



J. Serb. Chem. Soc. 78 (2) 281–294 (2013)
JSCS–4415

Journal of
the Serbian
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC *labelatol:544.6:544.275–128:
544.6.076.32–039.26

Original scientific paper

Electrochemical behavior of labetalol at an ionic liquid-modified carbon paste electrode and its electrochemical determination

YAN-MEI ZHANG¹, CHENG-QIAN DUAN^{1,2} and ZUO-NING GAO^{1*}

¹College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, 750021, China and ²Higher Vocational College of Ningxia Medical University, Yinchuan, 750004, China

(Received 14 April 2011, revised 28 August 2012)

Abstract: The electrochemical behavior of labetalol (LBT) at a carbon paste electrode (CPE) and an ionic liquid 1-benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) modified carbon paste electrode ([BnMIM]PF₆/CPE) in Britton–Robinson buffer solution (pH 2.0) was investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV). The experimental results showed that LBT at both the bare CPE and [BnMIM]PF₆/CPE showed an irreversible oxidation process, but at [BnMIM]PF₆/CPE its oxidation peak current increased greatly and the potential shifted negatively. The electrode reaction process is diffusion-controlled involving a one-electron transfer accompanied by the participation of one proton at [BnMIM]PF₆/CPE. In addition, the electrochemical kinetic parameters were determined. Under the optimized electrochemical experimental conditions, the oxidation peak currents were proportional to LBT concentration in the range of 7.0×10^{-6} – 1.0×10^{-4} mol L⁻¹ with a limit of detection (LOD, *S/N*=3) of 4.810×10^{-8} mol L⁻¹ and a limit of quantification (LOQ, *S/N* = 10) of 1.60×10^{-7} mol L⁻¹. The proposed method was successfully applied in the determination of the LBT content in commercial tablet samples.

Keywords: labetalol; carbon paste electrode; ionic liquid; electrochemical determination.

INTRODUCTION

Labetalol (LBT) (structure formula is shown in Fig. 1) is used in the treatment of hypertension, now clinically. It is most commonly prescribed as a first line agent for the treatment of hypertensive disorders of pregnancy, including pre-eclampsia.¹ Due to its clinical importance, many analytical techniques has been developed for its determination, including high performance liquid chromatography (HPLC),^{2,3} liquid chromatography coupled with mass spectrometry

* Corresponding author. E-mail: gaozn@nxu.edu.cn
doi: 10.2298/JSC120419113Z

(LC-MS),⁴ capillary electrophoresis (CE),^{5,6} spectrophotometry⁷ and electrochemical methods.^{8,9} Among the cited electrochemical methods, they mainly discuss the voltammetric determination of LBT in pharmaceuticals and the spiked human urine at a bare carbon paste electrode⁸ and the performance characteristics of labetalol-H on an ion selective membrane electrode.⁹ However, its electrochemical behaviors, electrochemical kinetics and electrochemical determination at an ionic liquid 1-benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) modified carbon paste electrode ([BnMIM]PF₆/CPE) have not hitherto been reported.

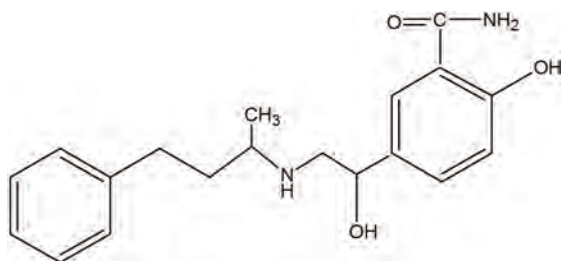


Fig. 1. The structure of labetalol (LBT).

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 have a number of valuable properties, such as high ionic conductivity, electrochemical thermal stability, negligible vapor pressure and wider electrochemical windows, *etc.*^{10,11} Due to their nature, ILs are non-flammable, non-volatile and non-hazardous, which makes them attractive as “green” solvents for many chemical processes on both the industrial and laboratory scale. Meanwhile, they have been widely used as a modifier or binder to fabricate electrodes in the research field of electrochemistry.

As continuations of previous work,^{12–15} an IL/CPE was fabricated using 1-benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) as a modifier and characterized by both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrochemical behaviors and the electrochemical determination of LBT were investigated at both bare a CPE and [BnMIM]PF₆/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 employed for the determination of LBT content 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, which included a carbon paste electrode (CPE) and 1-benzyl-3-methylimidazole hexafluorophos-

phate ([BnMIM]PF₆)-modified carbon paste electrode ([BnMIM]PF₆/CPE) as working electrodes, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. All the electrochemical experiments were performed at room temperature with a high purity nitrogen purge for 5 min before the experiments. All potentials measured and reported in this work are vs. a SCE.

Chemicals and reagents

Labetalol (batch No. 32780-64-6, purity 99 %) was purchased from Shanghai CpG Biotech Co., Ltd. (Shanghai, China) and used without further purification. LBT tablets (batch No. 110102) were purchased from Jiangsu Tianhe Disainuo Pharmaceutical Co. Ltd. (Jiangsu, China). 1-Benzyl-3-methylimidazole hexafluorophosphate ([BnMIM]PF₆) was purchased from Chengjie Chemical Reagent Co., Ltd. (Shanghai, China, Purity 99 %). All of the other chemicals were of analytical grade and double distilled water was used throughout this work.

Preparation of CPE and [BnMIM]PF₆/CPE

The bare CPE was prepared by thoroughly mixing 1.2 g of graphite with 0.40 mL of paraffin oil 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 the CPE was polished on a piece of weighing paper to obtain a smooth surface just before use.

The [BnMIM]PF₆/CPE was fabricated by dissolving 0.60 g of [BnMIM]PF₆ in 0.60 mL of *N,N*-dimethylformamide (DMF), and then added in 1.20 g of graphite powder in a mortar, ground until the DMF had totally volatilized, and finally mixed with 0.60 mL of paraffin oil in a mortar. A portion of the so-obtained carbon paste was processed in the same manner as the pure carbon paste.

RESULTS AND DISCUSSION

Characterization of the electrodes

Electrochemical behaviors of the bare CPE and [BnMIM]PF₆/CPE were first investigated by CV using K₃[Fe(CN)₆] as a redox probe. The cyclic voltammograms of both the electrodes in a solution containing 5.0×10⁻³ mol L⁻¹ K₃[Fe(CN)₆] in 1.0 mol L⁻¹ KCl in the potential range -0.30 to 0.60 V are shown in Fig. 2. The cyclic voltammogram curve of the bare CPE (Fig. 2, curve a) exhibited a pair of well-defined voltammetric peaks with a cathodic peak potential (E_{pc}) of 0.158 V and an anodic peak potential (E_{pa}) of 0.311 V. The peak-to-peak separation (ΔE_p) is 153 mV. The cyclic voltammogram curve of [BnMIM]PF₆/CPE, with an E_{pc} of 0.189 V, E_{pa} of 0.272 V and ΔE_p of 83 mV, is presented in Fig. 2, curve b. Compared with the bare CPE, the redox peak currents of [BnMIM]PF₆/CPE were increased dramatically and the peak-to-peak separation obviously decreased. Simultaneously, the peak current ratio R (I_{pa}/I_{pc}) is 1.053, suggesting a reversible electron transference process. The results indicated that the good conducting property of ILs could greatly promote the electron transference rate of [Fe(CN)₆]³⁻.

For further characterization of the electrodes, electrochemical impedance spectroscopy (EIS) was used. EIS could reflect the surface properties of the mo-

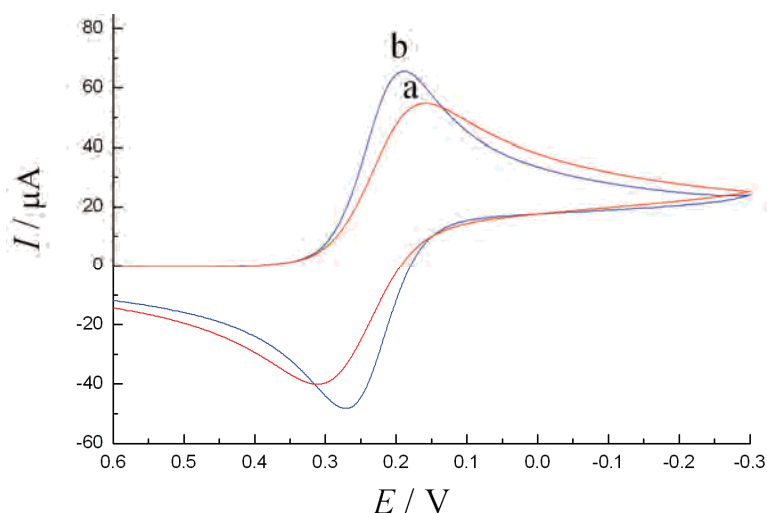


Fig. 2. CVs of the CPE (a) and the [BnMIM]PF₆/CPE (b) in 5.0×10^{-3} mol L⁻¹ K₃[Fe(CN)₆] + 1.0 mol L⁻¹ KCl. Scan rate: 50 mV s⁻¹.

dified electrodes¹⁶ using the [Fe(CN)₆]^{3-/4-} redox couple as an electrochemical probe. The EIS spectra consisted of two sections: one is the linear part at lower frequencies, representing a diffusion-limited process; the other one is a semicircle portion observed at higher frequencies, corresponding to an electron-transfer-limited process.¹⁷ Generally, the diameter of the semicircle is usually equal to the resistance to electron transfer (R_{et}).¹⁸ The Nyquist diagrams of 5.0×10^{-3} mol L⁻¹ [Fe(CN)₆]^{3-/4-} in 1.0 mol L⁻¹ KCl solution at the different electrodes in the frequency range from 1 Hz to 100 kHz are shown in Fig. 3. The bare CPE (Fig. 3, curve a) exhibited a large semicircle in the high frequencies range with a large resistance of electron transference (R_{et}), 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 occur. Meanwhile, the nonconductive paraffin oil increased the resistance of the Fe(CN)₆^{3-/4-} redox couple. However, the [BnMIM]PF₆/CPE (Fig. 3, curve b) showed a quasi-semicircle portion of much smaller diameter in the high frequencies range, which was attributed to the good ionic conductivity of ILs and the lower resistance to electron transfer of the [BnMIM]PF₆/CPE.^{10,11} At low frequencies, [BnMIM]PF₆/CPE presented a linearity with a larger slope than that of the bare CPE, which is a characteristic of a diffusion-limited electrochemical process. The experimental results of EIS confirmed that the [BnMIM]PF₆/CPE could effectively promote the electron transference rate of [Fe(CN)₆]^{3-/4-} and showed properties very different from those of the bare CPE.

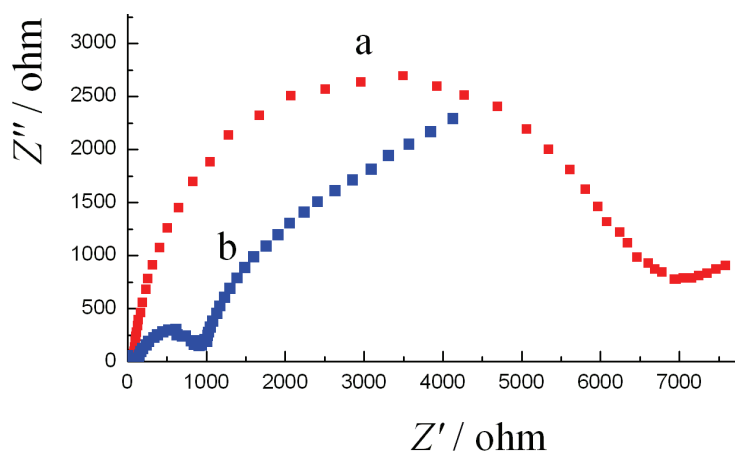


Fig. 3. EIS for the CPE (a) and the [BnMIM]PF₆/CPE (b) in $5.0 \times 10^{-3} \text{ mol L}^{-1} [\text{Fe}(\text{CN})_6]^{3-/4-} + 1.0 \text{ mol L}^{-1} \text{ KCl}$. Frequency range: $1-10^5 \text{ Hz}$.

Cyclic voltammetric behavior of LBT

The electrochemical behaviors of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ LBT at both the bare CPE and [BnMIM]PF₆/CPE were investigated by CV at a scanning rate of 100 mV s^{-1} in Britton–Robinson buffer solution (pH 2.0) over the potential range between 0.20 and 1.20 V (Fig. 4). From Fig. 4, curve a, it can be seen that no

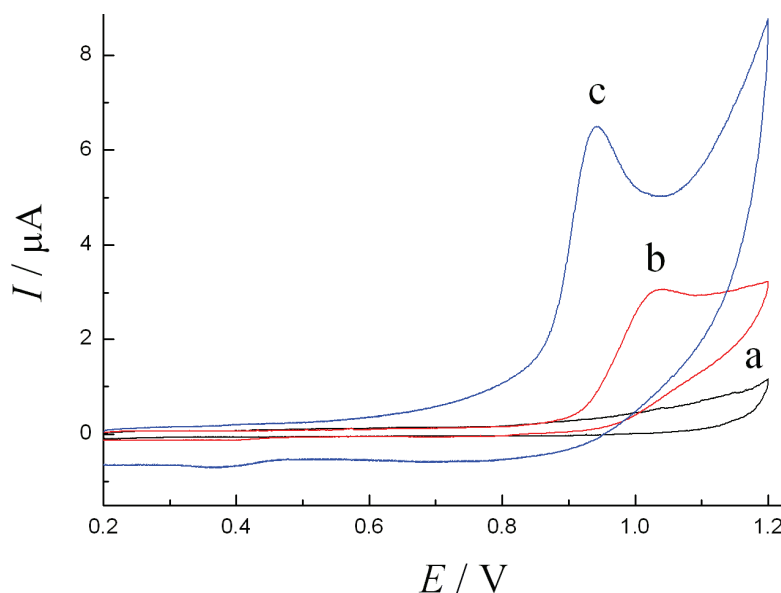


Fig. 4. CVs of the CPE in Britton–Robinson buffer solution (pH 2.0) in the absence (a) and the presence of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ LBT (b) and of the [BnMIM]PF₆/CPE in the presence of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ LBT (c). Scan rate: 100 mV s^{-1} .

oxidation peak could be observed in the blank Britton–Robinson buffer solution (pH 2.0) at the bare CPE. However, at the bare CPE (Fig. 4, curve b) and [BnMIM]PF₆/CPE (Fig. 4, curve c), irreversible oxidation peaks in the presence of LBT were observed with the oxidation peak potential and the oxidation peak currents of 1.040 V, 2.830×10⁻⁶ A (CPE) and 0.942 V, 5.956×10⁻⁶ A ([BnMIM]PF₆/CPE), respectively. The oxidation peak potential of LBT at [BnMIM]PF₆/CPE was shifted negatively by 98 mV and the oxidation peak current increased significantly by almost two times compared with that of CPE, and exhibited a great response of electrocatalytic activity. The above-mentioned experimental results indicated that the presence of the ionic liquid in the modified electrode showed good electrocatalytic ability, which was attributed to the specific advantages of ILs, including high conductivity and the inherent catalytic ability of ILs.¹⁹

The effect of the scan rate (ν) on the oxidation peak current (I_p) of 1.0×10⁻⁴ mol L⁻¹ LBT at [BnMIM]PF₆/CPE was investigated by CV (Fig. 5). With increasing scan rate from 20 to 1000 mV s⁻¹, the oxidation peak currents increased gradually. The oxidation peak currents vs. the square root of the scan rate exhibited a good linear relationship, the linear regression equation of which is expressed as $I_p/\mu\text{A} = -2.257 + 0.7231\nu^{1/2}$ (where ν is in mV s⁻¹) with the correlation coefficient (R) of 0.9982 and a relative standard deviation (RSD) of 2.8 %. The electrochemical oxidation of LBT at [BnMIM]PF₆/CPE was indicated to be a diffusion-controlled electrode reaction process.

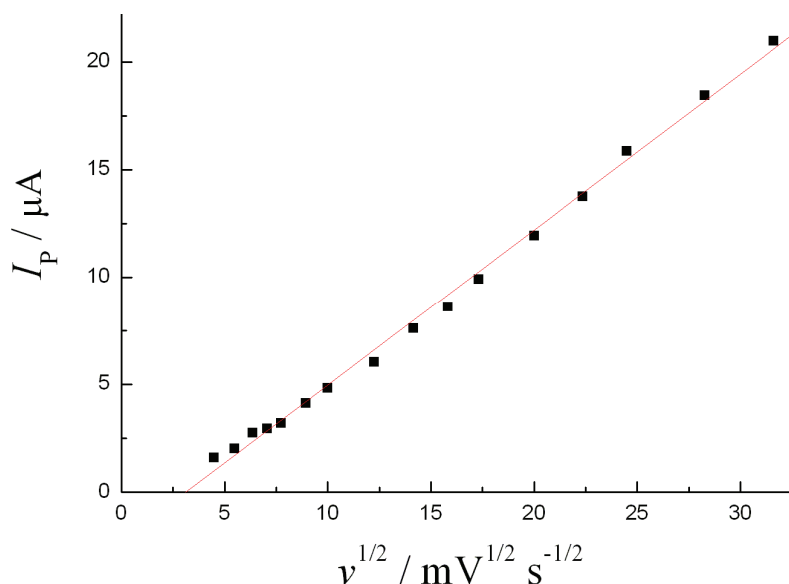


Fig. 5. The relationship of the oxidation peak current I_p vs. $\nu^{1/2}$ at the [BnMIM]PF₆/CPE.

The effect of experimental conditions on the peak currents and potentials

The effect of various media on the peak currents and potentials of LBT could be easily observed by CV. The CV of 1.0×10^{-4} mol L⁻¹ LBT at a scan rate of 100 mV s⁻¹ in different electrolyte solutions, *i.e.*, 0.10 mol L⁻¹ KNO₃, Na₂SO₄, NaCl, NaClO₄, NaAc, Na₂HPO₄-NaH₂PO₄ (PBS) and Britton–Robinson buffer solution was investigated. The experiment results showed that a well-defined electrochemical behavior was obtained in Britton–Robinson buffer solution. Therefore, Britton–Robinson buffer solution was adopted.

The effect of the pH of the Britton–Robinson buffer solution on the electrochemical response of 1.0×10^{-4} mol L⁻¹ LBT was investigated in the pH range from 2.0 to 10.0 (Fig. 6). It can be seen from Fig. 6 that the oxidation peak potential (E_p) of LBT decreased gradually with increasing pH from 2.0 to 10.0. A linear regression equation between E_p and pH was obtained as $E_p/\text{mV} = 1106.4 - 73.0 \text{ pH}$ with R 0.9987 and RSD 1.9 %. The slope of 73.0 mV/pH was close to the theoretical value of 59 mV/pH, which indicates that the number of electrons

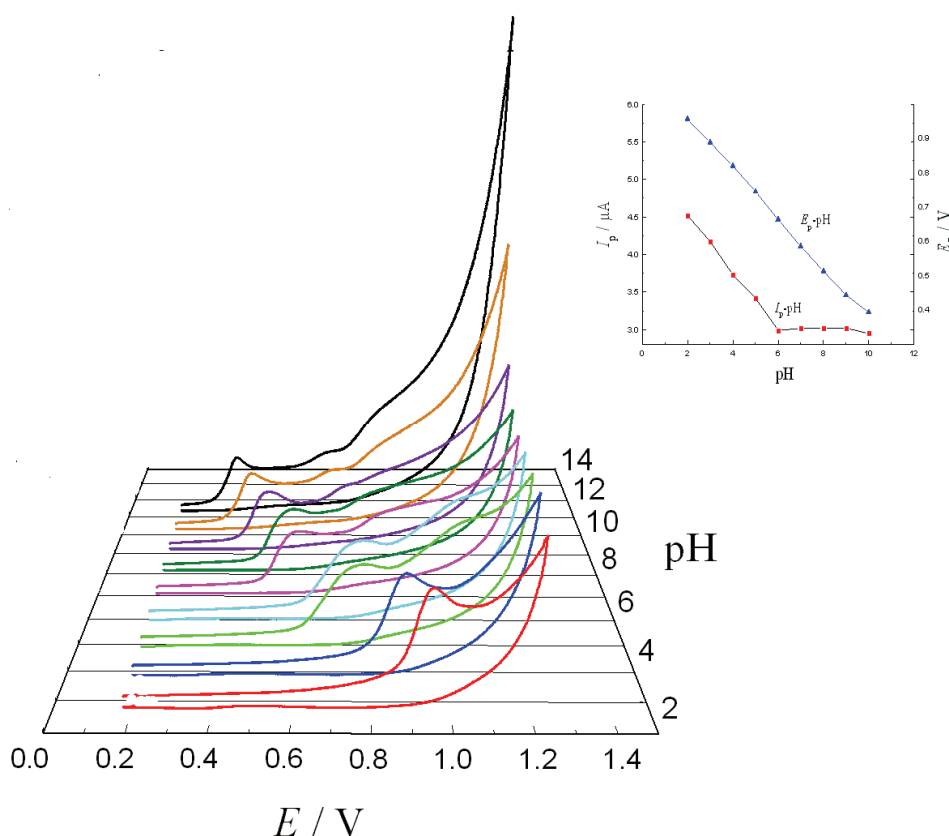


Fig.6 Effect of pH on E_p and I_p at the [BnMIM]PF₆/CPE.

and protons involved in the oxidation process of LBT were almost equal. It was also found that the oxidation peak current (I_p) of LBT decreased gradually with the increasing pH from 2.0 to 6.0, after which it remained almost constant. Therefore, Britton–Robinson buffer solution of pH 2.0 was chosen for the determination of LBT.

Electrode reaction kinetics

Electron transference number (n) and proton transference number (m). The effect of scanning rate (ν) on the oxidation peak potential (E_p) of 1.0×10^{-4} mol L^{-1} LBT at [BnMIM]PF₆/CPE was investigated by CV (Fig. 7). From Fig. 7, it can be seen that the oxidation peak potential shifted positively with increasing scan rate, a linear relationship was obtained in the range of 60–800 $mV s^{-1}$. The relationship can be expressed by the following equation:²⁰

$$E_p / mV = 855.2 + 43.60 \log (\nu / mV s^{-1}) \quad (1)$$

$$R = 0.9971, RSD = 1.8 \%$$

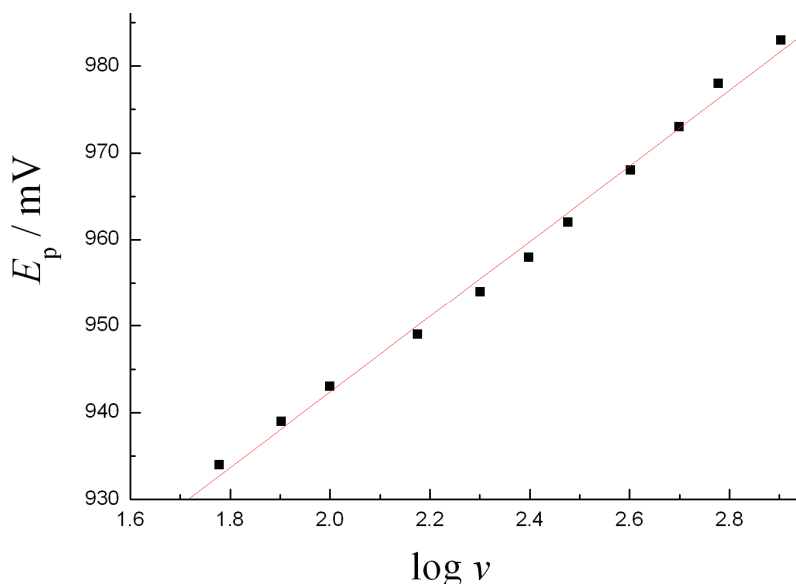


Fig. 7. The relationship of the oxidation peak potential E_p vs. $\log \nu$ at the [BnMIM]PF₆/CPE.

For a totally irreversible electrode process, the relationship between E_p and ν is defined by the following equation:²¹

$$E = E^\circ + \left(\frac{RT}{\alpha n F} \right) \left[0.780 + \ln \left(\frac{D_R^{1/2}}{k^\circ} \right) + \ln \left(\frac{\alpha n F \nu}{RT} \right)^{1/2} \right] \quad (2)$$

where E° is the formal potential; the k° , the standard heterogeneous rate constant; D_R , the diffusion coefficient of LBT, α , the charge transference coefficient. The other symbols have their usual significance. From Eqs. (1) and (2), one can obtain the slope ($2.303RT/2\alpha nF$) of the plot of $E_p - \log v$ as:

$$0.5 \times 2.303 (RT / \alpha nF) = 0.04360 \quad (3)$$

Generally, α in a totally irreversible electrode process is assumed as 0.5.²² Consequently, one electron is involved in the oxidation of LBT. Therefore, according to the experimental results, the above mentioned showed that the electrochemical oxidation of LBT on [BnMIM]PF₆/CPE is a one-electron and one-proton process.

Diffusion coefficient (D). The geometrical surface (A) for bare CPE and [BnMIM]PF₆ modified CPE can be calculated from the slope ($2nFAc\sqrt{D/\pi}$) of the plot of Q vs. $t^{1/2}$ by chronocoulometry (CC) using 5.0×10^{-3} mol L⁻¹ K₃[Fe(CN)₆] as the electrochemical model (the diffusion coefficient D of K₃[Fe(CN)₆] is 7.6×10^{-6} cm² s⁻¹)²³ from Eq. (4):²⁴

$$Q = 2nFAc\sqrt{Dt/\pi} + Q_{dl} + Q_{ads} \quad (4)$$

Based on the slopes of 8.709×10^{-6} ($RSD = 1.3\%$) for CPE and 9.255×10^{-6} ($RSD = 1.9\%$) for [BnMIM]PF₆/CPE of the plots of Q vs. $t^{1/2}$, A can be calculated as 0.0580 cm² for CPE and 0.0617 cm² for [BnMIM]PF₆/CPE when c (K₃[Fe(CN)₆] concentration), D (diffusion coefficient of 5.0×10^{-3} mol L⁻¹ K₃[Fe(CN)₆]), and n (electron transfer number) are known.

The diffusion coefficient D of LBT at the bare CPE and [BnMIM]PF₆/CPE can also be determined using CC based on Eq. (4). From the slopes of 3.630×10^{-6} ($RSD = 0.27\%$) for CPE and 8.645×10^{-6} ($RSD = 1.2\%$) for [BnMIM]PF₆/CPE of the plot of Q vs. $t^{1/2}$, D can be obtained as 3.303×10^{-5} cm² s⁻¹ for CPE and 1.655×10^{-4} cm² s⁻¹ for [BnMIM]PF₆/CPE.

The electrode reaction rate constant k_f . The electrode reaction rate constant (k_f) at both the bare CPE and [BnMIM]PF₆/CPE were calculated by chronoamperometry (CA) based on Eq. (5):²⁵

$$I(t) = nFAk_f c \left[1 - 2H\sqrt{t/\pi} \right] \quad (5)$$

where, $H = k_f / D_{Ox}^{1/2} + k_b / D_{Rd}^{1/2}$. For a totally irreversible electrochemical reaction, the value of k_b is 0, therefore, when t approaches 0, the plot of $I(t)$ vs. $t^{1/2}$ gives a good straight line (Fig. 8). Thus, k_f can be calculated from the intercept ($nFAk_f c$) of 3.393×10^{-7} ($RSD = 2.1\%$) for CPE and of 8.207×10^{-6} ($RSD = 1.5\%$) for [BnMIM]PF₆/CPE of the CA curves. The resulting values for k_f are 6.063×10^{-4} cm s⁻¹ for CPE and 1.379×10^{-2} cm s⁻¹ for [BnMIM]PF₆/CPE.

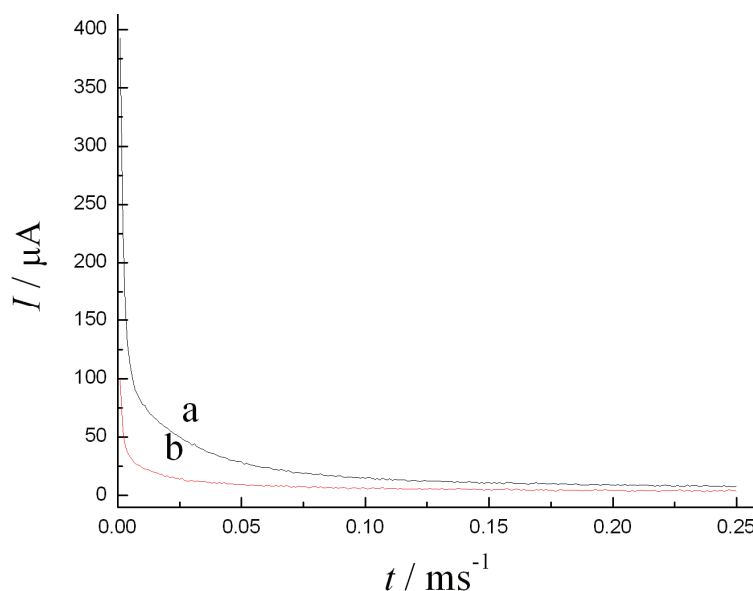


Fig. 8. Plots of the CA curves of 1.0×10^{-4} mol L $^{-1}$ LBT at the CPE (a) and the [BnMIM]PF $_6$ /CPE (b).

Application of the electrochemical determination

Square wave voltammetric (SWV) behaviors of LBT. The responses of square wave voltammetry are markedly dependent on the parameters of the exciting signals. Therefore, the optimization of the frequency, the pulse amplitude, and the scanning potential increment were investigated in the experiment. The dependence of the oxidation peak current on the frequency in the range 20–100 Hz was investigated. The peak current increased linearly with frequency from 20 up to 50 Hz, after which, it remained almost constant between 50 and 100 Hz. Thus, a frequency of 50 Hz was chosen. With a 50 Hz frequency, the pulse amplitude was changed in the range of 10–80 mV. It was found that between 10 and 30 mV, the peak current increased linearly with pulse amplitude, after 30 mV, it remained almost constant. A pulse amplitude of 30 mV was chosen. In addition, with a 50 Hz frequency and a pulse amplitude of 30 mV, a scanning potential increment of 5 mV was found to develop well-defined electrochemical behavior.

The SWV behaviors of 1.0×10^{-4} mol L $^{-1}$ LBT at both the bare CPE and [BnMIM]PF $_6$ /CPE in Britton–Robinson buffer solution (pH 2.0) under the optimized experimental conditions (frequency 50 Hz, pulse amplitude 30 mV, and scanning potential increment 5 mV) are shown in Fig. 9. From Fig. 9, curve a, it can be seen that no oxidation peak could be observed in the blank Britton–Robinson buffer solution (pH 2.0) at the bare CPE. While at the bare CPE (Fig. 9, curve b) and [BnMIM]PF $_6$ /CPE (Fig. 9, curve c), irreversible oxidation peaks in

the presence of LBT were observed with the oxidation peak potential and the oxidation peak currents of 1.005 V, 7.414×10^{-6} A (CPE) and 0.940 V, 1.734×10^{-5} A ([BnMIM]PF₆/CPE), respectively. The oxidation peak potential of LBT at [BnMIM]PF₆/CPE was shifted negatively by 65 mV and the oxidation peak current was significantly increased by almost two times compared with that at bare CPE, which confirmed its great electrocatalytic activity. These experimental results were in quite good agreement with those of CV.

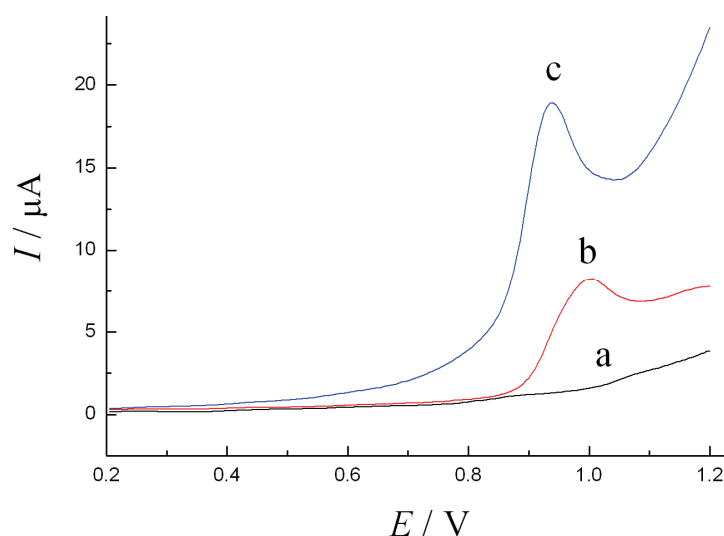


Fig. 9. SWV curves of the CPE (a) in Britton–Robinson buffer solution (pH 2.0) in the absence and the presence of 1.0×10^{-4} mol L⁻¹ LBT (b) and of the [BnMIM]PF₆/CPE in the presence of 1.0×10^{-4} mol L⁻¹ LBT (c).

The relationship between oxidation peak currents and LBT concentration were investigated at [BnMIM]PF₆/CPE. The oxidation peak currents increased linearly with increasing LBT concentration in the range of 7.0×10^{-6} – 1.0×10^{-4} mol L⁻¹. The linear regression equation is expressed as:

$$I_p (\mu\text{A}) = 2.214 + 60.59c \quad (c \text{ is in mM})$$

$$R = 0.9986, \text{ RSD} = 2.1 \%$$

Under the optimized experimental conditions, an LOD ($S/N = 3$) of 4.810×10^{-8} mol L⁻¹ and an LOQ ($S/N = 10$) of 1.60×10^{-7} mol L⁻¹ were obtained.

Reproducibility, stability and interference

After each experiment, the used carbon paste was carefully removed from the end cavity of the modified electrode, and then another new [BnMIM]PF₆/CPE was fabricated. The reproducibility of [BnMIM]PF₆/CPE was estimated by

comparing the oxidation peak current of 1.0×10^{-4} mol L⁻¹ LBT. The relative standard deviation (*RSD*) was 2.4 % for 10 determinations, revealing that the modified electrode had good reproducibility. After the modified electrode had been stored at room temperature for ten days, the current response obtained was within ± 5 % the immediately obtained response, which shows the excellent stability of the modified electrode.

Moreover, some common excipients were tested to check their levels of interference in the LBT determination. The results suggest that 100-fold concentrations of glucose, sucrose, amylum, magnesium stearate and dextrin had no influence on the signals of LBT with *RSD* below ± 5 %.

Analytical applications

In order to ascertain the potential application in commercial tablet samples analysis, the proposed method was used to determine LBT content in LBT tablets. Ten tablets of LBT with the labeled amount of 50.00 mg per tablet were homogeneously ground into powder in a mortar, and then an appropriate amount of the powder was accurately weighed, dissolved in doubly distilled water, transferred quantitatively into a 100 mL volumetric flask and doubly distilled water added to scale line. Finally, a known-amount of sample solution was added into pH 2.0 Britton–Robinson buffer solution and determined by SWV. The content of LBT in the sample solution, which was measured by the standard addition method, is given in Table I. An acceptable reproducibility with an *RSD* of 1.2–2.1 % for commercial tablet samples was obtained for six parallel measurements. By using the standard addition method, the recoveries for the determination of LBT were in the range of 98.30–104.2 %, indicating that the proposed method has good accuracy and could be used as an effective quantitative electrochemical determination of LBT in commercial tablet samples.

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

Samples	Labeled	Found, mg	<i>RSD</i> / %	Added, mg	Determined, mg	Recover, %
1	50.00 mg tablet ⁻¹	49.69	2.1	13.00	63.24	104.2
2		50.07	1.2	25.00	74.65	98.30
3		50.49	1.8	50.00	99.80	98.60

CONCLUSIONS

A modified carbon paste electrode ([BnMIM]PF₆) was successfully fabricated and characterized by CV and EIS. The electrochemical behaviors of LBT at the both a bare CPE and a [BnMIM]PF₆/CPE were investigated by CV and SWV. Compared with the bare electrode, the oxidation peak current of LBT increased greatly and the oxidation peak potential shifted negatively at the [BnMIM]PF₆/CPE, which revealed some advantages of [BnMIM]PF₆/CPE over CPE, such as high conductivity and inherent catalytic ability. The electrochemical behavior of

LBT at [BnMIM]PF₆/CPE is a diffusion-controlled electrode reaction process involving one electron transfer accompanied by the participation of one proton. Moreover, the electrochemical kinetic parameters (diffusion coefficient D and the electrode reaction rate constant k_f) of LBT were determined at the both the electrodes by CV, CC and CA. The oxidation peak currents increased linearly with the increasing LBT concentration in the range of 7.0×10^{-6} – 1.0×10^{-4} mol L⁻¹. The linear regression equation was expressed as I_p (μA) = 2.214 + 60.59c/10⁻³ mol L⁻¹ ($R = 0.9986$ and RSD of 2.1%). The limit of detection (LOD , $S/N = 3$) was 4.810×10^{-8} mol L⁻¹ and the limit of quantification (LOQ , $S/N = 10$) was 1.60×10^{-7} mol L⁻¹. A comparison of the present experimental results with those already existing in literature⁸ for similar electrochemical procedures, in which the LOD values were 1.0×10^{-6} mol L⁻¹ for LSV and 1.0×10^{-8} mol L⁻¹ for DPV, and the linear calibration curve ranges were 2.5×10^{-6} – 1.0×10^{-5} mol L⁻¹ for LSV and 2.5×10^{-8} – 1.0×10^{-5} mol L⁻¹ for DPV, shows that that the method presented herein is quite good and no preconcentration/medium exchange steps are necessary. Thus, the proposed method was successfully applied in the determination of the LBT content in commercial tablet samples with satisfactory results.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ПОНАШАЊЕ И ОДРЕЂИВАЊЕ ЛАБЕТАЛОЛА НА ЕЛЕКТРОДИ ОД УГЉЕНИЧНЕ ПАСТЕ КОЈА ЈЕ МОДИФИКОВАНА ЈОНСКОМ ТЕЧНОШЋУ

YAN-MEI ZHANG¹, CHENG-QIAN DUAN^{1,2} и ZUO-NING GAO¹

¹College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, 750021, People's Republic of China u ²Higher Vocational College of Ningxia Medical University, Yinchuan, 750004, People's Republic of China

Испитивано је електрохемијско понашање лабеталола (ЛБТ) на електроди од угљеничне пасте са и без модификације јонском течносту 1-бензил-3-метилимидазол хексафлуорофосфатом ([BnMIM]PF₆) у Бритон–Робинсоновом пуферском раствору рН 2,0. У поређењу са немодификованом електродом, електрода модификована [BnMIM]PF₆ је показује повећану струју за електрохемијску оксидацију ЛБТ, као и добро дефинисан и осетљив оксидациони пик. Одређени су и кинетички параметри електрохемијске оксидације ЛБТ. Под оптимизованим условима електрохемијског експеримента струјни пик оксидације линеарно зависи од концентрације у опсегу $7,0 \times 10^{-6}$ – $1,0 \times 10^{-4}$ М уз границу детекције ($S/N = 3$) од $4,81 \times 10^{-8}$ М и границу квантификације ($S/N = 10$) од $1,60 \times 10^{-7}$ М. Предложена метода је успешно примењена за одређивање количине ЛБТ у узорцима комерцијалних лекова.

(Примљено 14. априла, ревидирано 28. августа 2012)

REFERENCES

1. D. Kernaghan, G. McKay, *Pract. Diab. Int.* **28** (2011) 139
2. J. M. Dakers, D. W. Boulton, J. P. J. Fawcett, *J. Chromatogr., B* **704** (1997) 215
3. C. Ceniceros, M. I. Maguregui, R. M. Jimenez, R. M. Alonso, *J. Chromatogr., B* **705** (1998) 97

4. T. M. D. J. P. Carvalho, R. D. C. Cavalli, M. P. Marques, S. P. D. Cunha, C. D. O. Baraldi, V. L. Lanchote, *Chirality* **21** (2009) 738
5. T. V. Goel, J. G. Nikelly, R. C. Simpson, B. K. Matuszewski, *J. Chromatogr., A* **1027** (2004) 213
6. L. Potier, S. L. Tamisier-Karolak, P. Morin, F. Megel, M. Taverna, *J. Chromatogr., A* **829** (1998) 341
7. N. Rahman, H. Rahman, S. N. H. Azmi, *J. Chin. Chem. Soc.* **54** (2007) 185
8. A. Radi, Z. El-Sherif, A. Wassel, *Chem. Pap.* **58** (2004) 242
9. Voulgaropoulos, M. Sofoniou, E. Kazakou, *Electroanalysis* **5** (1993) 525
10. E. K. Goharshadi, M. Moosavi, *J. Mol. Liq.* **142** (2008) 41
11. M. C. Buzzeo, C. Hardace, R. G. Compton, *Anal. Chem.* **76** (2004) 4583
12. L. H. Liu, C. Q. Duan, Z. N. Gao, *Croat. Chem. Acta* **83** (2010) 409
13. Q. Duan, Y. M. Zhang, Z. N. Gao, *Croat. Chem. Acta* **85** (2012) 27
14. L. H. Liu, Z. N. Gao, *Chin. J. Pharm. Anal.* **30** (2010) 438
15. L. H. Liu, C. Q. Duan, Z. N. Gao, *J. Serb. Chem. Soc.* **77** (2012) 483
16. J. J. Feng, G. Zhao, J. J. Xu, H. Y. Chen, *Anal. Biochem.* **342** (2005) 280
17. X. G. Kong, J. W. Zhao, J. B. Han, D. Y. Zhang, M. Wei, X. Duan, *Electrochim. Acta* **56** (2011) 1123
18. E. Katz, I. Willner, *Electroanalysis* **15** (2003) 913
19. W. Sun, Y. Z. Li, Y. Y. Duan, K. Jiao, *Biosens. Bioelectron.* **24** (2008) 988
20. M. Golabi, H. R. Zare, *Electroanalysis* **11** (1999) 1293
21. A. J. Bard, L. R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, Wiley, New York, 1980, p. 223
22. K. B. Wu, Y. Y. Sun, S. S. Hu, *Sens. Actuators, B* **96** (2003) 658
23. R. N. Adams, *Electrochemistry at solid electrode*, Marcel Dekker, New York, 1969, p. 220
24. F. C. Anson, *Anal. Chem.* **38** (1966) 54
25. A. J. Bard, L. R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, Wiley, New York, 1980, p. 167.