 4th, 7th, 8th and 10th scan are shown. The arrow indicates the increasing number of scans; scan rate 10 mV s^{-1}.

3.3. Effect of MWCNT on the voltammetric responses for the biphasic oxidation of Fc

Figure 2 demonstrates Cyclic of the CPE containing MWCNT prepared with 0.01 mol dm^{-3} Fc solution in [OMIM]BF_4 immersed in 0.1 mol dm^{-3} aqueous $KClO_4$, at scan rate 10 mV s^{-1} . In this figure, the peaks potential are related to two the redox reaction of Fc and ions transfer in liquid-liquid interface.

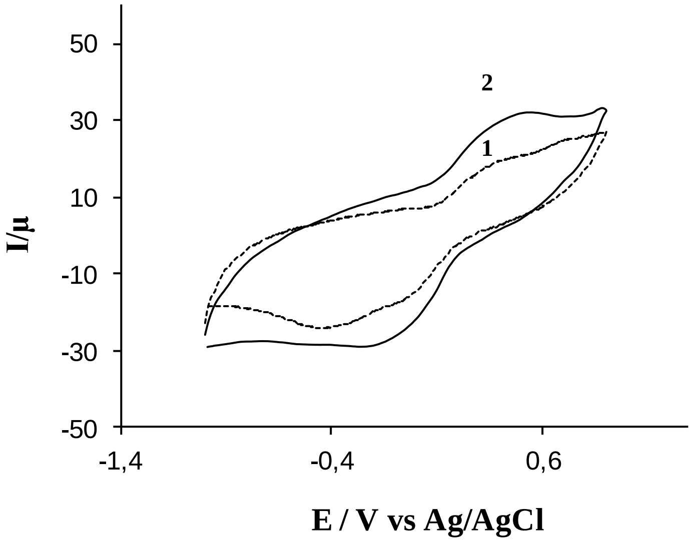


Figure 2. CVs of 2nd, 4th, 6th , 8th and 10th scan of CPE containing 0.01 mol dm^{-3} solution of Fc in [OMIM]BF$_4$ in absence (- - - - -) and present (———) of MWCNT, the CPE immersed in 0.1 mol dm^{-3} aqueous solution of KClO$_4$. Scan rate is 10 mV s^{-1}.

It can be seen that the peak current 2 is larger than peak 1 current, also during the forward scan the oxidation potential of peak 1 shifted to less positive potential values (503 mV) in presence of MWCNT. This suggests that MWCNT enhances the contact surface of the electrode and could facilitate the reaction 1. Consequently, the entrance of anions into the RTIL phase increases, which can be due to production of a large amount of the positive charges in non-aqueous phase. However, during the backward scan, the reduction peak at -454 mV shifted to -164 mV. It seems that the reduction of Fc$^+$ is also facilitated in presence of MWCNT at the electrode surface. The result shows that using MWCNT in the composition of CPE can improve in ITIES processes. Corresponding, the oxidation and reduction currents were enhanced in presence of MWCNT, indicating that the redox reaction of Fc and anion (ClO$_4^-$) transfer was facilitated.

3.4. The effect of the type of aqueous electrolyte

The potentials of both the oxidation and reduction peaks depend on the hydrophobicity of the aqueous anions. According to the equation (1), if reaction 3 is dominated, one should expect a linear plot of $E_{\mathrm{Re}d/Ox}$ vs. $\Delta_{aq}^{RTIL}\varphi_X^0$ with unit slope. In order to discriminate the mechanism of electron and ion transfer across the RTIL | aqueous solution interface, FFT-SWVs of Fc in the present of various aqueous salts are investigated in Figure 3. As can be seen in this figure, the shift of the voltammetric signals depends strongly on the nature of the anion present in the aqueous solution. With increase in the hydrophobicity of anions in the sequence ClO$_4^-$ - Cl$^-$, the SWV peaks shift toward more negative potentials. The shift of voltammetric signal as a result of increasing hydrophobicity can prove that reaction 3 is dominated and indicate that the anion transfer from the aqueous to the RTIL accompanies the oxidation of Fc to Fc$^+$ in the non-aqueous phase. Also this effect is consistent with equation (1).

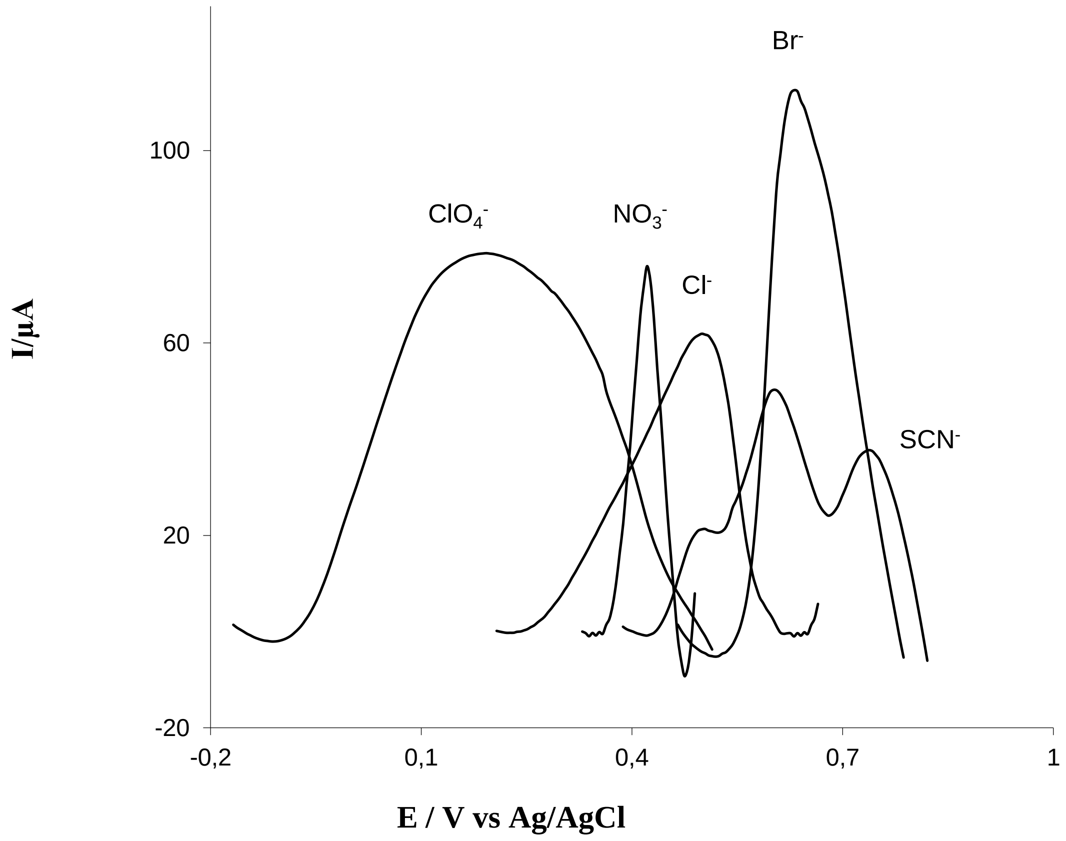


Figure 3. SW voltammetric responses (frequency 10 Hz, amplitude 50 mV and scan increment 1 mV) of MWCNT modified CPE containing 0.01 mol dm^{-3} Fc immersed in different anion solutions.

On the other hand, it is interesting that FFT-SWV response of SCN- (figure 3) is extraordinary and split into three peaks, probably because of reaction between SCN- and iron existing in Fc. Figure 4 shows $E_{\mathrm{Red}/Ox}$ vs. $\Delta_{aq}^{NB}\varphi_X^0$ of ClO_4^-, NO_3^-, Br^- and Cl^- obtained by FFT-SWV method. $\Delta_{aq}^{NB}\varphi_X^0$ describes the ability of the anion to be transferred across the water–non aqueous solvent interface, and therefore its hydrophilicity.

It appears that shift of the voltammetric signal depends on the hydrophobicity of ClO_4^- in aqueous phase, because after the heterogeneous electron transfer reaction, the anions predominantly entered the RTIL phase according to reaction (3).

Although the points on $E_{\mathrm{Red}/Ox}$ versus $\Delta_{aq}^{NB}\varphi_X^0$ plot are somewhat scattered, it is obvious that in the presence of more hydrophobic anions, oxidation potential of Fc shifted to less positive value. The correlations between $E_{\mathrm{Red}/Ox}$ vs. $\Delta_{aq}^{NB}\varphi_X^0$ were linear and the slope of this straight line was 1.096. This result was in accordance with equation (1). In this work, in spite of using a hydrophilic redox probe (Fc), which is cheaper and exceedingly available, the reaction 3 was dominated because of using a suitable ionic liquid.

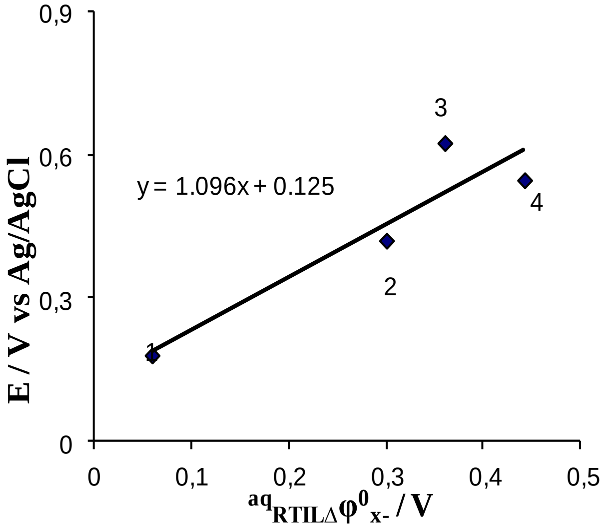


Figure 4. FFTSW voltammetric responses of MWCNT modified CPE containing 0.01 mol dm^{-3} Fc in [OMIM]BF$_4$ immersed in 0.1 mol dm^{-3} different anions solutions (1) ClO_4^- , (2) NO_3^-, (3) Br^-, and (4) Cl^-; All conditions as described in Figure 3.

3.5. The effect of the concentration of the aqueous electrolyte

According to the results obtained in Figure 5, when the concentration of ClO_4^- in water was higher than that concentration of Fc in RTIL, $E_{Red/Ox}$ for the oxidation of 0.01 mol dm^{-3} Fc in RTIL. The concentration of Fc linearly depended on the logarithm of the concentration of aqueous ClO_4^- solutions, with a slope of -0.62, which is close to that predicted (-0.59) by equation (1).

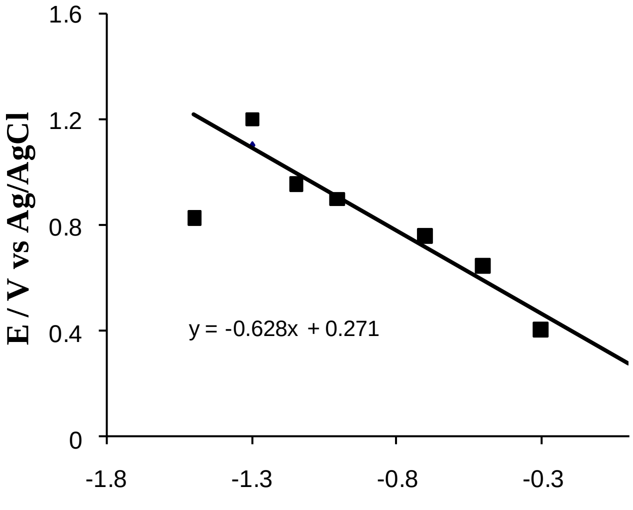


Figure 5. FFTSW voltammetry of MWCNT modified CPE containing 0.01 mol dm^{-3} Fc in [OMIM]BF$_4$ immersed in various concentrations of KClO$_4$ aqueous solutions. All conditions are like Figure 3.

It is clear that, in accordance with equation 1, $E_{\mathrm{Red/Ox}}$ shifted to more positive potentials as the ClO_4^- concentration decreased. In the case of the low concentration solutions, no dependency of potentials to the logarithm of concentration of the aqueous electrolyte was seen. This may due to the low concentration of ClO_4^- in aqueous phase leads to ejection of Fc^+ in to aqueous phase in order to maintain charge of the solution neutral. The difference between the theoretical slope and the experimental slope can be result of the deviation activity coefficients in theoretical model.

4. CONCLUSIONS

1. In this study, a new nanocomposite carbon paste electrode was prepared based on Fc as a redox probe and [OMIM]BF_4 as a binder. Using [OMIM]BF_4 was found to stabilize Fc^+ in the RTIL phase and dominate anion transfer from aqueous solution to the RTIL phase.
2. In the published, because of possible leakage of Fc^+ into the aqueous phase, Fc was reported as an unstable redox probe in comparison with DMFc and tBuFc. Using [OMIM]BF_4 makes it possible to use Fc, which is more available redox probe than the other ones.
3. Using MWCNT in the CPE composition facilitates the electron transfer rate and affected the ion transfer process. Because of obtaining well developed peak currents in presence of MWCNT.

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