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Enhancement effect of sodium dodecyl benzene sulfonate (SDBS) and its application into voltammetric determination of telmisartan

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Abstract

A sensitive and rapid electrochemical method was developed for the determination of telmisartan based on the enhancement effect of sodium dodecyl benzene sulfonate (SDBS). In 0.1 mol L^{-1} $HClO_4$ and in the presence of 7.5×10^{-5} mol L^{-1} SDBS, a well-defined and sensitive oxidation peak was observed for telmisartan at the acetylene black (AB) paste electrode. However, the oxidation peak is poor-shaped and the peak current is very low in the absence of SDBS, suggesting that SDBS shows obvious enhancement effect for the determination of telmisartan. After all the experimental parameters were optimized, a sensitive and simple electrochemical method was developed for determining telmisartan. The oxidation peak current is proportional to the concentration of telmisartan over the range from 2.5×10^{-7} to 2.0×10^{-5} mol L^{-1}. The detection limit is 7.5×10^{-8} mol L^{-1} after 2 min of accumulation. This new voltammetric method was successfully used to detect telmisartan in drugs.

Keywords: Telmisartan; Determination; Surfactant effect; Acetylene black; Drug analysis

1. Introduction

Drug analysis, an important branch of analytical chemistry, plays important role in drug quality control. Therefore, the development of sensitive, simple, rapid and reliable method for the determination of active ingredient is very important and interest.

Telmisartan, a substituted dibenzimidazole derivative (Fig. 1), is an antihypertensive drug, essentially used to control blood pressure. It is used alone or in combination with other medications to treat high blood pressure. It works by blocking the action of certain chemicals that tighten the blood vessels, so blood flows more smoothly. Therefore, developing simple, rapid and sensitive method for the determination of telmisartan is of great importance.

To date, various methods including high performance liquid chromatography (HPLC) [1,2], immunoassay [3], liquid chromatography–tandem mass spectrometry (LC–MS) [4–6], and spectrophotometry [7], were reported for telmisartan analysis. Electrochemical method possesses high sensitivity, good selectivity, rapid response, low cost and simplicity, so, it is widely used and becoming an important analytical method. Unfortunately, determination of telmisartan using electrochemical method is very limited although a linear sweep polarography (LSP) was reported for the determination of telmisartan [8]. In that work, toxic mercury electrode and time-consuming deaeration were used. What's more, the sensitivity is relatively poor. Therefore, it is necessary and important to develop a mercury-free, sensitive and simple electrochemical method for telmisartan.

The main objective of the current work is to develop a sensitive and rapid electrochemical method for the determination of telmisartan utilizing the enhancement effect of surfactant as well as the excellent properties of acetylene black (AB).

Surfactant with a long hydrophobic C–H chain and a hydrophilic head group, can adsorb at hydrophobic electrode surface and alter the properties of electrode/solution interface, heavily influencing the electrochemical process of electroactive species [9–11]. To date, surfactant was widely used in electroanalytical chemistry to improve the sensitivity and selectivity. Acetylene black (AB), a special type of carbon black, is made by the controlled combustion of acetylene in air under pressure and possesses many extraordinary properties such as large

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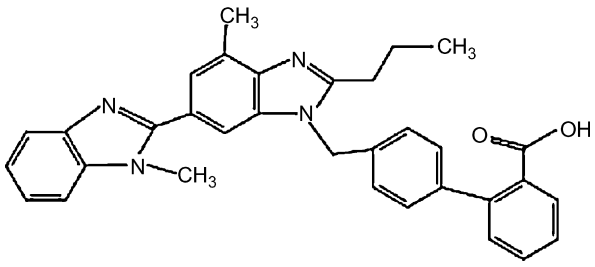

Fig. 1. Chemical structure of telmisartan.

specific surface area, excellent electric conductivity, and strong adsorptive ability.

To achieve this goal, AB paste electrode was employed and low concentration of sodium dodecyl benzene sulfonate (SDBS) was added into the bulk solution to change the electrode/solution interface as well as improve the electrochemical responses of telmisartan. It is found that a well-defined and sensitive oxidation peak is observed for telmisartan at AB paste electrode in the presence of 7.5×10^{-5} mol L^{-1} SDBS. Compared with that in the absence of SDBS, the oxidation peak current of telmisartan significantly increases in the presence of SDBS, suggesting that SDBS facilitates the electron transfer of telmisartan. Without a doubt, the sensitivity of determining telmisartan must be greatly improved under the enhancement effect of SDBS.

2. Experimental

2.1. Reagents

All chemicals were of analytical-reagent grade and used without further purification. 5.00×10^{-3} mol L^{-1} telmisartan stock solution was prepared by dissolving telmisartan (Sigma) into NaOH (0.1 mol L^{-1})–ethanol (1:1, v/v) mixed solution.

Sodium dodecyl benzene sulfonate (SDBS) (Shanghai Reagent Corporation, China) was made into 1.0×10^{-2} mol L^{-1} aqueous solutions. Acetylene black (AB, purity > 99.99%, particle size = 150–200 nm) was purchased from STREM Chemicals (USA). Paraffin oil was purchased from Sinopharm Group Chemical Reagent Co., Ltd., China.

2.2. Apparatus

All the electrochemical measurements were performed with a CHI 660A Electrochemical Workstation (CH Instrument, USA). A three-electrode system, including AB paste working electrode (3 mm in diameter), a platinum wire counter electrode and a saturated calomel reference electrode (SCE), was employed. The body of working electrode was a polytetrafluoroethylene (PTFE) cylinder that was tightly packed with AB paste. A copper wire inserts into the AB paste providing electrical contact.

2.3. Preparation of AB paste electrode

The AB paste electrode was prepared by mixing 100.0 mg AB, 100.0 μL paraffin oil and several drops of ethanol in a small mortar to form a homogeneous AB paste, and then dried under an infrared lamp. After that, the paste was pressed into the end cavity (3 mm in diameter, 1 mm in depth) of working electrode body, and the electrode surface was smoothed against a weighing paper. It is important to note that the amount of paraffin oil must be carefully controlled because excessive paraffin oil will lower the conductivity, while insufficient paraffin oil is not beneficial to obtain uniform AB paste.

2.4. Determination of telmisartan

Unless otherwise stated, 0.1 mol L^{-1} $HClO_4$ containing 7.5×10^{-5} mol L^{-1} SDBS was used as supporting electrolyte for telmisartan determination. The accumulation step was carried out under open-circuit with 2-min stirring solution, then the differential pulse voltammograms from 1.00 to 1.60 V were recorded after 15 s quiet time, and finally the peak current at 1.42 V was measured.

3. Results and discussion

3.1. Electrochemical behavior of telmisartan at AB paste electrode

The electrochemical behaviors of telmisartan at AB paste electrode and in the presence of low concentration of SDBS were investigated using cyclic voltammetry (CV). The results are shown in Fig. 2. In 0.1 mol L^{-1} $HClO_4$ containing 7.5×10^{-5} mol L^{-1} SDBS, 1.0×10^{-5} mol L^{-1} telmisartan yields a well-shaped and sensitive oxidation peak at 1.47 V during the first anodic sweep from 0.80 to 1.60 V. On the reverse scan, no corresponding reduction peak is observed, indicating that the electrode process of telmisartan is totally irreversible.

From Fig. 2, it is also known that the oxidation peak current of telmisartan gradually decreases as increasing the number of cyclic potential sweeps. The decreases in peak current may be caused by the fact that the adsorption of telmisartan or its oxidative product occurs at AB paste electrode surface. Therefore, the oxidation peak current in the first anodic sweep was recorded for

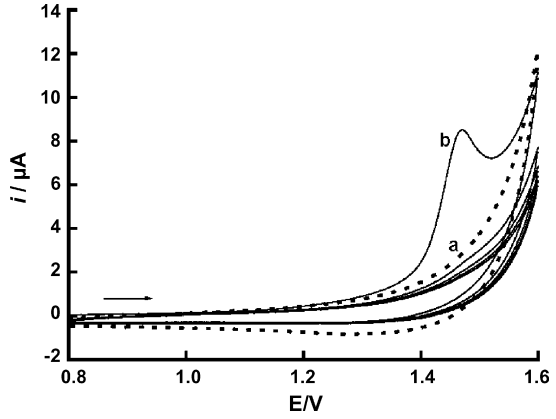

Fig. 2. Successive cyclic voltammograms of AB paste electrode in (a) 0.1 mol L^{-1} $HClO_4$ containing 7.5×10^{-5} mol L^{-1} SDBS; (b) (a) + 1.0×10^{-5} mol L^{-1} telmisartan. Scan rate: 100 mV s^{-1}.

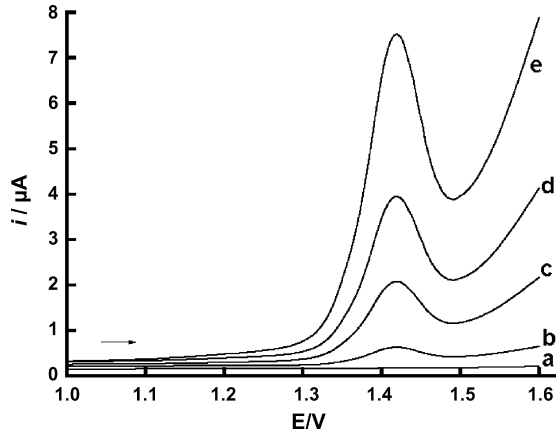

Fig. 3. DP voltammograms of 5.0×10^{-7} mol L^{-1} telmisartan in $HClO_4$. (a) Blank voltammograms; (b) 5.0×10^{-7} mol L^{-1} telmisartan; (c–e) 2.5×10^{-7}, 5.0×10^{-7}, and 1.0×10^{-6} mol L^{-1} telmisartan in the presence of 7.5×10^{-5} mol L^{-1} SDBS. Pulse amplitude = 50 mV; scan rate = 20 mV s^{-1}; pulse width = 50 ms; accumulation time: 2 min.

telmisartan analysis in the following studies to acquire higher sensitivity and better reproducibility.

3.2. Enhancement effect of SDBS to telmisartan

In order to elucidate the enhancement effect of SDBS for the determination of telmisartan, the electrochemical responses of telmisartan in the absence and presence of SDBS were examined by differential pulse voltammetry (DPV) with the following parameters: pulse amplitude = 50 mV, scan rate = 20 mV s^{-1}, pulse width = 50 ms, and accumulation time = 2 min.

In 0.1 mol L^{-1} $HClO_4$, a very poor oxidation peak is observed for 5.0×10^{-7} mol L^{-1} telmisartan at AB paste electrode (Fig. 3b). The oxidation peak potential is at 1.42 V and the peak current is very low (about 0.48 μA). However, the oxidation peak current increases greatly (from 0.48 to 3.36 μA) after adding 7.5×10^{-5} mol L^{-1} SDBS, and the oxidation peak potential is still at 1.42 V (Fig. 3d), suggesting that SDBS shows obvious enhancement effect to the oxidation of telmisartan. SDBS, an anionic surfactant, can adsorb at AB paste electrode surface via hydrophobic interaction and then change the structure of electrode/solution interface, which facilitating the electron transfer of telmisartan. Otherwise, the surface amount of telmisartan maybe greatly increases in the presence of SDBS. Therefore, the oxidation peak current of telmisartan significantly increases in the presence of SDBS.

Additionally, when improving the concentration of telmisartan to 1.0×10^{-6} mol L^{-1}, it is found that the oxidation peak current increases by two times (Fig. 3e); if we lower the concentration to 2.5×10^{-7} mol L^{-1}, the peak current also decreases by 50% (Fig. 3c), when the concentration further decreases to zero (without telmisartan), the oxidation peak current will disappear (Fig. 3a). These phenomena reveal that the oxidation peak at 1.42 V corresponds to telmisartan, and what's more, the oxidation peak current exhibits good linearity with concentration of telmisartan, which can be used as telmisartan analytical signal.

3.3. Supporting electrolyte

The electrochemical responses of telmisartan in a variety of determining mediums, such as pH 5.0–8.0 phosphate buffer, pH 3.5–5.5 HAc-NaAc buffer, $HClO_4$, KCl, HCl, NaOH (each 0.1 mol L^{-1}) containing different concentrations of SDBS from 0 to 1.5×10^{-4} were investigated in details. It is found that the oxidation peak current of telmisartan is highest in 0.1 mol L^{-1} $HClO_4$ containing 7.5×10^{-5} mol L^{-1} SDBS. Otherwise, the background current is very low and the oxidation peak is well-shaped. Thus, 0.1 mol L^{-1} $HClO_4$ containing 7.5×10^{-5} mol L^{-1} SDBS was used as supporting electrolyte for the determination of telmisartan.

3.4. Concentration of SDBS

Form Fig. 3, it is very clear that SDBS can enhance the oxidation peak current of telmisartan. However, the oxidation peak current of telmisartan is found to be closely related to the concentration of SDBS. Thus, the influence of SDBS concentration on the oxidation peak current of telmisartan was examined, and the results shown in Fig. 4. As gradual increasing the concentration of SDBS from 0 to 7.5×10^{-5} mol L^{-1}, the oxidation peak current of telmisartan also increases gradually; when further improving the SDBS concentration to 1.0×10^{-4} mol L^{-1}, the oxidation peak current almost keeps unchangeable; However, the oxidation peak current of telmisartan begins to decrease when the concentration of SDBS is higher than 1.0×10^{-4} mol L^{-1}. Therefore, the concentration of SDBS is chosen as 7.5×10^{-5} mol L^{-1} in this work.

3.5. Influence of scan rate

The oxidation peak currents of 1.0×10^{-5} mol L^{-1} telmisartan in the presence of 7.5×10^{-5} mol L^{-1} SDBS under different scan rates from 10 to 300 mV s^{-1} were measured by linear sweep voltammetry (LSV). It is found that the oxidation peak current is proportional to the scan rate, suggesting that the oxidation of telmisartan is adsorption-controlled.Otherwise, the oxidation peak potential (E_p) shifts towards positive direction as improving

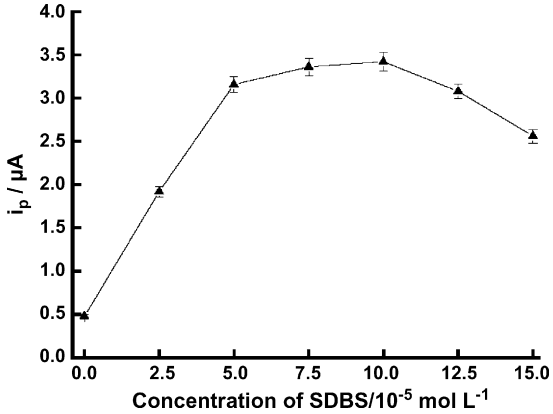

Fig. 4. Effect of the concentration of SDBS on the oxidation peak current of 5.0×10^{-7} mol L^{-1} telmisartan.

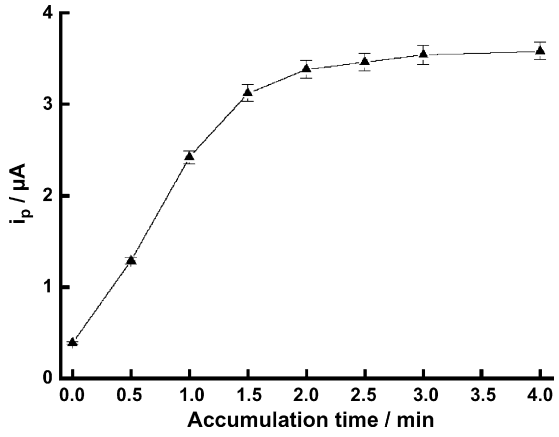

Fig. 5. Influence of accumulation time on the oxidation peak current of 5.0×10^{-7} mol L^{-1} telmisartan.

scan rate (υ), obeying the following equation:

$$E_p = 1.4546 + 0.0235 \ln \upsilon \quad (1)$$

For adsorption-controlled and totally irreversible electrode process, E_p and υ is defined by the following equation according to Laviron's conclusion [12]:

$$E_{pa} = E^{0'} + \left(\frac{RT}{\alpha n F}\right) \ln \left(\frac{RTk^0}{\alpha n F}\right) + \left(\frac{RT}{\alpha n F}\right) \ln \upsilon \quad (2)$$

where α is the transfer coefficient, k^0 the standard rate constant of the reaction, n the electron transfer number, υ the scan rate, and $E^{0'}$ is the formal potential. Other symbols have their usual significance.

From Eqs. (1) and (2), we can obtain:

$$\left(\frac{RT}{\alpha n_a F}\right) = 0.0235 \quad (3)$$

Therefore, the value of αn_a, calculated from Eq. (3), is 1.09. Generally, α is assumed as 0.5 in the totally irreversible electrode process. Hence two electrons are involved in the oxidation process of telmisartan, which maybe the imidazole group is oxidized.

3.6. Effect of accumulation time

Open-circuit accumulation is widely used in electroanalytical chemistry to improve the determining sensitivity. In this work, the effect of accumulation time on the oxidation peak current of telmisartan was investigated. As Fig. 5 showing, the oxidation peak current of telmisartan gradually increases as accumulation time increasing from 0 to 2 min. However, with further increasing the accumulation time, the plots become curved, revealing that the limiting value of the amount of telmisartan at AB paste electrode surface has been achieved. Considering both sensitivity and working efficiency, an accumulation time of 2 min was employed.

3.7. Calibration curve

The relationship between oxidation peak current and concentration of telmisartan was examined by DPV after 2-min open-circuit accumulation. The oxidation peak current is proportional to the concentration of telmisartan over the range from 2.5×10^{-7} to 2.0×10^{-5} mol L^{-1} and obeys the following equation: $i_p = 0.092 + 6.724 \times 10^6 C$ ($r = 0.998$, i_p in μA, C in mol L^{-1}). The detection limit is estimated to be 7.5×10^{-8} mol L^{-1}.

The reproducibility was also evaluated by successive measuring the same 5.0×10^{-7} mol L^{-1} telmisartan solution for 10 times at a single AB paste electrode. After each measurement, the AB paste electrode surface was re-polished against a clean weighing paper to remove any adsorbates and give a reproducible electrode surface. The relative standard deviation (R.S.D.) is 5.8%, suggesting that this method possesses good reproducibility and potential applications.

3.8. Interference

To estimate the interferences of foreign species on the determination of telmisartan, a systematic study was carried out (see Table 1). It is found that many other foreign substances have no influence on the determination of ciprofloxacin. For example, 1000-fold concentration of Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Cu^{2+}, 500-fold concentration of ascorbic acid (AA), uric acid (UA), dopamine (DA), xanthine (XA), caffeine and vitamin E, 200-fold concentration of L-glutamic acid, L-phenylalanine, L-cysteine, L-tryptophan and L-tyrosine, almost do not interfere with the current response of 5.0×10^{-7} mol L^{-1} telmisartan (signal change below 5%), suggesting that this newly proposed method has excellent selectivity toward telmisartan.

3.9. Drug analysis

In order to evaluate its potential application in the real sample analysis, this new method was used to detect telmisartan in telmisartan tablets.

The average mass of five tablets was determined and finely powdered, then the required amount of sample to prepare a solution of ca. 10^{-3} mol L^{-1} was transferred into a 100-mL standard flask containing 80 mL of 0.1 mol L^{-1} NaOH–ethanol mixed solution (1:1, v/v). The contents of flask were stirred magnetically for 30 min, then diluted to volume with ethanol, and kept overnight. After that, it was centrifugated for 20 min at the

Table 1
Interferences on the oxidation peak current of 5.0×10^{-7} mol L^{-1} telmisartan

Foreign species	Tolerance level (mol L^{-1})[a]
Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Cu^{2+}	5.0×10^{-4}
Ascorbic acid (AA), uric acid (UA), dopamine (DA), xanthine (XA), caffeine and vitamin E	2.5×10^{-4}
L-Glutamic acid, L-phenylalanine, L-cysteine, L-tryptophan and L-tyrosine	1.0×10^{-4}

[a]For 6% error.

Table 2
Determination of telmisartan in drugs

Samples	Declared content (mg/tablet)	Detected by HPLC (mg/tablet)	Detected by this method (mg/tablet)	Recovery (%)
A	80.0	79.6	79.2	99.0
B	80.0	79.4	78.9	99.4
C	80.0	79.2	80.2	99.2
D	80.0	80.1	79.6	99.6

speed of 3000 rpm. When determining telmisartan, 20.0 μL of the resulting clear solution was added into 10.0 mL supporting electrolyte and DP voltammograms were recorded as in standard telmisartan.

The content of telmisartan was determined by the standard addition method, and the results shown in Table 2. The results obtained by this method are in good agreement with the declared content as well as the results obtained by HPLC. Furthermore, in order to establish the suitability of this proposed method, known amounts of standard telmisartan were added into the analytical solution, and the same procedure was applied. The recovery is between 99.0 and 99.6%, indicating that the accuracy and repeatability of this method are very good. From above experimental results, it is very clear that this novel method has great potential for practical sample analysis.

4. Conclusion

SDBS can adsorb at AB paste electrode surface via strong hydrophobic interaction, altering the structure and property of the electrode/solution interface. Therefore, the electrochemical responses of telmisartan show great difference in the presence of SDBS. Under the obvious enhancement effect of SDBS, both the oxidation peak current and the determining sensitivity of telmisartan are significantly improved.

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