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Polyvinylpyrrolidone-enhanced electrochemical oxidation and detection of acyclovir

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ABSTRACT

Polyvinylpyrrolidone (PVP), a macromolecule surfactant, was used to modify the carbon paste electrode (CPE). The electrochemical behavior of acyclovir was studied, and a sensitive oxidation peak at 1.03 V was observed in pH 5 acetate buffer. Compared with the unmodified CPE, the resulting PVP-modified CPE greatly increased the oxidation signal of acyclovir, exhibiting strong surface enhancement effect. The oxidation mechanism of acyclovir was discussed. It was found that the oxidation of acyclovir involved two electrons and two protons. The influences of pH value, amount of PVP, accumulation potential and time were examined on the oxidation signal of acyclovir. As a result, a novel electrochemical method was developed for the detection of acyclovir. The linear range was from 1×10^{-8} to 7.5×10^{-7} M, and the detection limit was 2.5×10^{-9} M. The proposed method was demonstrated using acyclovir injection and tablets, and the accuracy was tested using high performance liquid chromatography.

1. Introduction

Polyvinylpyrrolidone (PVP) is a well known macromolecule surfactant with many advantages such as low toxicity, biocompatibility, high surface activity and strong adsorption ability. Until now, PVP has attracted considerable attention and been widely used in different fields, such as electrophoretic separation [1,2], electrospinning [3,4], and electrochemical deposition [5,6]. In addition, PVP was also used to modify electrode surface to improve the sensitivity of electrochemical detection. For example, the electrochemical response signals of Sudan I [7] and kojic acid [8] were greatly improved by PVP.

Acyclovir (9-carboxymethoxymethyl guanine) as shown in Fig. 1 is the most commonly used guanine analog antiviral drug. It is primarily applied for the treatment of herpes simplex as well as herpes zoster (shingles) infections. Up-to-date, various methods such as high performance liquid chromatography (HPLC) [9,10], near infrared spectroscopy [11], chemiluminescence [12], electrochemiluminescence [13], and spectrophotometry [14] have been employed for the determination of acyclovir. Because of high sensitivity, short analysis time, low cost and handling convenience, electrochemical method has also obtained application in the detection of acyclovir. For instance, a carbon nanotube-modified glassy carbon electrode (GCE) [15], a 2-mercaptobenzothiazol self-assembled monolayer-modified gold electrode [16], a GCE [17], and a copper nanoparticles-modified CPE [18] were published for acyclovir detection. However, to the best of our knowledge, electrochemical determination of acyclovir using PVP-modified electrode is still missing.

The main objective of this work is to elucidate the enhancement effect of PVP toward acyclovir and to develop a sensitive and rapid electrochemical method for the detection of acyclovir. Thus, a PVP-modified CPE was prepared and the electrochemical response of acyclovir was studied. It was found that the PVP-modified CPE remarkably increased the oxidation signal of acyclovir in comparison with the unmodified CPE. Undoubtedly, the determination sensitivity of acyclovir is greatly improved by PVP. As seen in Table 1, this new sensing system based on enhancement effect of PVP exhibited much higher sensitivity compared with the reported electrochemical methods.

2. Experimental section

2.1. Reagents

All chemicals were of analytical grade and used as received. Acyclovir (National Institute for the Control of Pharmaceutical Biological Products, Beijing, China) was dissolved in doubly distilled water to prepare 1×10^{-3} M standard solution. PVP with an average molecular weight of 29,000 was purchased from Sigma-Aldrich. Graphite powder (spectral reagent) and paraffin oil were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). The used water was doubly distilled.

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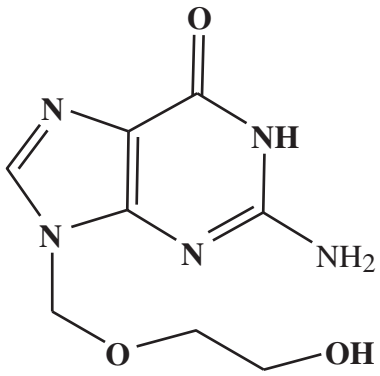

Fig. 1. Chemical structure of acyclovir.

2.2. Instruments

Electrochemical measurements were performed on a CHI 830C electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode system. The working electrode was a PVP-modified CPE, the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum wire.

High performance liquid chromatography (HPLC) detection of acyclovir was carried out with an Agilent 1100, coupled with a UV detector. The C18 analytical column (4.6 mm × 150 mm × 5 μm) was used. The mobile phase was 10 mM acetate/citrate buffer–3.7 mM aqueous octanesulfonic acid (87.5:12.5, v/v) adjusted to pH 3.08 with phosphoric acid. The flow rate was 1 mL min^{-1}, and the sample injection volume was 20 μL. The detection was performed at a wavelength of 254 nm.

2.3. Preparation of PVP-modified CPE

PVP (0.10 g) and graphite powder (0.90 g) were exactly weighed, and put in a carnelian mortar. The total mass was controlled at 1.00 g and the mass content of PVP was 10%. After that, 0.25 mL paraffin oil was added into, and then mixed homogeneously. Finally, the resulting carbon paste was tightly pressed into the end cavity of electrode body, and the surface was polished on a smooth paper. The bare CPE was prepared by the same procedure without addition of PVP.

2.4. Analytical procedure

0.1 M acetate buffer with pH of 5 was used for the detection of acyclovir. After 2-min accumulation under open-circuit, the differential pulse voltammograms were recorded from 0.6 to 1.2 V, and the oxidation peak current at 1.03 V was measured for acyclovir. The pulse amplitude was 50 mV, the pulse width was 40 ms and the scan rate was 40 mV s^{-1}.

Table 1
Comparison of electrochemical methods for acyclovir detection.

Electrode	Linear range/M	Detection limit/M	Reference
Carbon nanotube/GCE	8×10^{-8} to 1×10^{-5}	3×10^{-8}	[15]
Self-assembled monolayer/Au	1×10^{-8} to 1×10^{-6}	1×10^{-8}	[16]
GCE	2×10^{-6} to 1×10^{-4}	3.5×10^{-7}	[17]
Copper nanoparticles/CPE	2.7×10^{-5} to 5.2×10^{-4}	2.64×10^{-6}	[18]
PVP/CPE	1×10^{-8} to 7.5×10^{-7}	2.5×10^{-9}	This work

3. Results and discussion

3.1. Electrochemical enhancing of PVP

The oxidation responses of low concentration of acyclovir on CPE and PVP-modified CPE were studied using differential pulse voltammetry (DPV). As seen in Fig. 2, an oxidation peak was observed on the surface of CPE after 2-min accumulation in pH 5 acetate buffer (curve b). The peak potential was at 1.03 V, and the peak height was low, revealing that the oxidation activity of acyclovir on CPE surface is poor. However, the oxidation signal of acyclovir greatly increased on the surface of PVP-modified CPE (curve d). The notable peak current enlargement strongly indicates that PVP exhibits a remarkable enhancement effect toward the oxidation of acyclovir. PVP possesses strong accumulation ability to acyclovir, and greatly enhances its surface concentration. As a result, the oxidation peak current of acyclovir increases obviously on PVP surface. In addition, the DPV curves in the absence of acyclovir on CPE (curve a) and PVP-modified CPE (curve c) were given. It was found that their blank curves were featureless, suggesting that the oxidation peak at 1.03 V is attributed to acyclovir. In brief, the comparison of Fig. 2 demonstrates that PVP enhances the response of acyclovir remarkably and is thus more sensitive for the detection of acyclovir.

3.2. Oxidation mechanism of acyclovir

The electrochemical behavior of acyclovir on PVP-modified CPE was examined using cyclic voltammetry (CV) in different solutions. The applied solutions included (1) 0.1 M acetate buffer solutions with pH of 3.6, 4, 4.6, 5 and 5.6; (2) 0.1 M phosphate buffer solutions with pH of 5.7, 6, 6.5, 7, 7.5 and 8. Within the potential window from 0.4 to 1.4 V, just an oxidation peak was observed, suggesting that the oxidation of acyclovir is irreversible. Moreover, the oxidation peak potential (E_{pa}) shifted linearly to more negative potentials as improving pH value from 3.6 to 8. The slope was −54.6 mV/pH, suggesting that the number of transferred proton and electron was the same. In addition, the oxidation peak current of acyclovir enhanced gradually when improving pH value from 3.6 to 5, and then gradually decreased with further increasing pH value up to 8. Therefore, the oxidation activity of acyclovir on PVP-modified CPE is higher at a pH of 5.

The oxidation response of acyclovir at different scan rates was subsequently studied using linear sweep voltammetry (LSV) to discuss the oxidation mechanism. In pH 5 acetate buffer, the oxidation peak current of acyclovir on PVP-modified CPE increased linearly with the scan rate (ν) over the range from 0.025 to 0.5 V s^{-1}, indicating that

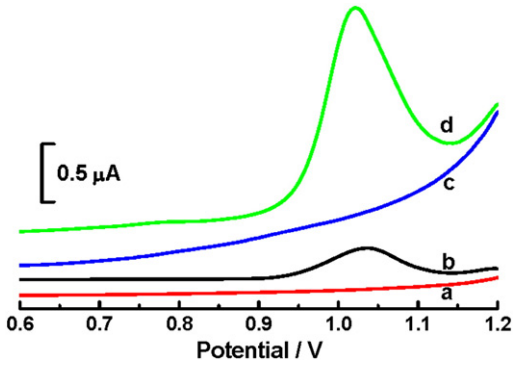

Fig. 2. DPV curves of 1×10^{-7} M acyclovir on CPE (b) and PVP-modified CPE (d) in pH 5 acetate buffer solution. (a) and (c): blank curves for CPE and PVP-modified CPE. Accumulation was under open-circuit for 2 min.