Electrochemical Behaviors of Methocarbamol at an Acetylene Black-Ionic Liquid Modified Carbon Paste Electrode and its Electrochemical Determination

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Abstract. Electrochemical behaviors of methocarbamol (MET) at the bare carbon paste electrode (CPE), acetylene black (AB) modified carbon paste electrode (AB/CPE), an ionic liquid 1-Benzyl-3-Methylimidazole hexafluorophosphate ([BnMIM]PF$_6$) modified carbon paste electrode ([BnMIM]PF$_6$/CPE) and AB-[BnMIM]PF$_6$ modified carbon paste electrode (AB-[BnMIM]PF$_6$/CPE) in PBS (pH = 6.8) were investigated by cyclic voltammetry (CV) and square wave voltammetric (SWV). The experimental results showed that MET at the above metioned four electrodes showed an irreversible electrochemical oxidation process, but at the AB-[BnMIM]PF$_6$/CPE, the oxidation peak potential keep almost constant and the oxidation peak current of MET increased greatly. At the same time, the electrochemical kinetic parameters were determined. Under the optimized electrochemical experimental conditions, the oxidation peak currents were proportional to MET concentration range from 4.0×10^{-5} to 1.0×10^{-2} mol L^{-1} with the detection limit (S/N = 3) of 1.5×10^{-6} mol L^{-1}. The proposed method was successfully applied in the determination of MET content in commercial tablet samples. (doi: 10.5562/cca2094)

Keywords: AB-[BnMIM]PF$_6$/CPE, Methocarbamol, Electrochemical behaviors, Electrochemical determination

INTRODUCTION

Methocarbamol (MET), 3-(2-methoxyphenoxy)-1,2-propandiol-1-carbamate (structure formula shown in Figure 1.) is a central muscle relaxant that is used to treat skeletal muscle spasms and relieve pain and discomfort caused by strains, sprains, and the other muscle injuries for human and the other mammals.[1,2] MET is easily absorbed from the intestine and widely distributed in all body tissues, especially the liver and the kidney.[3] Hence, it is very necessary to determine the amount of MET in drug formulations. To date, the widely used techniques for the determination of MET are high performance liquid chromatography (HPLC),[4,5] high performance liquid chromatography coupled with mass spectrometry (HPLC-MS),[6] spectrophotometry,[7] spectrophotometry-LC,[8] reversed phase liquid chromatography (RP-LC),[9] spectrofluorometric,[10] H-NMR spectroscopy[11] and the electrochemical method.[12] Among the electrochemical one mentioned above, it mainly discuss the electrochemical determination of MET on a montmorillonite-Ca modified carbon paste electrode in formulation and the human blood.[12]

Ionic liquids (ILs) are ionic compounds consisting of organic cations and various kinds of anions, which are liquids at temperatures around 298 K and below. ILs has a number of valuable properties such as high ionic conductivity, electrochemical thermal stability, negligible vapor pressure and wider electrochemical windows, etc.[13,14] Due to their nature, ILs are non-flammable, non-volatile and non-hazardous which makes them attractive as "green" solvents for many chemical processes in both industrial and laboratory scales. Meanwhile, they have been widely used as a modifier or binder to fabricate electrodes in the field of electrochemistry.
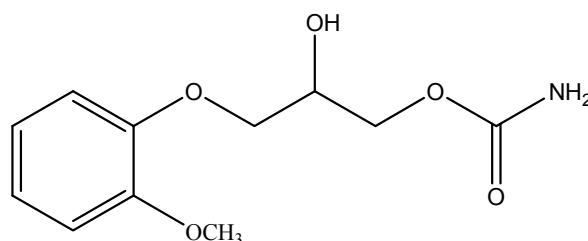

Figure 1. Structural formula of Methocarbamol (MET).

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Acetylene black (AB), a special type of carbon black, is made by the controlled combustion of acetylene in air under pressure.[15] AB has porous structure and possesses many fascinating properties such as good conductivity, large surface area and strong adsorptive ability.[16,17] Thus, AB was used as a substitute of graphite powder in preparation of carbon paste electrode[18–20] and was also successfully used as a modifier to fabricate electrodes in electrochemistry to increase the determining sensitivity of different species such as rutin,[17] 6-benzylaminopurine,[21] colchicine,[22] 1-Naphthylacetic Acid,[23] 2-chlorophenol.[24] However, electrochemical behaviors, electrochemical kinetics and electrochemical determination of MET using AB and ionic liquid 1-Benzyl-3-Methylimidazole hexafluorophosphate ([BnMIM]PF$_6$) modified carbon paste electrode (AB-[BnMIM]PF$_6$/CPE) have not been reported yet.

As continuations of our previous work,[25–28] an AB-[BnMIM]PF$_6$/CPE had been fabricated by using acetylene black (AB) and 1-Benzyl-3-Methylimidazole hexafluorophosphate ([BnMIM]PF$_6$) as a modifier and characterized by both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrochemical behaviors and the electrochemical determination of MET were investigated at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE by CV and the square wave voltammetry (SWV). Its electrochemical kinetic parameters were also determined. Meanwhile, an electrochemical quantitative determination was established which was successfully used for MET content determination in commercial tablet samples.

EXPERIMENTAL

Apparatus

All electrochemical experiments were performed using an Electrochemistry Workstation CHI660A (CHI Instrument, USA). A conventional three-electrode system was used including carbon paste electrode (CPE), 1-Benzyl-3-Methylimidazole hexafluorophosphate ([BnMIM]PF$_6$) modified carbon paste electrode ([BnMIM]PF$_6$/CPE), acetylene black (AB) modified carbon paste electrode (AB/CPE) and AB-[BnMIM]PF$_6$ modified carbon paste electrode (AB-[BnMIM]PF$_6$/CPE) as the working electrodes, a saturated calomel electrode (SCE) as the reference electrode, and platinum wire as the auxiliary electrode, respectively. All of the electrochemical experiments were carried out at room temperature with the nitrogen purged for 5 min before the experiments. All potentials measured and reported in this work were *vs.* SCE.

Chemicals and Reagents

MET (Batch No. G7012-5G, Purity 99 %) was purchased from sigma-aldrich Co. (USA) and used without further purification. MET tablets (Batch No. 100901069) was purchased from Nanjing Baijingyu Pharmacentical Co. Ltd. (Nanjing, China). 1-Benzyl-3-Methylimidazole hexafluorophosphate ([BnMIM]PF$_6$) was purchased from Chengjie Chemical Reagent Co. Ltd (Shanghai, China, Purity 99 %). Acetylene black (AB) was purchased from Baishun chemical technology Co., Ltd. (Beijing, China, AR). All of the other chemicals were of analytical grade and double distilled water was used throughout this work. In addition, 0.10 mol L^{-1} Na$_2$HPO$_4$/NaH$_2$PO$_4$ buffer solution (PBS, pH = 6.8) was used as the supporting electrolyte.

Fabrication of Modified Electrodes

The bare CPE was prepared by mixing 1.2 g of graphite powder with 0.40 mL of paraffin oil thoroughly in a mortar to form a homogeneous carbon paste. A portion of the carbon paste was filled firmly into one end of a polytetrafluoroethylene (PTFE) tube, and a copper wire was inserted through the opposite end to establish an electrical contact. The surface of CPE was polished on a piece of weighing paper to get a smooth surface just before use. The AB/CPE was fabricated using the same procedure except that 0.12 g AB was mixed with 1.2 g of graphite powder firstly. The surface of AB/CPE was polished on a piece of weighing paper to get a smooth surface just before use lastly.

The [BnMIM]PF$_6$/CPE was fabricated by dissolving 0.60 g of [BnMIM]PF$_6$ in 0.60 mL of *N,N*-dimethyl-Formamide (DMF), and then added in 1.2 g of graphite powder in a mortar, grounded until DMF totally volatilized, and finally mixed with 0.60 mL of paraffin oil in a mortar. A portion of the carbon paste was filled firmly into one end of a polytetrafluoroethylene (PTFE) tube, and a copper wire was inserted through the opposite end to establish an electrical contact. The surface of [BnMIM]PF$_6$/CPE was polished on a piece of weighing paper to get a smooth surface just before use. The AB-[BnMIM]PF$_6$/CPE was fabricated in a similar way, except that 0.12 g AB was mixed with 1.2 g of graphite powder. The surface of AB-[BnMIM]PF$_6$/CPE was polished on a piece of weighing paper to get a smooth surface just before use.

RESULTS AND DISCUSSION

Characterization of Electrodes

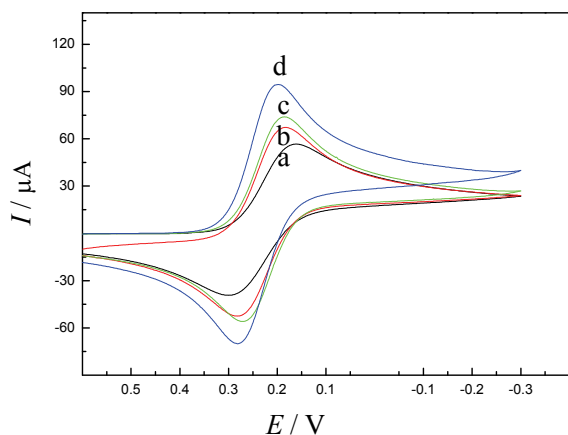Electrochemical behaviors of the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE were

Figure 2. CVs of the bared CPE (a), AB/CPE (b), [BnMIM]PF$_6$/CPE (c) and AB-[BnMIM]PF$_6$/CPE (d) in 5.0 × 10^{-3} mol L^{-1} K$_3$[Fe(CN)$_6$] + 1.0 mol L^{-1} KCl. Scan rate: 50 mV s^{-1}.

Figure 3. EIS for the bared CPE (a), AB/CPE (b), [BnMIM]PF$_6$/CPE (c) and AB-[BnMIM]PF$_6$/CPE (d) in 5.0 × 10^{-3} mol L^{-1} [Fe(CN)$_6$]$^{3-/4-}$ + 1.0 mol L^{-1} KCl. The frequency range is 1–10^5 Hz.

investigated using K$_3$[Fe(CN)$_6$] as a redox probe by CV firstly. Figure 2. shows the cyclic voltammograms of 5.0 × 10^{-3} mol L^{-1} K$_3$[Fe(CN)$_6$] containing 1.0 mol L^{-1} KCl in potential range of −0.3 to 0.6 V at four electrodes. Figure 2a. is cyclic voltammogram curve of bare CPE, which has a pair of redox peaks with the cathodic peak potential (E_{pc}) as 0.161 V and the anodic peak potential (E_{pa}) as 0.300 V. The cathodic peak current (I_{pc}) and the anodic peak current (I_{pa}) is got as 5.534 × 10^{-5} A and 4.890 × 10^{-5} A, respectively. The peak-to-peak separation (ΔE_p) is 139 mV and the ratio of I_{pa}/I_{pc} is 1.1. The results indicated the electrode reaction was a quasi-reversible process. Figure 2b. is cyclic voltammogram curve of AB/CPE with E_{pc} of 0.183 V, E_{pa} of 0.282 V, and ΔE_p of 99 mV. Figure 2c. is cyclic voltammogram curve of [BnMIM]PF$_6$/CPE with E_{pc} of 0.185 V, E_{pa} of 0.272 V, and ΔE_p of 87 mV. Compared with the bare CPE, the redox peak currents of [BnMIM]PF$_6$/CPE and AB/CPE increased greatly and the peak-to-peak separation decreased obviously. Figure 2d. is cyclic voltammogram curve of AB-[BnMIM]PF$_6$/CPE with E_{pc} of 0.198 V, E_{pa} of 0.282 V. The cathodic peak current (I_{pc}) and the anodic peak current (I_{pa}) is got as 9.392 × 10^{-5} A and 9.045 × 10^{-5} A, respectively. The redox peak currents is about 1.5 folds larger than that on [BnMIM]PF$_6$/CPE and AB/CPE. Simultaneously, The peak-to-peak separation (ΔE_p) is 84 mV and the ratio of I_{pa}/I_{pc} is 1.0, suggesting a reversible electron transfer process. The results indicated that the good conducting property of AB and ILs could greatly promote the electron transfer rate of [Fe(CN)$_6$]$^{3-}$.

For further characterization of the modified electrode, electrochemical impedance spectroscopy (EIS) was used. EIS could reflect the surface properties of the modified electrodes[29] by using [Fe(CN)$_6$]$^{3-/4-}$ redox couples as an electrochemical probe. The EIS consists of two sections: one is the linear part at lower frequen-
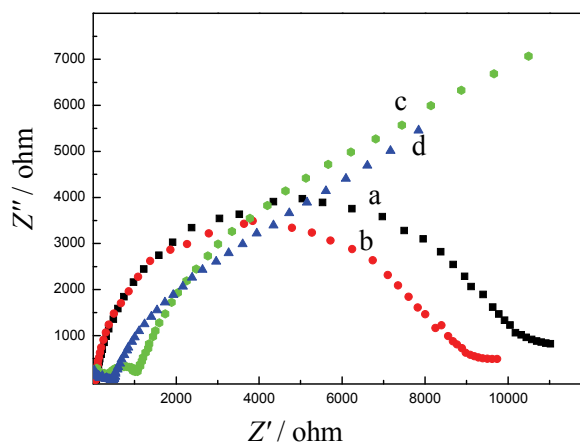
cies representing the diffusion-limited process; the other one is a semicircle portion observed at higher frequencies corresponding to the electron-transfer-limited process.[30] Generally, the diameter of the semicircle is usually equal to the electron transference resistance (Ret).[31] Figure 3. shows Nyquist diagrams of 5.0 × 10^{-3} mol L^{-1} [Fe(CN)$_6$]$^{3-/4-}$ at different electrodes with the frequencies from 1 Hz to 100 kHz. From curve a in Figure 3. it can be seen that the bare CPE exhibited a large semicircle in the high frequencies range with a large electron transfer resistance (Ret), suggesting a sluggish electrochemical performance of the redox probe on the bare CPE. This might be due to the presence of nonconductive paraffin oil in the carbon paste, which played an important role in hindering the electron transfer and made it more difficult for the electron transfer reaction to take place. Mealwhile, the nonconductive paraffin oil increased the resistance of Fe(CN)$_6^{3-/4-}$ redox couple. From Figure 3. curve b it can be seen that the AB/CPE showed a smaller semicircle than that on the bare CPE in the high frequencies range. From Figure 3. curve c it can be seen that the [BnMIM]PF$_6$/CPE showed a quasi-semicircle portion with much smaller diameters than that of the AB/CPE in the high frequencies range. Whereas, the AB-[BnMIM]PF$_6$/CPE (Figure 3d.) showed a quasi-semicircle portion with smallest diameters in the high frequencies range, which was attributed to the good conductivity of AB[16] and ILs,[13,14] and the least charge transfer resistance of AB-[BnMIM]PF$_6$/CPE. At low frequencies, [BnMIM]PF$_6$/ CPE and AB-[BnMIM]PF$_6$/CPE represented a linear with a larger slope than that of the bare CPE and the AB/CPE, which is a characteristic of diffusion limited electrochemical process. The experimental results of EIS confirmed that the AB-[BnMIM]PF$_6$/CPE could promote the electron transfer rate of [Fe(CN)$_6$]$^{3-/4-}$ effectively.
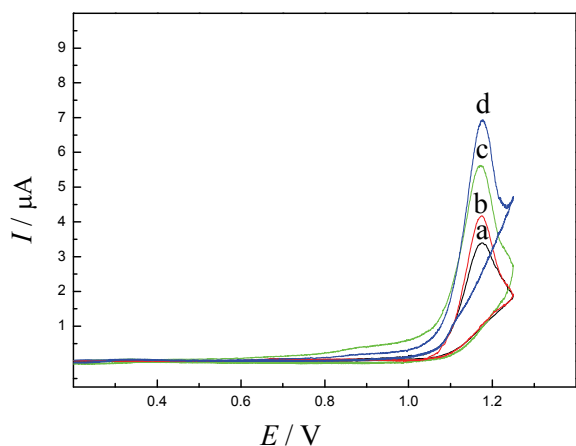
Figure 4. CV curves of 1.0×10^{-4} mol L^{-1} MET in PBS at the bared CPE (a), AB/CPE (b), [BnMIM]PF$_6$/CPE (c) and AB-[BnMIM]PF$_6$/CPE (d). Scan rate: 100 mV s^{-1}.

Cyclic Voltammetric Behaviors of MET

The electrochemical behaviors of 1.0×10^{-4} mol L^{-1} MET at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE were investigated with the scanning rate of 100 mV s^{-1} in PBS (pH = 6.8) over the potential range between 0.20 V and 1.25 V by CV (Figure 4.). From Figure 4. curve a, it can be seen that an irreversible oxidation peak in the presence of MET are observed at the bare CPE with the oxidation peak potential and the oxidation peak current of 1.178 V, 3.351×10^{-6} A, respectively. From the comparision of CPE (curve a), AB/CPE (curve b) and [BnMIM]PF$_6$/CPE (curve c) in Figure 4., it is very clear that the oxidation peak current of MET at the AB/CPE and [BnMIM]PF$_6$/CPE were larger than that of CPE about 1 times and 1.7 times, respectively. While at the AB-[BnMIM]PF$_6$/CPE (Figure 4d), there was a sensitive oxidation peak located at 1.178 V with the oxidation peak current as 6.915×10^{-6} A. The oxidation peak potential of MET at AB-[BnMIM]PF$_6$/CPE keep almost constant and the oxidation peak current increased significantly by 2.1 times compared with that of CPE, which exhibited a great response of electrocatalytic activity. The above mentioned experiment results indicated that the presence of AB and ionic liquid in the modified electrode showed a good electrocatalytic ability to oxidation of MET, which was attributed to the high conductivity, the large surface area of AB[16] and the inherent catalytic ability of ILs.[32]

The effect of scanning rate (v) on the oxidation peak current (I_p) of 1.0×10^{-4} mol L^{-1} MET at AB-[BnMIM]PF$_6$/CPE was investigated by CV as shown in Figure 5. With the increasing scanning rate from 10 to 1000 mV s^{-1}, the oxidation peak currents increased gradually. The oxidation peak currents (I_p) *vs.* the square roots of the scanning rate ($v^{1/2}$) had a good linear relationship, which the linear regression equation is
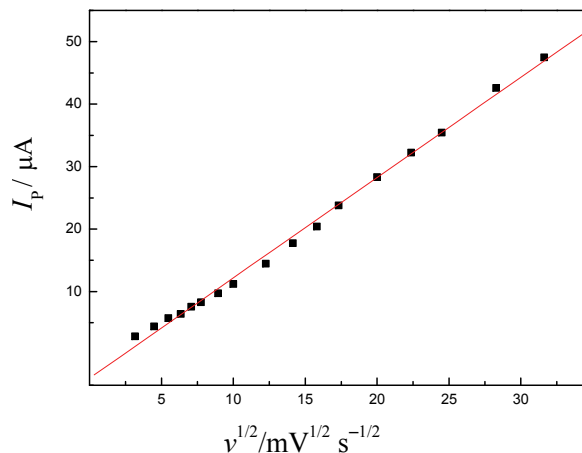

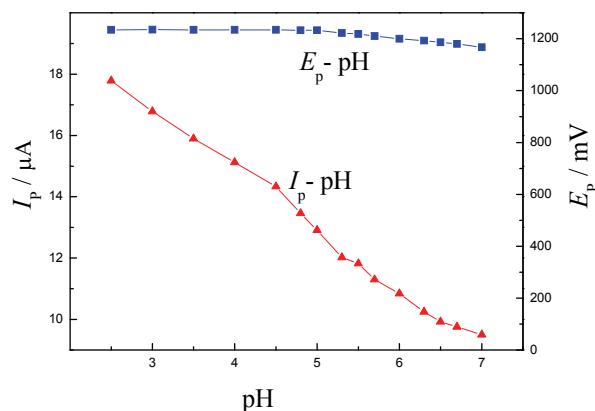**Figure 5.** The relationship of the oxidation peak current I_p *vs.* $v^{1/2}$ at AB-[BnMIM]PF$_6$/CPE.

Figure 6. Effect of pH on E_p and I_p of 1.0×10^{-4} mol L^{-1} MET at AB-[BnMIM]PF$_6$/CPE.

expressed as $I_p/\mu A = -3.868 + 1.606 \; v^{1/2}/mV^{1/2} \; s^{-1/2}$ ($R = 0.9981$). It indicated that the electrochemical oxidation of MET at AB-[BnMIM]PF$_6$/CPE was a diffusion-controlled electrode reaction process.

The Effect of Experimental Conditions on the Peak Currents and Potentials

The effect of various media on the peak currents and potentials of MET could be easily observed from CV. The CV of 1.0×10^{-4} mol L^{-1} MET at scanning rate of 100 mV s^{-1} in different electrolyte solutions such as 0.10 mol L^{-1} NaNO$_3$, Na$_2$SO$_4$, NaCl, NaClO$_4$, Na$_2$HPO$_4$/NaH$_2$PO$_4$(PBS), NaAc and 0.04 mol L^{-1} Britton-Robinson buffer solution had been investigated. The experiment results showed that in 0.10 mol L^{-1} PBS, MET had a well-defined electrochemical behavior. Therefore, 0.10 mol L^{-1} PBS was chosen as supporting electrolyte.

The effect of pH on the electrochemical response of 1.0×10^{-4} mol L^{-1} MET was investigated in the pH range from 2.5 to 10.0 as shown in Figure 6.

From Figure 6., it can be seen that the oxidation peak potential (E_p) of MET keep constant with the increase of pH from 2.5 to 5.0. But the oxidation peak potential (E_p) of MET negatively move slightly from 5.0 to 7.0. 1.0×10^{-4} mol L^{-1} MET at AB-[BnMIM]PF$_6$/CPE have no oxidation peak from 7.0 to 10.0. It was also found that the oxidation peak currents (I_p) of MET decreased gradually with the increase of pH from 2.5 to 7.0.

Electrode Reaction Kinetics

The Charge-transfer Coefficient α
The effect of scanning rate (v) on the oxidation peak potential (E_p) of 1.0×10^{-4} mol L^{-1} MET at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE was also investigated by CV in the range from 10 to 1000 mV s^{-1}, respectively. From the experiment results, we can see that with the increasing of v the oxidation peak potential was positively shifted. A linear relationship can be obtained in the range of 10–1000 mV s^{-1} at AB-[BnMIM]PF$_6$/CPE as shown in Figure 7. The linear regression equation can be expressed as E_p / mV = 1087.0 + 52.4 log v / mV s^{-1} (R = 0.9990). According to the slope of $E_p \sim$ log v, it can be got as $\partial E_{pa} / \partial (\log v) = 52.4$ mV.

For an irreversible diffusion-controlled process, the Tafel slope b was determined using the following equation:[33]

$$E_p = (b \log v) / 2 + \text{constant} \quad (1)$$

From the Eq. (1), we know that the slope of E_p *vs.* log v curve is $b/2$, where b indicates the Tafel slope. so, $b = 2 \times \partial E_{pa} / \partial (\log v) = 104.6$ mV. While $b = 2.303 RT/n(1-\alpha)F$, the number of electrons involved in the electrochemical oxidation reaction of MET is 2[12], F is the Faraday's constant (96,485 C mol^{-1}), and the other symbols have their usual meanings, so α can
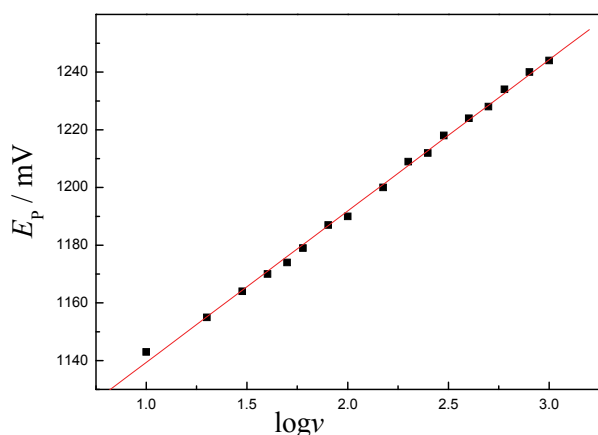

Figure 7. The relationship of the oxidation peak potential E_p *vs.* log v at AB-[BnMIM]PF$_6$/CPE.

be obtained. In the same way, α can be obtained at the bare CPE, AB/CPE and [BnMIM]PF$_6$/CPE as shown in Table 1.

Diffusion Coefficient D
The electrode area (A) for the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE can be calculated by the slope of Q *vs.* $t^{1/2}$ by chronocoulometry (CC) using 5.0×10^{-3} mol L^{-1} K$_3$[Fe(CN)$_6$] as model complex (the diffusion coefficient D of K$_3$ [Fe(CN)$_6$] is 7.6×10^{-6} cm^2 s^{-1})[34] based on Eq. (2)[35]

$$Q = 2nFAc\sqrt{Dt/\pi} + Q_{dl} + Q_{ads} \quad (2)$$

Based on the slope of Q *vs.* $t^{1/2}$, A can be calculated when c (MET concentration), D (diffusion coefficient of 5.0×10^{-3} mol L^{-1} K$_3$[Fe(CN)$_6$]), and n (electron transfer number) are known.

The diffusion coefficient D of MET at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE can also be determined using CC based on Eq. (2). From the slope of Q *vs.* $t^{1/2}$, D can be obtained as shown in Table 1.

The electrode Reaction Rate Constant k_f
The electrode reaction rate constant (k_f) at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE were calculated by Chronoampertry (CA) based on Eq. (3).[36]

$$I(t) = nFAk_f c \left[1 - 2H\sqrt{t/\pi} \right] \quad (3)$$

in which, $H = k_f / D_{Ox}^{1/2} + k_b / D_{Red}^{1/2}$. For the totally irreversible electrochemical reaction, the value of k_b is 0, therefore, when t approaches to 0, the plot of $I(t)$ *vs.* $t^{1/2}$ gives a good straight line. So, k_f can be calculated from the intercept of CA curve at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE as shown in Table 1.

From the comparison of α, D and k_f value of 1.0×10^{-4} mol L^{-1} MET at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE in Table 1, it was founded that α, D, and k_f value increased gradually at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE. But at the AB-[BnMIM]PF$_6$/

Table 1. Kinetic parameters for MET at bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE

Electrodes	a	D/cm^{2}s^{-1}	k_f/cms^{-1}
Bare CPE	0.612	2.485×10^{-5}	2.244×10^{-3}
AB/CPE	0.622	3.035×10^{-5}	2.466×10^{-3}
[BnMIM]PF$_6$/CPE	0.707	3.277×10^{-4}	7.609×10^{-3}
AB-[BnMIM]PF$_6$/CPE	0.723	5.465×10^{-4}	1.095×10^{-2}

CPE, α, D, and k_f value was largest, thus the experiment results showed that the presence of AB and [BnMIM]PF$_6$ in the modified electrode showed a good electrocatalytic ability to oxidation of MET. Meanwhile, the experimental result was in quite good agreement with that of CV.

Electrochemical Determination Application

Square Wave Voltammetric (SWV) Behaviors of LBT
The SWV behaviors of 1.0×10^{-4} mol L^{-1} MET at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE in PBS under the optimized experimental conditions (the frequency 50 Hz, the pulse amplitude 40 mV, and the scanning potential increment 4 mV) was shown in Figure 8. From Figure 8. curve a, it can be seen that an irreversible oxidation peak in the presence of MET are observed at the bare CPE with the oxidation peak potential and the oxidation peak current of 1.172 V, 1.495×10^{-5} A, respectively. From the comparison of CPE (curve a), AB/CPE (curve b), and [BnMIM]PF$_6$/CPE (curve c) in Figure 8., it is very clear that the oxidation peak current of MET at the AB/CPE and [BnMIM]PF$_6$/CPE were larger than that of CPE about 1.2 times and 1.8 times, respectively. While at the AB-[BnMIM]PF$_6$/CPE (Figure 8. curve d), there was a sensitive oxidation peak located at 1.188 V with the oxidation peak current as 4.010×10^{-5} A. The oxidation peak potential of MET at AB-[BnMIM]PF$_6$/CPE keep almost constant and the oxidation peak current increased significantly by almost 3 times compared with that of CPE. The above mentioned experiment exhibited a great response of electrocatalytic activity of MET at the AB-[BnMIM]PF$_6$/CPE. Meanwhile, the experimental result was in quite good agreement with that of CV.

The relationship between oxidation peak currents for MET and its concentration were investigated at the AB-[BnMIM]PF$_6$/CPE. The oxidation peak currents increased linearly with the increasement of MET concentration in the range of 4.0×10^{-5}–1.0×10^{-2} mol L^{-1}. The linear regression equation was expressed as $I_p/\mu A = 40.58 + 62.49c/10^{-3}$ mol L^{-1} ($R = 0.9996$) and the detection limit (S/N = 3) was 1.5×10^{-6} mol L^{-1} for MET under the optimized experimental conditions.

Reproducibility, Stability and Interference
After each experiment, the used carbon paste was carefully removed from the end cavity of the modified electrode. The electrode surface was polished to a mirror manually on a piece of weighting paper and rinsed with redistilled water. Then another new AB-[BnMIM]PF$_6$/CPE was fabricated again. The reproducibility of AB-[BnMIM]PF$_6$/CPE was estimated by comparing the oxidation peak current of 1.0×10^{-4} mol L^{-1} MET. The relative standard deviation (RSD) is 1.8 % with 10 determinations, revealing that this method have good re-
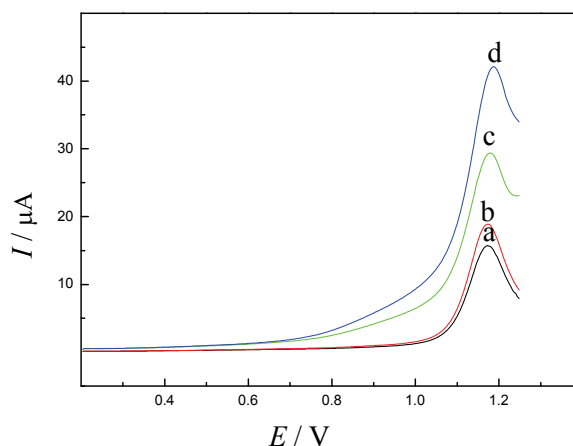

Figure 8. SWV curves of 1.0×10^{-4} mol L^{-1} MET in PBS at the bared CPE (a), AB/CPE (b), [BnMIM]PF$_6$/CPE (c) and AB-[BnMIM]PF$_6$/CPE (d).

producibility. After the modified electrode was stored in the room temperature for ten days, the current response obtained was within less than ±5 %, which can be attributed to the excellent stability of the modified electrode.

On the other hand, some common compounds or inorganic ions were tested to check their levels of interference in MET determination. The results suggest that 100-fold concentration of glucose, sucrose, amylum, magnesium stearate and dextrin have no influence on the signals of MET with relative standard deviations below ±5 %. Otherwise, some inorganic ions such as 300-fold concentration of K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}, Zn^{2+}, SO$_4^{2-}$, NO$_3^-$, Cl$^-$ have no interference in the determination of MET.

Analytical Applications

In order to ascertain the potential application in commercial tablet samples analysis, this proposed method was used to determined MET content in MET tablets. Ten tablets of MET, with labeled amount of 0.250 g of MET per tablet, were grinded evenly into powder in a mortar. Then a right amount of this powder was accurately weighed approximately 0.2412 g, which dissolved by doubly distilled water, then transferred accurately into a 100 mL volumetric flask and added doubly distilled water to scale line. Finally, a known-amount of sample solution was added into PBS determined by SWV. Table 2. shows the content of MET in sample solution which measured by the standard addition method. An acceptable reproducibility with the relative standard deviation of 0.1–0.4 % for commercial tablet samples was obtained for six parallel measurements. By using the standard addition method, the recoveries for the determination of MET were in the range of 98.50–103.2 %, indicating that this method has good accuracy and can be used as an effective electrochemical quantitative determination of MET in commercial tablet samples.

Table 2. Determination results of the samples ($n = 6$)

Samples	Labeled	Founded / g	RSD / %	Added / g	Determined / g	Recoverage / %
1		0.241	0.1	0.065	0.305	98.5
2	0.250 g per tablet	0.249	0.4	0.125	0.378	103.2
3		0.251	0.3	0.250	0.505	101.2

CONCLUSIONS

AB and [BnMIM]PF$_6$ modified carbon paste electrode was successfully fabricated and characterized by CV and EIS. The electrochemical behaviors of MET were investigated at the bare CPE, AB/CPE, [BnMIM]PF$_6$/CPE and AB-[BnMIM]PF$_6$/CPE by CV and SWV. Compared with the bare CPE electrode, the oxidation peak potential keep almost constant and the oxidation peak current of MET increased greatly at AB-[BnMIM]PF$_6$/CPE. Meanwhile, the electrochemical kinetic parameters (charge-transfer coefficient α, diffusion coefficient D and electrode reaction rate constant k_f) of MET were determined at four electrodes by CV, CC and CA. The oxidation peak currents increased linearly with the increasing MET concentration in the range of 4.0×10^{-5}–1.0×10^{-2} mol L^{-1}. The linear regression was expressed as $I_p/\mu A = 40.58 + 62.49 c/10^{-3}$ mol L^{-1} ($R = 0.9996$) with the detection limit (S/N = 3) of 1.5×10^{-6} mol L^{-1} for MET under the optimized experimental conditions. Thus, the proposed method was successfully applied in the determination of MET content in commercial tablet samples with satisfactory results.

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