



J. Serb. Chem. Soc. 77 (4) 483–496 (2012)
JSCS–4284

Electrochemical behavior and electrochemical determination of carbamazepine at an ionic liquid modified carbon paste electrode in the presence of sodium dodecyl sulfate

LI-HONG LIU^{1,2}, CHENG-QIAN DUAN^{1,3} and ZUO-NING GAO^{1*}

¹Key Lab of Energy Sources and Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China, ²Department of Chemistry, Heihe College, Heihe 164300, China and ³Higher Vocational College, Ningxia Medical University, Yinchuan 750004, China

(Received 20 April, revised 9 October 2011)

Abstract: The electrochemical behavior and electrochemical determination of carbamazepine (CBZ) at a hydrophobic ionic liquid 1-benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) modified carbon paste electrode ([BnMIM]PF₆/CPE) in the presence of sodium dodecyl sulfate (SDS) were investigated. A well-defined and sensitive oxidation peak was observed at the [BnMIM]PF₆/CPE in the presence of SDS and a 0.10 M phosphate buffer solution (pH 6.80). The oxidation peak current of CBZ increased significantly at the [BnMIM]PF₆/CPE in the presence of SDS compared with that in the absence of SDS at the carbon paste electrode. It suggested that both SDS and [BnMIM]PF₆/CPE show an obvious enhancing effect on the electrochemical oxidation of CBZ. The electrochemical kinetic parameters for CBZ at the [BnMIM]PF₆/CPE in aqueous SDS solutions were also determined by chronocoulometry and chronoamperometry. Finally, the experimental conditions were optimized, and a new electrochemical method for the determination for CBZ was established. The oxidation peak current was linearly dependent on the CBZ concentration in the range 7.0 μM to 0.7 mM, with a detection limit of 0.98 μM (signal to noise ratio, *S/N* = 3). The relative standard deviation for six determinations of 0.10 mM CBZ was between 1.40 and 2.13 %. The proposed method was applied in the determination of CBZ in commercial tablet samples.

Keywords: carbamazepine; sodium dodecyl sulfate; ionic liquid modified carbon paste electrode; electrochemistry.

INTRODUCTION

Carbamazepine (5*H*-dibenz[*b,f*]azepine-5-carbox-amide, CBZ, structure presented in Fig. 1) has been extensively used in the treatment of epilepsy.¹ Now it

* Corresponding author. E-mail: gaozn@nxu.edu.cn
doi: 10.2298/JSC110420188L

is considered as the most frequently prescribed front-line anticonvulsant in complex partial seizures.² Due to its clinical importance, many analytical techniques have been developed for its determination and also its metabolite in biological fluids (plasma, urine), including high performance liquid chromatography (HPLC),^{3,4} HPLC with an electrochemical detector,⁵ liquid chromatography with mass spectrometry (LC-MS),⁶ gas chromatography,^{7,8} capillary electrokinetic chromatography,⁹ mass spectrometry,¹⁰ chemiluminescence,¹¹ spectrofluorimetry¹² and spectrophotometry.¹³ Electroanalytical techniques bring with them important advantages, such as high sensitivity, relative simplicity, low costs and portable field-based equipment. They therefore offer interesting alternatives to replace the methods that are currently in use. Voltammetric and polarographic methods have been reported for the determination of CBZ. These included polarography in which the electrochemical reduction of CBZ at a mercury drop electrode was studied,^{14,15} potentiometry with polymer membrane-based ion-selective electrodes,¹⁶ more recently, described by Garcia *et al.*¹⁷, the determination of carbamazepine in pharmaceutical solutions using differential-pulse adsorptive stripping voltammetry and the oxidation properties of the molecule with different modified and the unmodified carbon electrodes. Thus, Rodriguez *et al.*¹⁸ studied the electrochemical behavior and determination of carbamazepine on glassy carbon electrodes and microelectrodes. Teixeira *et al.*¹⁹ described the voltammetric determination of carbamazepine at a multi-walled carbon nanotubes (MWCNTs) film-coated glassy carbon electrode (GCE) and Jaldappagari *et al.*²⁰ investigated the electrochemical behavior of carbamazepine (CBZ) at a fullerene-C₆₀ modified glassy carbon electrode. However, its electrochemical behavior and electrochemical determination at an ionic liquid 1-benzyl-3-methylimidazole hexafluorophosphate modified carbon paste electrode ([BnMIM]PF₆/CPE) in the presence of sodium dodecyl sulfate (SDS) has, to the best of our knowledge, not been reported in the literature.

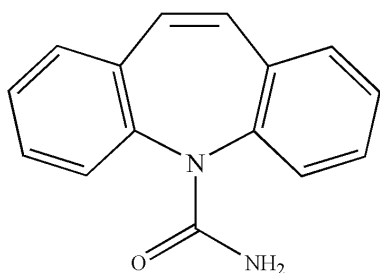


Fig. 1. Structure of carbamazepine.

Recently, the application of room temperature ionic liquids (RTILs) in the fields of analytical chemistry and electrochemical biosensors has attracted much attention. Ionic liquids (ILs) are composed of an organic cation and either an organic or an inorganic anion, preserved in the liquid state over a wide tem-

perature range.²¹ Due to their specific physicochemical characteristics, such as high chemical and thermal stability, good ionic conductivity, negligible vapor pressure and wider electrochemical windows,^{22–27} RTILs have been used as a new modifier on the surface of electrodes or binders to make a carbon ionic liquid electrode (CILE). For example, Safavi *et al.*^{28,29} fabricated an ionic liquid, *i.e.*, octylpyridinium hexafluorophosphate (OPFP), modified carbon paste electrode and investigated the electrochemical oxidation of some phenolic compounds. Zheng *et al.*³⁰ fabricated an ionic liquid, *i.e.*, 1-pentyl-3-methylimidazolium bromide modified carbon paste electrode and investigated the voltammetric determination of rutin. Liu *et al.*³¹ reported a CILE constructed of graphite powder mixed with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) and the electrode had an increased sensitivity of the response toward potassium ferricyanide. Sun *et al.*^{32–34} also combined butylpyridinium hexafluorophosphate (BPPF₆) with graphite powder to fabricate an ILs modified electrode and applied it in the electrochemical determination of different inorganic, organic and biomolecules.

As a continuation of previous work,^{35–38} in this study, the hydrophobic ionic liquid 1-benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) was used as a modifier to fabricate [BnMIM]PF₆/CPE and the electrochemical behavior and electrochemical kinetics of carbamazepine (CBZ) at [BnMIM]PF₆/CPE in the presence of sodium dodecyl sulfate (SDS) were investigated.

Surfactants are a kind of amphiphilic molecule with hydrophilic head on one side and a long hydrophobic tail on the other. They can be adsorbed at an electrode surface and alter the properties of the electrode/solution interface and subsequently influence the electrochemical processes of electroactive species.^{39,40} Now surfactants are extensively used in the fields of electrochemistry and electroanalytical chemistry.⁴¹ Hu and coworkers successfully employed surfactants for the analysis of some biomolecules,^{42,43} and found that the electrochemical responses of the analyzed compounds were remarkably enhanced in the presence of the surfactants. Moreover, they proposed a synergistic adsorption mechanism to interpret the enhancing effects of the surfactants. For example, surfactants might combine with the substrate in certain forms and strengthen their adsorption on the electrode surface, which facilitated the electron or the substance transfer between the electrode and the solution.^{44–47} Kaifer colleagues reported significant changes in the redox potentials and peak currents of methyl viologen in a sodium dodecyl sulfate (SDS) micellar solution.^{48,49}

In the present work, the oxidation peak currents of CBZ were found to increase greatly at [BnMIM]PF₆/CPE in the presence of SDS compared with those at bare CPE and [BnMIM]PF₆/CPE in the absence of SDS. The experimental results indicated that both [BnMIM]PF₆ and SDS can greatly enhance the electrochemical responses of CBZ. Simultaneously, a quantitative electroche-

mical determination method was developed which was successfully used to determine CBZ in commercial samples.

EXPERIMENTAL

Apparatus

All electrochemical experiments were performed using an electrochemistry workstation CHI660A (CH Instrument, USA). The working electrodes were a carbon paste electrode (CPE) and a 1-benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) modified carbon paste electrode ([BnMIM]PF₆/CPE). A CHI115 platinum wire and a CHI150 saturated calomel electrode (SCE) served as the auxiliary electrode and reference electrode, respectively. All potentials measured and reported in this work are *versus* a SCE.

Reagents

Carbamazepine was manufactured by China Drug and Biological Products Testing Organization and was used as received without further purification. Carbamazepine tablets were from FuDan FuHua Pharmaceutical Corporation (Shanghai, China), 1-benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) from Chengjie Chemical Reagent Ltd. (Shanghai, China, purity 99 %) and sodium dodecyl sulfate (SDS) from Beijing Chemistry Factory (Beijing, China, analytical grade). All solutions were prepared using deoxygenated and doubly distilled water. All other chemicals were of analytical grade and were used as received.

Preparation of CPE and [BnMIM]PF₆/CPE

The carbon paste electrode was prepared as follows: 1.50 g of graphite and 0.50 mL of paraffin oil were mixed in a mortar to form a homogeneous mixture. The mixture was pressed by hand into the end cavity of a polytetrafluoroethylene (PTFE) cylindrical electrode body and the surface was polished on a piece of weighing paper.

The [BnMIM]PF₆/CPE was prepared as follows: 0.50 g of [BnMIM]PF₆ was first dissolved in 2.0 mL of DMF, and then added to 1.50 g of graphite powder in a mortar, ground until the DMF had entirely volatilized, and finally mixed with 0.50 mL of paraffin oil in the mortar. The mixture was pressed by hand into the end cavity of a PTFE cylindrical electrode body and the surface was polished on a piece of weighing paper.

Experimental procedure

The electrochemical experiments were performed in a conventional electrochemical cell, containing 0.10 M phosphate buffer solutions (PBS) as the supporting electrolyte and a certain concentration of CBZ and SDS. A 0.01 M ethanolic stock solution of CBZ was prepared in and diluted solutions were prepared daily with doubly distilled water just before use. All experiments were realized at room temperature.

RESULTS AND DISCUSSION

Cyclic voltammetric behavior of CBZ

The cyclic voltammetric behavior of 0.10 mM CBZ in 0.10 M PBS were investigated at the CPE and [BnMIM]PF₆/CPE in the absence and the presence of SDS at a scanning rate of 50 mV s⁻¹ over the potential range from 0.30 to 1.20 V. As shown in Fig. 2, a less sensitive electrochemical response was observed for 0.10 mM CBZ at CPE in the absence of SDS (curve *a*). Moreover, the oxidation peak potential shifted negatively by about 50 mV and the oxidation peak current

increased about two times of that at the [BnMIM]PF₆/CPE (curve *b*) in the absence of SDS. Due to the decrease of the oxidation peak potentials and the increase of the oxidation peak currents, the good enhancing effect on the electrochemical oxidation of CBZ was attributed to the specific advantages of RTILs, including high conductivity and the promotion of the electron transfer rate.³⁴ After the addition of 0.40 mM SDS, the oxidation peak potential shifted negatively by about 70 mV and the oxidation peak current increased to nearly four times that at the CPE (curve *c*) and the oxidation peak potential remained almost constant and the oxidation peak current increased to nearly three times that at [BnMIM]PF₆/CPE in the presence of SDS (curve *d*). It is well known that surfactants can be adsorbed on a hydrophobic surface to form a surfactant film,⁵⁰ which may alter the overvoltage of CBZ on the electrode surface and facilitate the electron transfer rate.⁵¹ Moreover, CBZ surface concentration on the CPE and [BnMIM]PF₆/CPE can be greatly increased in the presence of SDS, therefore, the oxidation peak current of CBZ significantly increased at both the CPE and the [BnMIM]PF₆ in the presence of SDS. Hence, the conclusion can be drawn from the comparisons that both CPE and [BnMIM]PF₆/CPE in the presence of SDS are more active to CBZ than that in the absence of SDS and can greatly enhance the electrochemical sensitivity. Therefore, both RTILs and SDS

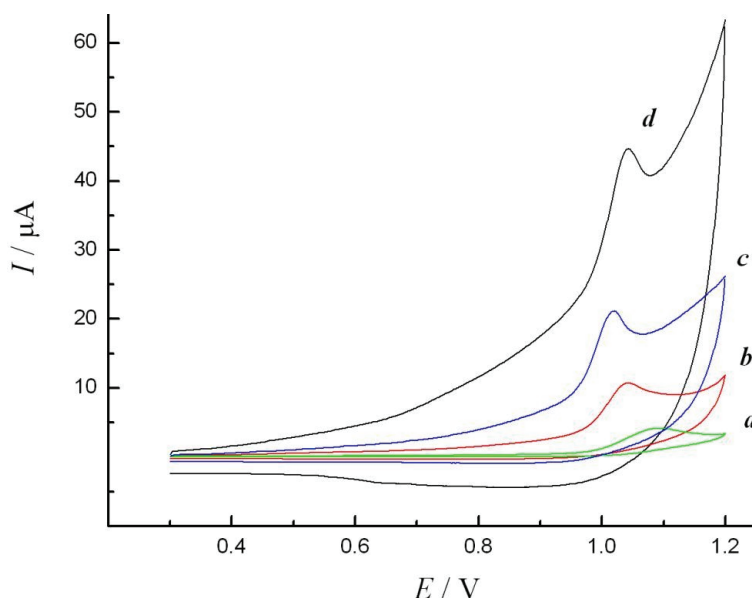


Fig. 2. Cyclic voltammograms of CBZ in 0.10 M PBS (pH 6.8) at the CPE in the absence (a) and the presence (c) of SDS, at the [BnMIM]PF₆/CPE in the absence (b) and the presence (d) of SDS. Scanning rate: 50 mV·s⁻¹, CBZ concentration: 0.10 mM, SDS concentration: 0.40 mM. Accumulation time: 160 s.

have synergetic effect on the CBZ electrochemical oxidation process. In addition, no corresponding reduction peak was observed in the reverse scanning, indicating the irreversibility of the electrochemical oxidation.

Furthermore, the effect of scanning rate on the electrochemical behavior of 0.10 mM CBZ at [BnMIM]PF₆/CPE in the presence of 0.40 mM SDS at different scan rates of 30 to 500 mV s⁻¹ were investigated by CV. With increasing potential scanning rate, the peak currents increased and the peak potentials shifted positively, which implied the irreversible nature of the electrode reaction processes. The oxidation peak currents versus the square roots of the scanning rate gave a straight line, as expected for a diffusion-limited electrode reaction process. The linear regression equation is expressed as $I_{pa} (\mu\text{A}) = -2.469 + 1.469 v^{1/2}$ (where v is in mV s⁻¹), with a correlation coefficient (R) of 0.9977.

The effects of the experimental conditions on the oxidation peak currents and potentials

The effect of various media on the peak currents and potentials of CBZ could be easily observed from CV. The CV of CBZ at a scanning rate of 50 mV s⁻¹ in different electrolyte solutions, *i.e.*, aqueous NaCl, NaAc, NaNO₃, Na₂SO₄ and NaAc-HAc, Britton-Robinson buffer (B-R), Na₂HPO₄-NaH₂PO₄ (PBS) solutions containing NaCl were investigated. The experimental results showed that in an aqueous 0.10 M PBS solution, CBZ had a well-defined electrochemical behavior. Thus, a 0.10 M aqueous PBS solution was chosen as the supporting electrolyte.

The influence of the surfactant, *i.e.*, the anionic surfactants sodium dodecyl benzene-sulfonate (SDBS), sodium dodecyl sulfate (SDS) and the cationic surfactants cetyltrimethylammonium bromide (CTAB), cetylpyridine bromide (CPB), dodecyltrimethylammonium bromide (DTAB) on the oxidation peak current of CBZ were also examined. It was observed that all the anionic surfactants could improve the oxidation peak current of CBZ over a certain concentration range (below the critical micelle concentration (CMC)), but the degree of enhancement varied. Among these surfactants, the oxidation peak current of CBZ was the highest and the background current the smallest in the presence of SDS. The SDS concentration also affects the oxidation peak current of CBZ. Thus, the influence of the SDS concentration on the oxidation peak current of CBZ was examined, and the experimental results showed that with gradual increasing concentration of SDS from 0.01 to 0.40 mM, the oxidation peak current of CBZ also obviously increased, while on further increasing the SDS concentration from 0.40 to 0.90 mM, the oxidation peak currents remained almost constant. Therefore, the SDS concentration was chosen as 0.40 mM.

The effect of solution pH on the oxidation peak current and peak potential for CBZ at [BnMIM]PF₆/CPE were studied in 0.10 M PBS over the pH range from 2.0 to 9.0. It was found that the oxidation peak currents remained almost

constant from pH 2.0 to 7.5 and then decreased as the pH was further increased. Therefore, an aqueous PBS solution of pH 6.8 was chosen as the electrolyte. Furthermore, the peak potentials shifted only slightly in the pH range 2.0 to 9.0, suggesting that no proton was involved in the electrode reaction.

Accumulation potential and time

The effects of the accumulation potential on the oxidation peak current were investigated. When the accumulation potential was shifted from 0.10 to 0.80 V, the oxidation peak current of CBZ altered very slightly. This reveals that the accumulation potential has no obvious influence on the oxidation current of CBZ under these conditions.

The influences of the accumulation time from 20 to 200 s on the peak current were investigated and it was found that the peak current increase linearly with the accumulation time in the range of 20 to 160 s. However, the peak current did not increase, as when the accumulation time was extended beyond 160 s. Usually, an accumulation time of 160 s employed in this study.

Electrochemical kinetics

The charge-transfer coefficient α . According to the experimental results mentioned above, the oxidation of CBZ is a diffusion-limited electrochemical process at [BnMIM]PF₆/CPE in the presence of SDS. For an irreversible diffusion-controlled process, the peak potential (E_{pa}) is proportional to the logarithm of potential scanning rate (ν) according to the equation:⁵²

$$E_{pa} = (b \log \nu)/2 + \text{constant} \quad (1)$$

Based on this equation, the slope of an E_{pa} vs. $\log \nu$ plot is $b/2$, in which b indicates the Tafel slope. The dependence of E_{pa} on $\log \nu$ for oxidation of CBZ at the [BnMIM]PF₆/CPE in the presence of SDS is shown in Fig. 3. Its linear regression equation is expressed as E_{pa} (mV) = 989.6 + 40.44 $\log \nu$, with a correlation coefficient (R) of 0.9970. Thus $b = 2\partial E_p/\partial(\log \nu) = 81$ mV was obtained. Thus, from the equation $b = 2.303 RT/n(1-\alpha)F$ ($n = 2$,^{15,16}, $T = 298$ K, $F = 96485$ C mol⁻¹), the charge-transfer coefficient $\alpha = 0.63$.

The diffusion coefficient D . The apparent diffusion coefficient D of CBZ and the geometrical surface area of electrode were also determined in this work by chronocoulometry (CC):⁵³

$$Q = \frac{2nFACD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads} \quad (2)$$

where Q is the total charge, n is number of electrons transferred in the electrochemical oxidation reaction. A is the electrode area (cm²), c is the concentration of the electroactive species, D is the diffusion coefficient (cm² s⁻¹) and t is the time (ms). The geometrical surface area of the modified electrode and CPE were

calculated from the slopes of Q vs. $t^{1/2}$ curves obtained using 5.0 mM of $\text{Fe}(\text{CN})_6^{3-}$ as a model compound. As the number of electron transferred of CBZ is 2,^{15,16} the surface area (A) of $[\text{BnMIM}]\text{PF}_6/\text{CPE}$ is 0.0686 cm^2 . For a CBZ concentration (C) of 0.10 mM, the diffusion coefficient (D) of CBZ in the presence of SDS was calculated to be $8.10 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$.

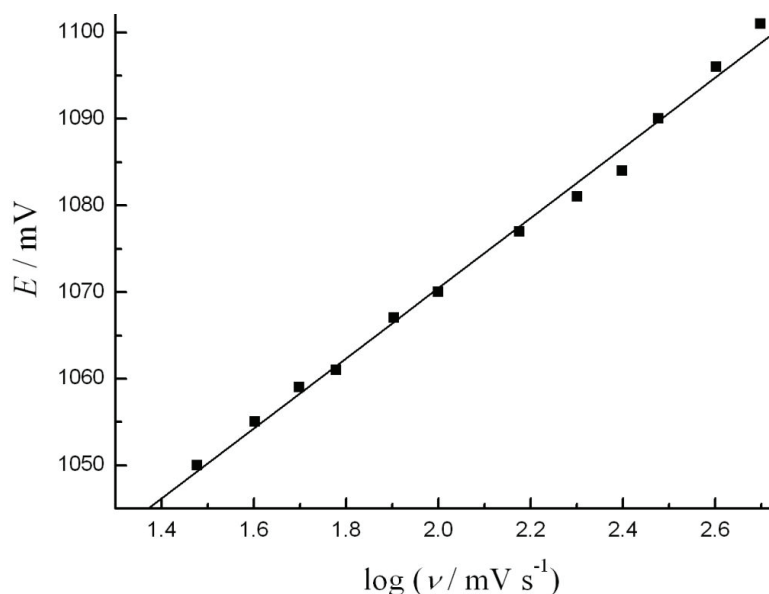


Fig. 3. Dependence of the voltammetric peak potentials on the logarithm of the scanning rate for CBZ oxidation at the $[\text{BnMIM}]\text{PF}_6/\text{CPE}$ in the presence of SDS.

The electrode reaction rate constant k_f . Due to the increase of the electrochemical oxidation of CBZ in the presence of SDS, it should obey the following chronoamperometric equation.^{36,54}

$$I_C / I_L = \lambda^{1/2} \left[\pi^{1/2} \operatorname{erf}(\lambda^{1/2}) + \exp(-\lambda) / \lambda^{1/2} \right] \quad (3)$$

The CA curves are shown in Fig. 4, where I_C is the catalytic current in the presence of SDS, I_L is the diffusion-limited current in the absence of SDS. $\lambda = kc_0t$ (k is the rate constant and c_0 is the bulk initial concentration of SDS) is the argument of the error function. In cases where λ exceeds 1.5, the error function is almost equal to unity and the reaction zone is in the pure kinetic region; hence, the above equation can be reduced to:

$$I_C / I_L = \pi^{1/2} \lambda^{1/2} = \pi^{1/2} (kc_0t)^{1/2} \quad (4)$$

This equation can be used to calculate the rate constant (k) of the oxidation process. Knowing that the value of I_C/I_L is proportional to $\lambda^{1/2}$, a plot of I_C/I_L vs.

$\lambda^{1/2}$ can be given by combining Eq. (3) with Eq. (4) and used as a working curve for chronoamperometry. In this way, $\lambda^{1/2}$ can be determined from the working curve after measuring I_C and I_L , and then the value of the electrode reaction rate constant k can simply be calculated from the slope if c_0 (a given concentration of SDS) and t are known. Both I_C and I_L were measured at $t = 17$ ms where $I_C/I_L > 1.5$, and the rate constant k was calculated to be $(1.07 \pm 0.10) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

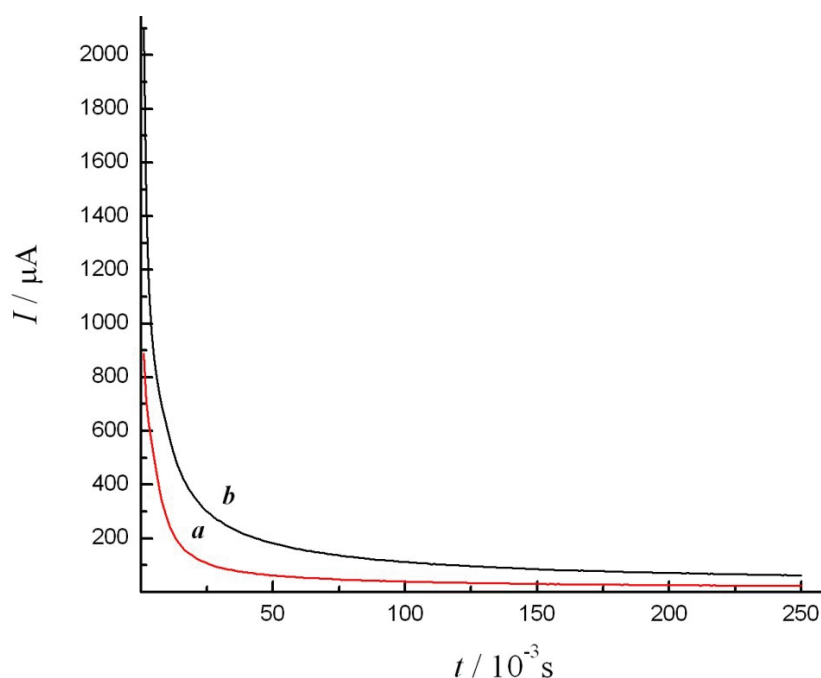


Fig. 4. Chronoamperometry plots of CBZ at the [BnMIM]PF₆/CPE in the absence (a) and the presence (b) of 0.40 mM SDS.

Electrochemical reaction order. The cyclic voltammetric behavior of the oxidation of different concentrations of CBZ at the [BnMIM]PF₆/CPE in the presence of SDS was examined. In the given concentration range, it was found that the logarithm of the peak current, I_{pa} , depended linearly on the logarithm of c_{CBZ} . The linear relationship equation was $\log I_{pa} = 22.261 + 0.9519 \log c_{CBZ}$ with a correlation coefficient (R) of 0.9958. The slope close to 1 implies that the electrochemical oxidation of CBZ obeys first-order kinetics with respect to CBZ.⁵⁵

Electrochemical determination of CBZ

Optimization of the operational parameters of differential pulse voltammetry. Differential pulse voltammetry (DPV) responses are markedly dependent on the parameters of the excitement signals. Therefore, optimization of the pulse width and amplitude, and the scan potential increment was performed. The de-

pendence of the oxidation peak current on the pulse amplitude was examined in the range 10–85 mV. Between 10 and 75 mV, the variation of the peak current with pulse amplitude was linear one, above 75 mV, the peak current remained almost constant. Thus, a pulse amplitude of 75 mV was chosen to improve the sensitivity without distortion of the peak. Using a pulse amplitude of 75 mV, the pulse width was varied in the range of 0.01 to 0.035 s. It was found that between 0.01 and 0.02 s, the peak current increased linearly with increasing pulse width, above 0.02 s, the variation of the peak current with the pulse width remained almost constant. A pulse width of 0.02 s was applied. In addition, using a pulse amplitude of 75 mV and a pulse width of 0.02 s, a scanning potential increment of 6 mV was found to develop a well-defined peak and a higher current response.

Differential pulse voltammetry of CBZ. The DPV behavior of 0.10 mM CBZ at the [BnMIM]PF₆/CPE in the presence of 0.40 mM SDS and 0.10 M aqueous PBS solution under the optimal experimental conditions (amplitude of 75 mV, pulse width of 0.02 s and scanning potential increment of 6 mV) is shown in Fig. 5. From the curves in Fig. 5, it can be seen that CBZ itself showed a weak DPV response at the CPE in the absence of SDS, but the electrochemical response was greatly enhanced using the [BnMIM]PF₆/CPE in the presence of SDS. The experimental result is in quite good agreement with that of CV.

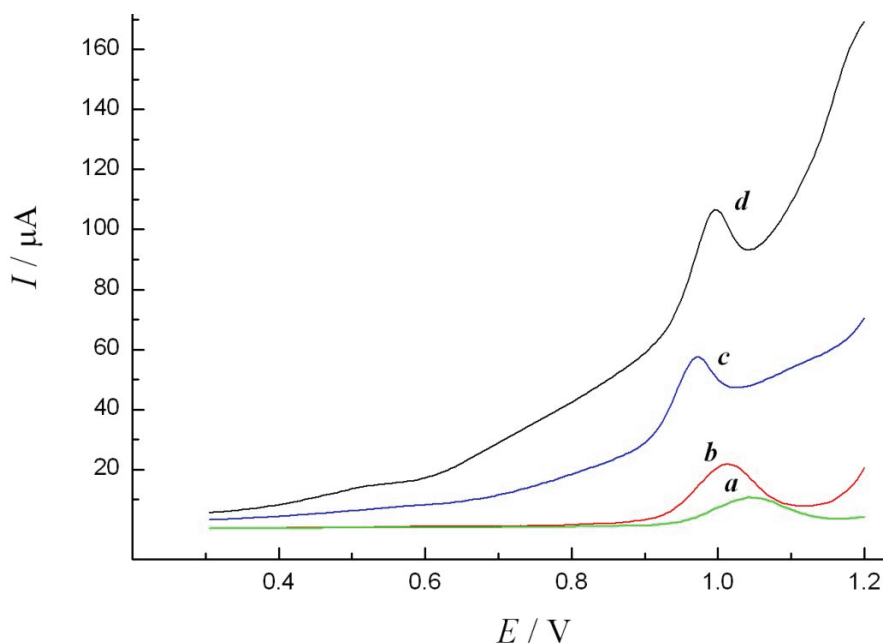


Fig. 5. DPV of 0.10 mM CBZ at the CPE in the absence (a) and the presence (c) of SDS, and at the [BnMIM]PF₆/CPE in the absence (b) and the presence (d) of 0.40 mM SDS. Accumulation time 160 s.

The relationship between the anodic peak currents for CBZ and its concentration were investigated at the [BnMIM]PF₆/CPE in the presence of SDS. Linear calibration curves were obtained over the range 7.0 μM–0.70 mM in 0.10 M PBS solution (as shown in Fig. 6) with a linear fitting regression equation of $I_{pa} (\mu A) = 3.337 + 161.11c$, where c is in mM, with a correlation coefficient (R) of 0.9959. The detection limit defined as a signal-to-noise ratio of 3 ($S/N = 3$) was 0.98 μM for CBZ under the optimized experimental conditions.

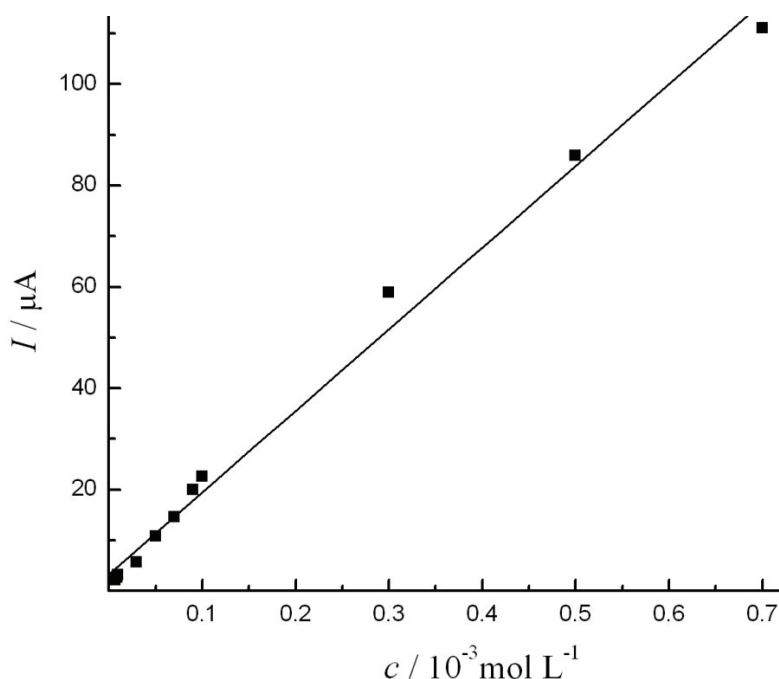


Fig. 6. The relationships between peak current and the CBZ concentration for CBZ oxidation at the [BnMIM]PF₆/CPE in the presence of SDS.

Interferences and reproducibility

The influences of various possible interferences were also studied by analyzing a standard solution of 0.10 mM CBZ in the presence of 0.40 mM SDS. The amount of the foreign species tolerated was that which caused a change in the responding signal of $\pm 5\%$. The interferences of some metal ions and organic compounds were examined. The experimental results showed that 1000-fold of the inorganic ions K^+ , Na^+ , Cl^- , NO_3^- and SO_4^{2-} , and 100-fold of glucose, saccharose, urea and tartaric acid did not affect the CBZ currents response.

In order to inspect the reproducibility of the electrode, ten sequential determination were made using the same electrode in the presence of 0.40 mM SDS, almost the same results were obtained. A relative standard deviation (RSD) value

of about 3.6 % was obtained by measuring the oxidation peak current for CBZ electrochemical oxidation with CV. The experimental results showed the good reproducibility of the modified electrode.

Sample determination

The proposed determination was successfully applied in the determination of CBZ in commercial pharmaceutical samples. A 1.0 mM CBZ sample was prepared in ethanol solutions, and 0.10 mM CBZ samples were analyzed using the proposed method. An acceptable reproducibility with a relative standard deviation (*RSD*) of 1.40–2.13 % was obtained for six parallel measurements. The determination was performed by standard addition. In addition, the recoveries based on this method were in the range of 101.2–103.7 %. The result indicates that the proposed determination could be used as an effective electrochemical determination of CBZ in commercial tablet samples.

CONCLUSIONS

In this work, the electrochemical behavior of CBZ in the presence of SDS at a [BnMIM]PF₆/CPE was investigated. It was found that the oxidation peak current of CBZ remarkably increased at the [BnMIM]PF₆/CPE in the presence of SDS. The results indicated that the electrochemical responses of CBZ were facilitated by SDS and the ionic liquid [BnMIM]PF₆. The electrochemical kinetic parameters were also determined. The proposed method is simple, rapid and inexpensive, which was demonstrated by its application in the determination of CBZ in commercial samples.

Acknowledgements. This work was financially supported by the Natural Science Foundation of Ningxia (NZ1147) and the Scientific Research Fund of Heilongjiang Provincial Education Department (12511348).

ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ПОНАШАЊЕ И ОДРЕЂИВАЊЕ КАРБАМАЗЕПИНА У ПРИСУСТВУ НАТРИЈУМ-ДОДЕЦИЛСУЛФАТА НА ЕЛЕКТРОДИ ОД УГЉЕНИЧНЕ ПАСТЕ МОДИФИКОВАНОЈ ЈОНСКОМ ТЕЧНОШЋУ

LI-HONG LIU^{1,2}, CHENG-QIAN DUAN^{1,3} и ZUO-NING GAO¹

¹Key Lab of Energy Sources and Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China, ²Department of Chemistry, Heihe College, Heihe 164300, China и ³Higher Vocational College, Ningxia Medical University, Yinchuan 750004, China

Испитивано је електрохемијско понашање и могућност електрохемијског одређивања карбамазепина (KBZ) на електроди од угљеничне пасте која је модификована хидрофобном јонском течношћу 1-бензил-3-метилимидазол хексафлуорофосфатом ([BnMIM]PF₆/CPE), у присуству натријум-додецил-сулфата (SDS). Добро дефинисан и осетљив струјни пик оксидације KBZ је запажен на [BnMIM]PF₆/CPE у присуству SDS у фосфатном пуферу вредности рН 6,80. Висина струјног пика у присуству SDS је била знатно већа него када он није био присутан на електроди. Претпостављено је да и SDS и [BnMIM]PF₆ значајно повећавају бр-

зину електрохемијске оксидације KBZ. Кинетички параметри оксидације KBZ на [BnMIM]PF₆/CPE у присуству SDS су одређени и хронокулометријом и хроноамперометријом. Након оптимизације експерименталних параметара предложена је нова електрохемијска метода одређивања KBZ. Оксидациони пик је зависио линеарно од концентрације KBZ у опсегу од 7,0 μ M до 0,7 mM уз границу детекције од 0,98 μ M (однос сигнала и шума је 3). Релативна стандардна девијација одређивања у раствору 0,10 mM KBZ у 6 експеримената је износила од 1,40 до 2,13 %. Предложена метода је примењена и на одређивање KBZ у узорку комерцијалних таблета.

(Примљено 20. априла, ревидирано 9. октобра 2011)

REFERENCES

1. I. Bernus, R. G. Dickinson, W. D. Hooper, M. J. Eadie, *Epilepsy Res.* **24** (1996) 163
2. H. Breton, M. Cociglio, F. Bressolle, H. Peyriere, J. P. Blayac, D. Hillaire-Buys, *J. Chromatogr., B* **828** (2005) 80
3. R. G. Kelmann, G. Kuminek, H. F. Teixeira, L. S. Koester, *Chromatographia* **66** (2007) 427
4. M. Zhang, W. John, *Ther. Drug Monit.* **19** (1997) 92
5. F. S. Messiha, *Alcohol* **3** (1986) 135
6. G. F. V. Rooyen, D. Badenhorst, K. J. Swart, H. K. L. Hundt, T. Scanes, A. F. Hundt, *J. Chromatogr., B* **769** (2002) 1
7. J. T. Burke, J. P. Thenot, *J. Chromatogr., B* **340** (1985) 199
8. J. C. Duran-Alvarez, E. Becerril-Bravo, V. S. Castro, B. Jimenez, R. Gibson, *Talanta* **78** (2009) 1159
9. E. Marziali, M. A. Raggi, N. Komarova, E. Kenndler, *Electrophoresis* **23** (2002) 3020
10. J. L. Maggs, M. Pirmohamed, N. R. Kitteringham, B. K. Park, *Drug. Metab. Dispos.* **25** (1997) 275
11. S. H. Lee, M. Li, J. K. Suh, *Anal. Sci.* **19** (2003) 903
12. L. D. L. Pena, A. Gomez-Hens, D. Perez-Bendito, *Fresenius J. Anal. Chem.* **338** (1990) 821
13. Z. Rezaei, B. Hemmateenejad, S. Khabnadideh, M. Gorgin, *Talanta* **65** (2005) 21
14. Z. Q. Zhang, S. Z. Chen, W. L. Huang, F. Xu, *Acta Pharmacol. Sin.* **28** (1993) 312
15. U. Dunnbier, W. Jugelt, K. Hanig, B. Vieth, *Pharmazie* **41** (1986) 567
16. D. J. Turk, S. A. McClintock, W. C. Purdy, *Anal. Lett.* **18** (1985) 2605
17. M. A. García-García, O. Domínguez-Renedo, A. Alonso-Lomillo, M. J. Arcos-Martínez, *Sensor Lett.* **7** (2009) 586
18. S. Atkins, J. M. Sevilla, M. Blazquez, T. Pineda, J. Gonzalez-Rodriguez, *Electroanal.* **22** (2010) 2961
19. A. Veiga, A. Dordio, A. J. Palace Carvalho, D. M. Teixeiraa, J. G. Teixeira, *Anal. Chim Acta* **674** (2010) 182
20. S. S. Kalanur, S. Jaldappagari, S. Balakrishnan, *Electrochim. Acta* **56** (2011) 5295
21. Q. Zhang, W. Wei, G. C. Zhao, *Electroanal.* **20** (2008) 1002
22. M. Galinski, A. Lewandowski, I. Stepniak, *Electrochim. Acta* **51** (2006) 5567
23. D. R. McFarlane, J. Sun, J. Golding, P. Meakin, M. Forsyth, *Electrochim. Acta* **45** (2000) 1271
24. C. A. Brooks, A. P. Doherty, *Electrochem. Commun.* **6** (2004) 867
25. F. Zhao, X. Wu, M. Wang, Y. Liu, L. Gao, S. Dong, *Anal. Chem.* **76** (2004) 4960
26. P. He, H. T. Liu, Z. Y. Li, Y. Liu, X. D. Xu, J. H. Li, *Langmuir* **20** (2004) 10260
27. N. Nishi, S. Imakura, T. Kakiuchi, *Anal. Chem.* **78** (2006) 2726

28. A. Safavi, N. Maleki, O. Moradlou, F. Tajabadi, *Anal. Biochem.* **359** (2006) 224
29. A. Safavi, N. Maleki, F. Tajabadi, *Analyst* **132** (2007) 54
30. Y. Zhang, J. B. Zheng, *Talanta* **77** (2008) 325
31. H. T. Liu, P. He, Z. Y. Li, C. Y. Sun, L. H. Shi, Y. Liu, G. Y. Zhu, J. H. Li, *Electrochem. Commun.* **7** (2005) 1357
32. W. Sun, R. F. Gao, K. Jiao, *J. Phys. Chem. B.* **111** (2007) 4560
33. W. Sun, R. F. Gao, X. Q. Li, D. D. Wang, M. X. Yang, K. Jiao, *Electroanal.* **20** (2008) 1048
34. W. Sun, Y. Z. Li, Y. Y. Duan, K. Jiao, *Biosens. Bioelectron.* **24** (2008) 988
35. J. Peng, Z. N. Gao, *Anal. Bioanal. Chem.* **384** (2006) 1525
36. Z. N. Gao, J. Peng, X. X. Han, *Pol. J. Chem.* **81** (2007) 441
37. X. X. Han, Z. N. Gao, *Acta Pharmacol. Sin.* **42** (2007) 413
38. L. H. Liu, Z. N. Gao, *Chin. J. Pharm. Anal.* **30** (2010) 438
39. R. Vittal, H. Gomathi, K. J. Kim, *Adv. Colloid Interface. Sci.* **119** (2006) 55
40. M. Plavsic, D. Krznaric, B. Cosovic, *Electroanal.* **6** (1994) 469
41. P. Manisankar, G. Selvanathan, C. Vedhi, *Talanta* **68** (2006) 686
42. P. P. Xie, X. X. Chen, F. Wang, C. G. Hu, S. S. Hu, *Colloids Surf., B* **48** (2006) 17
43. Q. He, X. P. Dang, C. G. Hu, S. S. Hu, *Colloids Surf., B* **35** (2004) 93
44. S. S. Hu, Y. Q. Yan, Z. F. Zhao, *Anal. Chim. Acta* **248** (1991) 103
45. H. C. Yi, K. B. Wu, S. S. Hu, D. F. Cui, *Talanta* **55** (2001) 1205
46. S. H. Zhang, K. B. Wu, S. S. Hu, *Talanta* **58** (2002) 747
47. S. S. Hu, K. B. Wu, H. C. Yi, D. F. Cui, *Anal. Chim. Acta* **464** (2002) 209
48. A. E. Kaifer, A. J. Bard, *J. Phys. Chem.* **89** (1985) 4876
49. P. A. Ouintela, A. Diaz, A. E. Kaifer, *Langmuir* **4** (1988) 663
50. T. F. Connors, J. F. Rusling, A. Owlia, *Anal. Chem.* **57** (1985) 170
51. J. B. Zheng, X. L. Zhou, *Bioelectrochem.* **70** (2007) 408
52. S. M. Golabi, H. R. Zare, *Electroanal.* **11** (1999) 1293
53. A. J. Bard, L. R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, Wiley, New York, 1980, p. 200
54. Z. Galus, *Fundamentals of Electrochemical Analysis*, Ellis Horwood Press, New York, 1994, p. 398
55. H. H. Wu, *Electrochemistry*, Chemical Industry Press, Beijing, China, 2004, p. 84 (in Chinese).