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ORIGINAL PAPER

Electrochemical determination of phloroglucinol using a carbon nanotube modified electrode enhanced by surfactant

Xiao-gang Wang · Ya-juan Fan

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Abstract A novel technique is utilized to detect trace amounts of phloroglucinol. In pH 5.0, 0.1 mol L^{-1} HAc–NaAc buffer solution, phloroglucinol exhibited a stable and sensitive oxidation signal at a glassy carbon electrode modified with multi-wall carbon nanotube. By using the surfactant cetyl pyridinium chloride, the electrochemical response was greatly enhanced. The mechanism was systematically explored. In the range 9.0×10^{-7}–3.0×10^{-4} mol L^{-1}, the oxidation peak currents of phloroglucinol have a linear relationship with concentration: the limit of detection was estimated to be 2.5×10^{-7} mol L^{-1} (S/N = 3). The method was adopted to detect the content of phloroglucinol injection, and the recovery was from 97.5% to 103.0%.

Keywords Multi-walled carbon nanotube · Modified electrode · Phloroglucinol · Surfactant · Determination

1 Introduction

As an essential phenolic compound, phloroglucinol (benzene-1,3,5-triol) is widely used in the food, leather and chemical industries. More importantly, phloroglucinol is employed as a smooth muscle relaxant. It has no anticholinergic potency and appears to be less toxic than most other antispasmodic agents.

X.-g. Wang (✉)
Chemistry Department, Tongji University, Shanghai 200092, People's Republic of China
e-mail: xgwang@mail.tongji.edu.cn

Y.-j. Fan
Maths Department, Tongji University, Shanghai 200092, People's Republic of China

Up to now, only a few analytical methods have been developed for the determination of phloroglucinol, including fluorimetry [1], thin-layer chromatography [2, 3], high performance liquid chromatography (HPLC) [4, 5] and gas chromatography mass spectrometry (GC-MS) [6]. However, HPLC and GC-MS methods have disadvantages such as being time consuming and having high cost. For fluorimetry detection, derivatization is required because phloroglucinol is not fluorescent [7]. Thus, it is necessary to explore a new method for fast and simple detection of phloroglucinol.

Electrochemical methods have received considerable interest due to their quick response, ease of operation and capability of direct detection in aqueous media without pretreatment. Several electrochemical approaches have been reported for the quantitative determination of phenolic compounds [8–10]. As far as we know, however, there have been no reports on the detection of phloroglucinol using electrochemical methods. The main problem is that phloroglucinol does not give sensitive electrochemical responses at several electrodes. In our present work, a multi-wall carbon nanotubes (MWCNTs) modified electrode was developed to enhance the voltammetric signal of phloroglucinol. Moreover, a cationic surfactant, cetyl pyridinium chloride (CPC), was used to further improve the sensitivity. The novel method was applied to the detection of the content of a phloroglucinol injection sample with excellent analytical performance.

2 Experimental

2.1 Reagents

All the chemicals used were of analytical reagent grade. Phloroglucinol, CPC and Nafion (5%) were purchased from

Shanghai Chemical. Phloroglucinol injection was obtained from Shanghai Pharmaceutical Company. Sample solutions were freshly prepared with twice-distilled water, and they were used immediately without deoxygenation in consideration that the treatment showed no obvious difference in experimental results. MWCNTs used in this paper were synthesized by an arc-charge method [11], and then refluxed under stirring for 5 h in concentrated nitric acid. The diameter of CNTs was about 50 nm and the length was about 300 nm.

2.2 Apparatus

Electrochemical experiments were carried out with a CHI-660C electrochemical workstation (Shanghai, China). A three-electrode system was employed comprising a MWCNT modified glassy carbon (GC) electrode (3 mm diameter) as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials in this work are referred to the reference electrode.

2.3 Preparation of the MWCNT modified electrode

A MWCNT–ethanol–Nafion suspension was prepared by dispersing 3 mg MWCNTs into 1 mL ethanol and 0.5 mL Nafion (5%) solution with ultrasonication for about 40 min. Before preparation, the GC electrode was polished successively with emery paper, 0.30 and 0.05 μm γ-Al_2O_3 powder on a polishing cloth. Residual polishing material was removed from the electrode surface by ultrasonication in concentrated nitric acid, twice-distilled water and ethanol. The MWCNT modified electrode was then fabricated by dripping 5 μL of suspension onto a cleaned GC electrode surface, and drying in air before use.

2.4 Analytical procedure

A 0.1 mol L^{-1}, pH 5.0, HAc–NaAc buffer was used as the supporting electrolyte for phloroglucinol determination. The accumulation step proceeded under open circuit while stirring the solution for 3 min, and the voltage-scanning step was performed after 2 s quiet time. Cycle voltammograms (CV) or linear sweep voltammograms (LSV) were carried out at the rate of 0.05 V s^{-1}. The peak currents were recorded by subtracting the background. After every measurement, the modified electrode was swept 10 times in blank solution to remove materials adsorbed on the surface. All experiments were carried out at room temperature.

3 Results and discussion

3.1 Electrochemical behavior of phloroglucinol

Figure 1 shows the CVs of phloroglucinol and blank solution at different electrodes. Phloroglucinol only gave an oxidation peak and no reduction peak appeared, meaning that the electrochemical process was irreversible. At the bare GC electrode, the oxidation peak potential was 0.745 V, and the peak current was 7.2 μA (curve 4). At the MWCNT modified electrode, the oxidation peak potential shifted negatively to 0.710 V, meanwhile, the peak current increased about 4 times up to 27.3 μA (curve 2), indicating that MWCNT had excellent electro-catalytic effect on the oxidation of phloroglucinol. This electrochemical behavior may be explained as follows: the MWCNTs have huge specific surface area. When purified by concentrated nitric acid, MWCNTs open their active groups [12], e.g., –COOH, –C=O and –OH, which become active sites and lower the activity energy of electrochemical reaction. Thus, the oxidation current of phloroglucinol increases significantly. Another phenomenon has also been found in the experiment: the electrochemical signal of phloroglucinol can be greatly enhanced when cationic surfactant is added to the solution. The oxidation current increased about 31% in the presence of 8×10^{-5} mol L^{-1} of CPC (see curve 1).

3.2 Possible enhancement mechanism

Surfactants, with an amphiphilic character, are widely used in the field of electroanalysis. They may change the

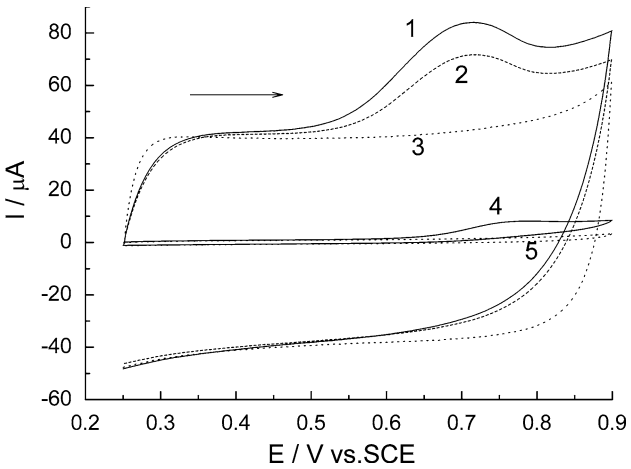

Fig. 1 CV curves of phloroglucinol solution at different electrode 1. Phloroglucinol + CPC; 2. Phloroglucinol; 3. Blank solution at modified electrode; 4. Phloroglucinol + CPC; 5. Blank solution at GC electrode; phloroglucinol 2.0×10^{-4}, CPC 8×10^{-5} mol L^{-1}, pH 5.0

electrical properties of the electrode/solution interface and enhance the voltammetric responses in electrochemical reactions. The enhancement of several surfactants on different materials has been reported, such as estradiol [13], progesterone [14], and dinitrophenol [15]. However, the mechanism has not been explained clearly. In this paper, a number of surfactants, including polyethylene glycol, cyclodextrin, CPC, dodecyl sodium sulfate, 8-hydroxy-7-iodoquinoline-5 sulfonic acid, tetramethyl ammonium bromide, cetyl sodium sulfate, and triton X-100, were tested to study the enhancement mechanism. It was found that these surfactants, except CPC, did not enhance the oxidation current of phloroglucinol. Based on the experimental results, we propose the following mechanism. CPC is a cationic surface-active agent with a long-chain hydrophobic group, which makes it easy to adsorb onto the hydrophobic surface of a MWCNT modified electrode and form a positively charged film. The positively charged film accelerates electron transfer in the electrochemical reaction through the electrostatic effect. Second, the surfactant hydrophobic groups adsorb onto the electrode surface with the positively charged head groups facing the water phase [16]. The N atom in the head group forms a hydrogen bond with the –OH groups in the phloroglucinol molecule, which increases the concentration of phloroglucinol adsorbed on the electrode surface. For these two reasons, the oxidation signal of phloroglucinol is greatly enhanced. Compared with CPC, tetramethyl ammonium bromide only has a short-chain hydrophobic group that does not favor adsorption on the electrode surface. Therefore, it does not exhibit similar behavior to phloroglucinol.

In the next test, phloroglucinol was detected quantitatively using the LSV technique in the presence of CPC.

3.3 Optimization of the experimental conditions

3.3.1 Effect of pH value

NaOH was used to adjust the pH value of 0.1 mol L^{-1} HAc–NaAc buffer solution. When the pH was over 7 borax buffer was used instead. As shown in Fig. 2, the oxidation peak potential of phloroglucinol shifted negatively with increase in pH value. Figure 3 shows the relationship between oxidation peak current and pH value. The current was highest when the pH was in the range 4.0–6.0, thus, pH 5.0 was chosen in this work.

3.3.2 Effect of scan rate

A solution of mixed phloroglucinol (2.0×10^{-4} mol L^{-1}) and CPC (8.0×10^{-5} mol L^{-1}) was tested by CV at different scan rates (see Fig. 4). In the range 0.02–0.09 V s^{-1}, the oxidation peak currents increased linearly with scan rate,

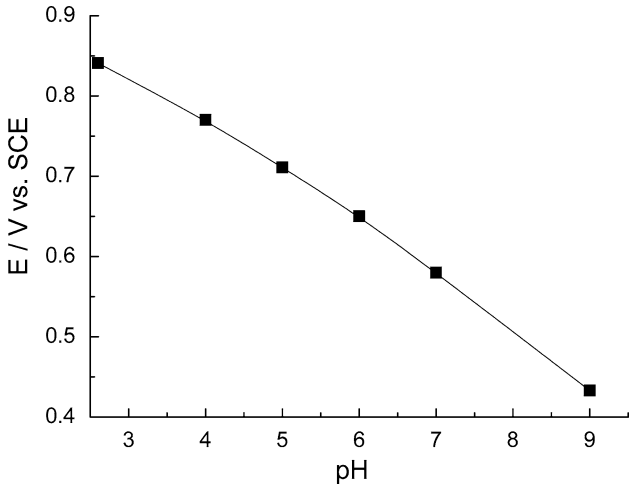

Fig. 2 The influence of pH on the oxidation peak potential (phloroglucinol 1.0×10^{-4} mol L^{-1}, CPC 8.0×10^{-5} mol L^{-1})

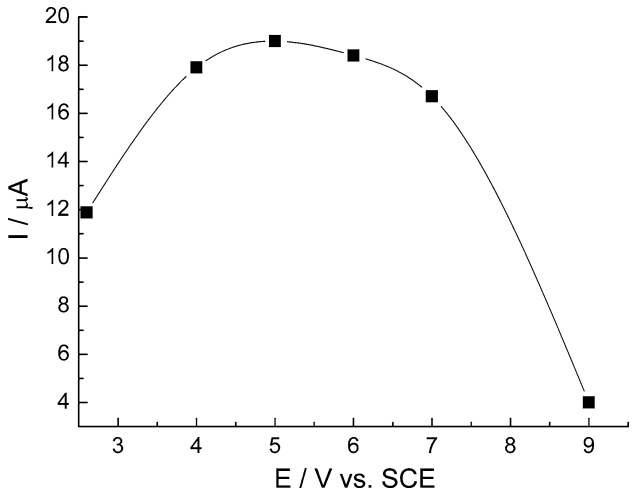

Fig. 3 The influence of pH on the oxidation peak current (phloroglucinol 1.0×10^{-4} mol L^{-1}, CPC 8.0×10^{-5} mol L^{-1})

with the linear regression equation $I = 552.5v + 7.398$, $R = 0.995$ (I in μA, v in V s^{-1}). This suggests that the electro-oxidation of phloroglucinol is adsorption-controlled. A scan rate of 0.05 V s^{-1} was chosen in the test.

3.3.3 Effect of the amount of surfactant

As shown in Fig. 5, at first, the oxidation peak current of phloroglucinol increased significantly with increase in CPC concentration. However, when the concentration exceeded 1.5×10^{-4} mol L^{-1}, the peak currents gradually decreased, probably because the resistance at the surface of the modified electrode increased due to the CPC. So, we chose 8.0×10^{-5} mol L^{-1} as the optimum concentration of CPC.

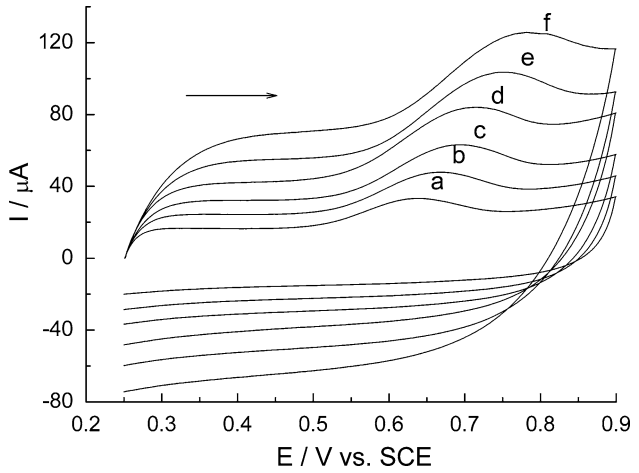

Fig. 4 CV curves of phloroglucinol at different scan rates (phloroglucinol 2.0×10^{-4} mol L^{-1}, CPC 8.0×10^{-5} mol L^{-1}, pH 5.0) *a* 0.02, *b* 0.03, *c* 0.04, *d* 0.05, *e* 0.07, *f* 0.09 V s^{-1}

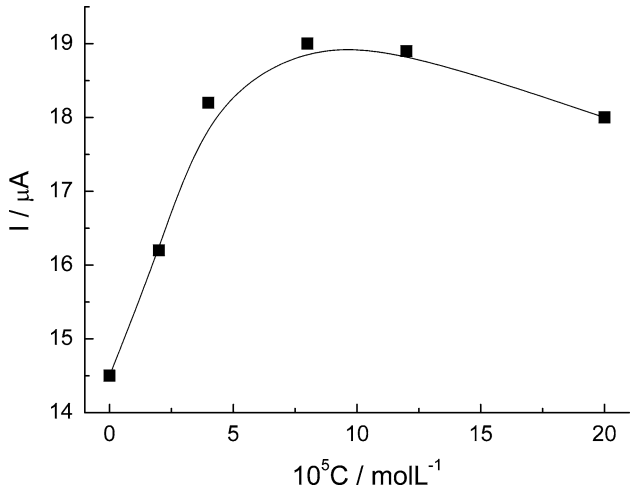

Fig. 5 The influence of concentration of CPC on the oxidation peak current (phloroglucinol 1.0×10^{-4} mol L^{-1}, pH 5.0)

3.4 The calibration equations

At the optimum conditions, the sample solutions were investigated by LSV. The oxidation peak current of phloroglucinol is proportional to its concentration from 9.0×10^{-7} mol L^{-1} to 3.0×10^{-4} mol L^{-1} ($I = 1.651C + 2.607$, $R = 0.999$; I in μA, 10^5C in mol L^{-1}) as shown in Fig. 6.

3.5 Interferences

In the interference test, a number of inorganic ions, such as K^+, Na^+, Ca^{2+}, Pb^{2+}, Ba^{2+}, Co^{2+}, NO_3^-, Cl^-, SO_4^{2-} (each 1.0×10^{-2} mol L^{-1}), and a number of phenols, including *m*-nitrophenol, *o*-nitrophenol, *p*-nitrophenol,

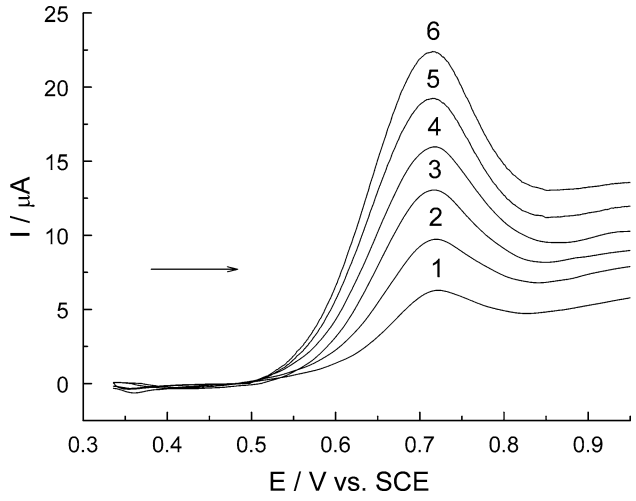

Fig. 6 The calibration of phloroglucinol 1: 2.0×10^{-5}, 2: 4.0×10^{-5}, 3: 6.0×10^{-5}, 4: 8.0×10^{-5}, 5: 10.0×10^{-5}, 6: 12.0×10^{-5} mol L^{-1} (CPC 8.0×10^{-5} mol L^{-1}, pH 5.0)

o-dihydroxybenzene, *p*-dihydroxybenzene, 2,4-dinitrophenol, 2,5-dinitrophenol and 1-naphthol (10-fold), had no influence on the signal of phloroglucinol, with deviation below 5%. However, 2-naphthol and *m*-dihydroxybenzene would disturb the measurement of phloroglucinol.

3.6 Reproducibility and detection limit

One modified electrode was used to detect phloroglucinol (1.0×10^{-4} mol L^{-1}) for five times in succession. The relative standard deviation (RSD) was 3.6%. The modified electrode was fabricated four times and then immersed in sample solution (1.0×10^{-4} mol L^{-1}); the RSD was 4.1%. The peak current attenuation was <5% when the modified electrode was stored at room temperature for 10 days. These results implied that the modified electrode was stable and had good reproducibility. Using 3-fold signal–noise ratio method, the detection limit was estimated to be 2.5×10^{-7} mol L^{-1}.

3.7 Determination of phloroglucinol in injection

One ampoule of phloroglucinol injection (4 mL) was dispersed into pH 5.0, 0.1 mol L^{-1} HAc–NaAc buffer (1,000 mL in total volume). The solution was then diluted 10 times as the analysis sample, and CPC was used as additive. The amount of phloroglucinol was detected by the Standard Addition Method. One sample solution was measured by LSV three times, as shown in Table 1, the recovery was from 97.5% to 103.0%. Thus, the concentration of phloroglucinol in the injection was about 7.81×10^{-2} mol L^{-1}.

Table 1 Determination of phloroglucinol in injection

Sample	10^4C Original (mol L^{-1})	10^4C Added (mol L^{-1})	10^4C Found (mol L^{-1})	Recovery (%)	x (%)
1	0.312	0.200	0.499	97.5	99.7
2	0.312	1.000	1.351	103.0	
3	0.312	2.000	2.281	98.7	

4 Conclusion

In 0.1 mol L^{-1} HAc–NaAc buffer, phloroglucinol exhibited a sensitive oxidation peak at the MWCNT modified GC electrode. A cationic surfactant of CPC was used to change the properties of the interface between solution and the modified electrode, by which the electrochemical signal of phloroglucinol was further enhanced. The influence of substrate, pH, interference and enhancement mechanism were investigated systematically. On this basis, a fast and convenient electrochemical method has been established for determination of phloroglucinol. The novel method has the advantages of higher sensitivity and wider linear range, and can be applied to detect phloroglucinol in aqueous solution without previous treatment.

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