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ORIGINAL PAPER

Docosyltrimethylammonium chloride modified glassy carbon electrode for simultaneous determination of dopamine and ascorbic acid

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Abstract A glassy carbon electrode (GCE) modified with docosyltrimethylammonium chloride (DCTMACl) is used for simultaneous determination of dopamine (DA) and ascorbic acid (AA) using differential pulse voltammetry (DPV) technique in 0.10 mol·L^{-1} phosphate buffer solution of pH 5.0. The cationic surfactant DCTMACl modified film has a positive charge. DA exists as the positively charged species, whereas AA is the negatively charged one in the solution. Thus, at DCTMACl film-modified GCE, the oxidation peak potential of AA shifts toward less negative potential and the peak current of AA increases a little, while the oxidation peak potential of DA shifts toward more positive potential and peak current decreases greatly in comparison with that on bare electrode. The two anodic peaks are separated around 200 mV. Under optimal conditions, the catalytic peak currents obtained from DPV increase linearly with concentrations of DA and AA in the ranges of 1.0×10^{-5} to 1.0×10^{-3} mol·L^{-1}. This electrode has good reproducibility, high stability in its voltammetric response, and low detection limit (micromolar) for both AA and DA. The modified electrode has been applied to the determination of DA and AA in injection.

Keywords Docosyltrimethylammonium chloride · Simultaneous determination · Dopamine · Ascorbic acid

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Introduction

Dopamine (3,4-dihydroxyphenyl ethylamine, DA) plays an important physiological role as an extracellular chemical messenger in the function of the central nervous, renal, hormonal, and cardiovascular systems [1]. Furthermore, neurobiological investigations have suggested that DA system dysfunction plays a critical role in some clinical manifestations of HIV infection [2]. In the extracellular fluid of the central nervous system, the basal DA concentration is very low, which provides a large challenge for detection of DA. It has been also found that patients with Parkinson's disease show an almost complete depletion of DA in this region. Common instrumental techniques like high performance liquid chromatography have been used for the determination of DA [3]. However, such methods of detection are often complicated and very expensive. Electrochemical methods have advantages such as simplicity, speed, and sensitivity, and electrochemical detection is a feasible method as the electrochemical oxidation of DA is a two-electron irreversible process with transfer of two protons [4].

A major problem in detection of DA using electrochemical methods is the presence of high concentrations of ascorbic acid (AA), because AA is oxidized at a potential close to that of DA on the solid electrodes, which results in overlapping of the voltammetric response [5]. AA is a vital vitamin in the diet of humans. AA has been used for preventing and treating common cold, mental illness, infertility, cancer, and AIDS [6]. It is present in many biological systems and multivitamin preparations, which are commonly used to supply inadequate dietary intake. Furthermore, AA is widely used in foods as an antioxidant for the stabilization of color and aroma with subsequent extension of the storage time of the products [1]. Thus, the determination of AA content is particularly important in the pharmaceutical and food industry. Direct oxidation of AA at conventional electrodes

is totally irreversible. Moreover, because of large anodic overpotential and the electrode surface fouling by the oxidation products, the determination of AA by its direct electrochemical oxidation is very complicated [7].

In order to solve the problem of simultaneous determination of DA and AA, one of the most common routes is to use a modified electrode. For example, electrodes with covalent modification [8, 9], polymer film [10–14], ruthenium oxide modification [15], carbon ionic liquid [16], thionine-nafion supported on multi-walled carbon nanotube [7], and binuclear copper complex [17] have been applied to detect DA and AA together. And other methods and materials have been also adopted, such as chemometrics [18], molecularly imprinted polymers [19], chemiluminescence [20], ion-exchange voltammetry [21], boron-doped diamond electrodes [22], and catechin hydrate [23]. In this work, we use a surfactant-modified electrode to measure the concentration of DA and AA simultaneously.

Surfactants, a kind of amphiphilic molecules with a hydrophilic head on one side and a hydrophobic tail on the other side, have been widely applied in electrochemistry to improve the property of the electrode/solution interface [24–26]. The surfactant-modified electrodes have been reported previously. Shahrokhian et al. have modified carbon-paste electrode with tetraoctylammonium bromide and cobalt-5-nitrosalophen for simultaneous voltammetric detection of AA and DA [27]. Didodecyldimethylammonium bromide film-modified electrode has been used for simultaneous measurement of various combinations of neurotransmitters and AA [28].

Our group has fabricated cetyltrimethylammonium bromide/chitosan composite modified glassy carbon electrodes for simultaneous determination of DA and AA [29]. In this report, we describe a differential pulse voltammetric (DPV) determination of AA, DA, and their mixture at docosyltrimethylammonium chloride (DCTMACl) film-modified electrode. DCTMACl is a kind of surfactant, which is ionized for a large cation and anion in aqueous solution. The large cation contains hydrophobicity of hydrocarbon chains and DCTMACl could be aggregated by hydrophobic interaction.

Experimental

Apparatus and reagents

All electrochemical experiments were performed with a CHI660C electrochemical workstation (Shanghai Chenhua Co., China). A three-electrode electrochemical cell was employed. DCTMACl/GCE was used as working electrode, with a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. All potentials reported were versus the SCE.

All reagents such as DA (Sigma–Aldrich), AA (Sigma–Aldrich), and DCTMACl (Nanjing Wuniu Technology Enterprise Co., Ltd) were used as received without further purification. All chemicals were of analytical grade. The phosphate buffer solution (PBS, 0.10 mol·L^{-1}) with various pH values was prepared by mixing stock standard solution of KH_2PO_4 and K_2HPO_4, and the pH value was adjusted with HCl. Freshly prepared solution of DA and AA was used in all experiments. All solutions were prepared with doubly distilled water. All experiments were carried out at room temperature.

Preparation of the DCTMACl film-modified electrode

Before modification, the GCE was polished using a chammy cloth with 0.3 and 0.05 μm alumina slurry, rinsed, and ultrasonicated in 1:1 nitric acid, ethanol, and double distilled deionized water, respectively. Various concentrations of DCTMACl with volume of 10 μL were dropped on the electrode surface which had been treated before and dried at room temperature.

Results and discussion

Optimization of DCTMACl concentration for DPV response of DA and AA oxidation

In this work, the concentration of DCTMACl is vital to the simultaneous determination of AA and DA. As is well known, the bare glassy carbon electrode fails to separate the voltammetric signals of AA and DA. When DCTMACl is modified on electrode, the surfactant concentration dependence of variation of the difference of peak potentials (ΔE_p) of DA and AA is illustrated in Fig. 1, which exhibits that the ΔE_p values reach a plateau in the concentration range of DCTMACl from 4.0 to 10.0 mmol·L^{-1}. The plot of peak current versus the surfactant concentration is shown in Fig. 2. It shows that the peak current reached maximum at the DCTMACl concentration of 8.0 mmol·L^{-1}. Taking into account effective separation and sensitivity, the concentration of DCTMACl was chosen as 8.0 mmol·L^{-1} for further experiments.

The influence of pH on the oxidation of DA and AA in the mixture

The pH value of the supporting electrolyte had significant influence on the separation of AA and DA. The effect of pH on the response of AA and DA in the mixture at DCTMACl film-

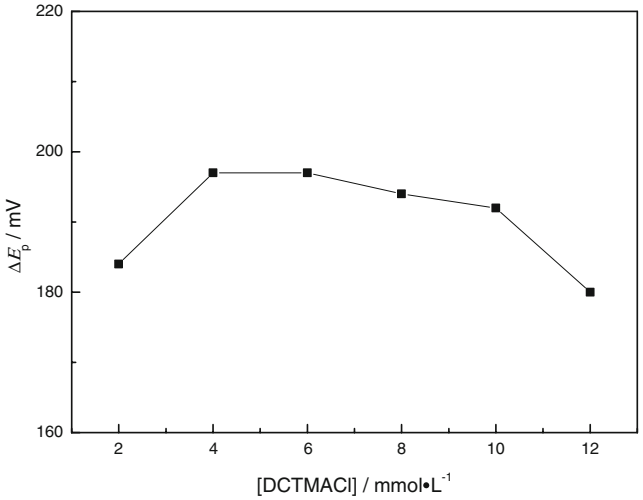

Fig. 1 Effect of DCTMACl concentration on variation of the difference of peak potentials (ΔE_p) of AA and DA. In the mixture of DA (5.0×10^{-4}mol·L^{-1}) and AA (5.0×10^{-4}mol·L^{-1}) in 0.10 mol·L^{-1} PBS (pH 5.0)

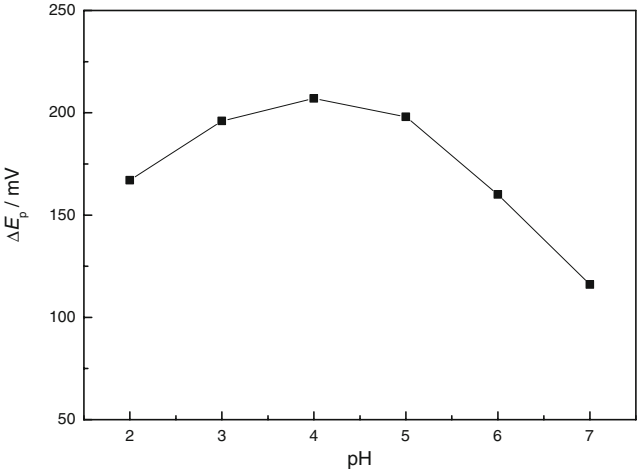

Fig. 3 Effect of pH on variation of the difference of peak potentials (ΔE_p) of DA and AA, in the mixture of DA (5.0×10^{-4}mol·L^{-1}) and AA (5.0×10^{-4}mol·L^{-1}) in 0.10 mol·L^{-1} PBS of different pH

modified electrode was investigated using DPV in 0.10 mol·L^{-1} PBS of pH 2.0–7.0 containing 5.0×10^{-4}mol·L^{-1} AA and 5.0×10^{-4}mol·L^{-1} DA. AA (pK_a=4.10) and DA (pK_a=8.87) exist in different ion forms in supporting electrolyte of distinct pH [30], which can be observed by the difference of peak potentials (Fig. 3) and peak currents (Fig. 4).

It can be seen from Fig. 3 that the difference of peak potentials reached a plateau in the pH range of 3.0–5.0. Figure 4 depicts the peak currents of AA coming to the maximum, whereas those of DA reach the minimum of around pH 4.0–5.0. And the peak currents of AA are much smaller than the peak current of DA at other pH. Taking into account pK_a of AA, we chose pH 5.0 to the subsequent study. The amine group of DA is positively charged, whereas the hydroxyl next to the carbonyl group of AA is negatively charged at pH 5.0. Thus, AA and DA can be completely separated, allowing simultaneous determination of AA and DA in the mixture.

Electrochemical behavior of AA and DA at the DCTMACl film-modified electrode

DPV is often used to make electrochemical measurements. It can be considered as a derivative of linear sweep voltammetry or staircase voltammetry, with a series of regular voltage pulses superimposed on the potential linear sweep or stair steps. DPV is characteristic of higher current

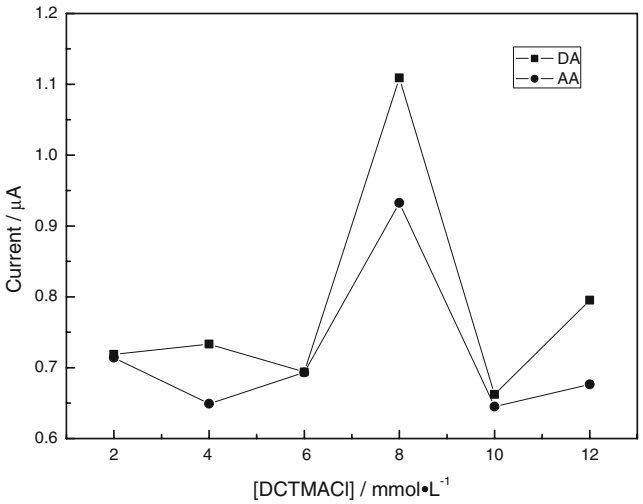

Fig. 2 Effect of DCTMACl concentration on variation of peak currents of DA and AA. Experimental conditions were the same as indicated in Fig. 1

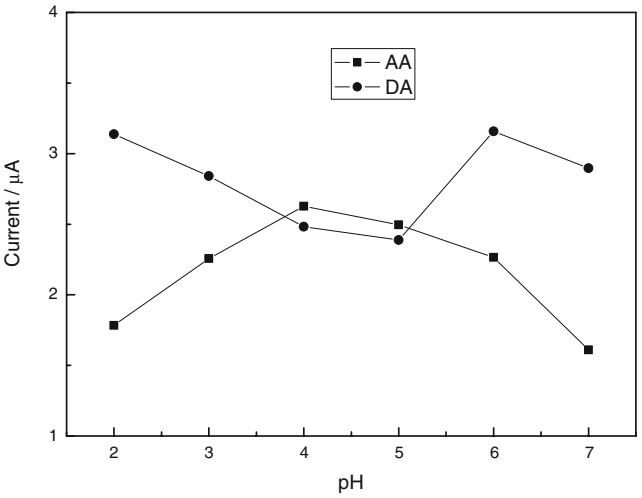

Fig. 4 Effect of pH on variation of peak currents of DA and AA. Experimental conditions were the same as indicated in Fig. 3

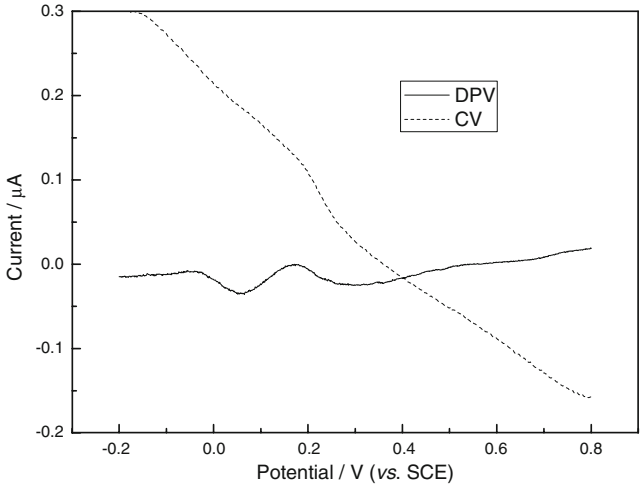

Fig. 5 DPV and cyclic voltammetry of the DCTMACl/GCE in 0.10 mol·L^{-1} PBS (pH 5.0) with 2.0×10^{-5} mol·L^{-1} of AA and DA

sensitivity and better resolution than cyclic voltammetry. Figure 5 shows the DPV and cyclic voltammetry of the DCTMACl/GCE in 0.10 mol·L^{-1} PBS (pH 5.0) with 2.0×10^{-5} mol·L^{-1} of AA and DA. It can be clearly seen that the peak current response in DPV is much better than that in cyclic voltammetry. Figure 6 indicates the electrocatalytic behavior of AA at the DCTMACl/GCE (Fig. 6a–k) and the bare GCE (Fig. 6l) in 0.10 mol·L^{-1} PBS (pH 5.0) which contains various concentrations of AA. As shown in Fig. 6, at a bare GCE, AA shows a broad oxidation peak at 0.21 V, indicating a slow electron transfer kinetic, while the oxidation peak shifts to 0.17 V with well-defined peak shape at the DCTMACl composite film-modified electrode, showing the modified electrode has electrocatalytic activity toward AA. About 40 mV negative shift and enhanced current of the anodic peak indicate that the DCTMACl film-modified electrode plays a key role in catalyzing AA oxidation. The reason behind this can be explicated as: on the bare electrode, fouling of the electrode surface caused by the adsorption of the oxidation product of AA makes the electron transfer rate rather sluggish; however, on the modified electrode, excellent electrocatalytic activity for AA is obtained due to electrostatic attraction between AA and DCTMACl on the electrode surface, which reduces the overpotential of the electrode and increases the electron transfer rate as well. Figure 6 also indicates the DPV peak currents of AA increased linearly with the increase of concentrations of AA in the range of 1.0×10^{-5} to 1.0×10^{-3} mol·L^{-1} (I_p=0.00365c+0.04385, r=0.9982).

Figure 7 depicts the electrochemical oxidation behavior of DA at the DCTMACl film-modified electrode (Fig. 7a–k), and bare GCE (Fig. 7l) in 0.10 mol·L^{-1} PBS (pH 5.0) containing various concentrations of DA. As shown in Fig. 7, the oxidation of DA occurred at 0.27 V on bare GCE, while the oxidation of DA was at 0.32 V on the DCTMACl film-modified electrode. Due to the electrostatic repulsion of the film against DA, the peak current of DA decreased greatly and the anodic peak potential shifted toward positive in contrast with that on bare GCE. The decrease in the rate of electron transfer is well indicated by the higher oxidation overpotential. It is clear that the oxidation of DA is lagged at the modified electrode. This

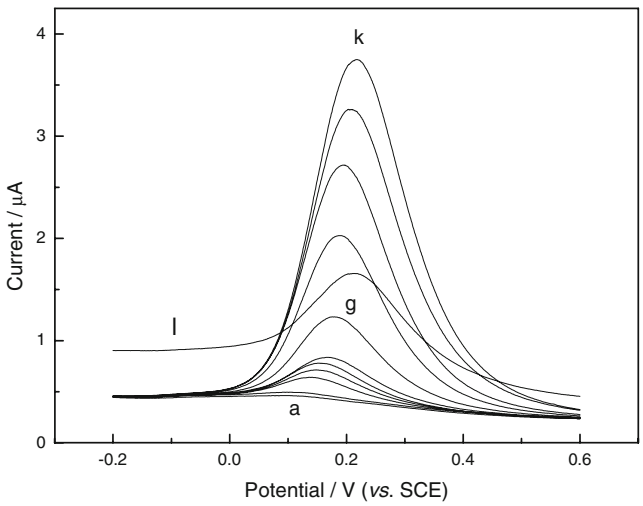

Fig. 6 DPVs of the DCTMACl/GCE in 0.10 mol·L^{-1} PBS (pH 5.0) with different concentrations of AA: *a* 1.0×10^{-5}, *b* 2.0×10^{-5}, *c* 4.0×10^{-5}, *d* 6.0×10^{-5}, *e* 8.0×10^{-5}, *f* 1.0×10^{-4}, *g* 2.0×10^{-4}, *h* 4.0×10^{-4}, *i* 6.0×10^{-4}, *j* 8.0×10^{-4}, *k* 1.0×10^{-3} mol·L^{-1}. *l* DPV of bare glassy carbon electrode and the concentration of AA=2.0×10^{-4} mol·L^{-1}. Potential amplitude of 50 mV; pulse width of 0.04 s; pulse period of 0.2 s

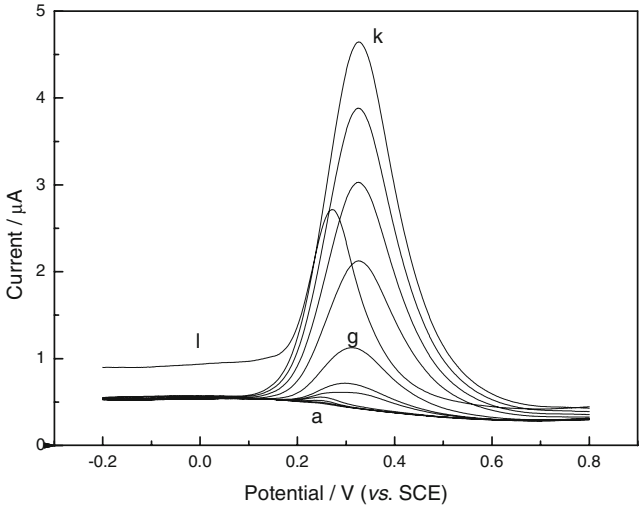

Fig. 7 DPVs of the DCTMACl/GCE in 0.10 mol·L^{-1} PBS (pH 5.0) with different concentrations of DA: *a* 1.0×10^{-5}, *b* 2.0×10^{-5}, *c* 4.0×10^{-5}, *d* 6.0×10^{-5}, *e* 8.0×10^{-5}, *f* 1.0×10^{-4}, *g* 2.0×10^{-4}, *h* 4.0×10^{-4}, *i* 6.0×10^{-4}, *j* 8.0×10^{-4}, *k* 1.0×10^{-3}. *l* DPV of bare glassy carbon electrode and the concentration of DA=2.0×10^{-4} mol·L^{-1}. Potential amplitude of 50 mV; pulse width of 0.04 s; pulse period of 0.2 s

figure also shows that the peak currents of DA were proportional to its concentrations in the range of 1.0×10^{-5} to 1.0×10^{-3} mol·L^{-1} (I_p=0.00453c+0.03854, r=0.9990).

DPV technique for simultaneous determination of AA and DA

In order to distinguish between DA and AA, the problem of their overlapped signals on bare GCE must be resolved. From the above discussion, we can know that the electrostatic attraction of the DCTMACl film towards AA and the electrostatic repulsion of the film against DA separate the overlapping anodic peaks in DPV detection of the two compounds. Using DCTMACl/GCE, two well-defined oxidation peaks corresponding to AA and DA with a peak potential difference of 200 mV are achieved. The synergic effect of AA with DA was tested in the experiments. The results show that there is no obvious synergic effect of AA concentration on the analytical signal of DA and vice versa. The DPVs were obtained at the DCTMACl/GCE during the simultaneous change of the concentrations of AA and DA (Fig. 8). It is demonstrated that the calibration curves for AA and DA were linear for a wide range of concentrations from 1.0×10^{-5} to 1.0×10^{-3} mol·L^{-1} for AA (I_p=0.00437c+0.05216, r=0.9988) and also for DA (I_p=0.00675c+0.07225, r=0.9993). The detection limit for AA is 4.0×10^{-6} and DA is 6.5×10^{-6} mol·L^{-1}. The above results hence confirm that the responses of DA and AA at the DCTMACl/GC electrode were independent. The renewal of the film is easily accomplished by soaking the electrode in 0.10 mol·L^{-1} PBS (pH 5.0) and cycling its potential in the range of −0.2 and 0.8 V (0.1 V·s^{-1}).

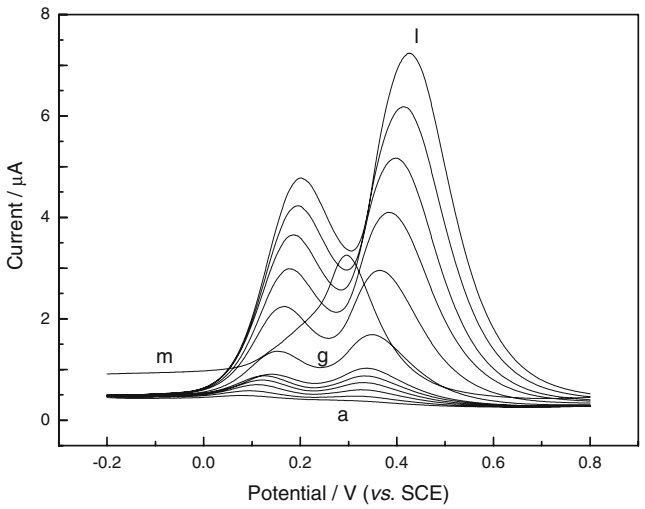

Fig. 8 DPVs of the DCTMACl/GCE in 0.10 mol·L^{-1} PBS (pH 5.0) with different concentrations of AA: *a* 1.0×10^{-5}, *b* 2.0×10^{-5}, *c* 4.0×10^{-5}, *d* 6.0×10^{-5}, *e* 8.0×10^{-5}, *f* 1.0×10^{-4}, *g* 2.0×10^{-4}, *h* 4.0×10^{-4}, *i* 5.5×10^{-4}, *j* 7.0×10^{-4}, *k* 8.0×10^{-4}, *l* 1.0×10^{-3} mol·L^{-1}. Concentration of DA was the same as that of AA. *m* DPV of bare glassy carbon electrode and the concentration of AA=2.0×10^{-4} mol·L^{-1}, also for DA. Potential amplitude of 50 mV; pulse width of 0.04 s; pulse period of 0.2 s

Table 1 Determination of DA in hydrochloride injection solutions (n=5)

Labeled (10^{-4}M)	Spiked (10^{-4}M)	Found (10^{-4}M)	RSD (%)	Recovery
3.17	1.00	4.06	1.7	97
3.17	1.00	4.08	1.9	98
3.17	1.00	4.34	1.6	104

Reproducibility, stability, and selectivity against interferences

The reproducibility test using six biosensors was investigated, which were modified in the same way. The same measurements using the six biosensors were carried out at the concentration level of DA 2.0×10^{-4} mol·L^{-1}. The relative standard deviation (RSD) of the potential responses is within 0.5%. The stability test was done in which the electrode was tested after 1 month. When not in use, the electrode was stored in a dry state at room temperature. The biosensor retained more than 90% of its original response after 1 month of testing. No interference was observed for the following compounds: K^+, Ca^{2+}, Fe^{3+}, L-cysteine, and glucose.

Determination of DA in dopamine hydrochloride injection and AA in hydrochloride injection solutions

One hundred and fifty microliters of the dopamine hydrochloride injection solution (10 mg·mL^{-1}, 2 mL per injection, from Shanghai Harvest Pharmaceutical Co., Ltd.) and 7 μL of the AA hydrochloride injection solution (200 mg·mL^{-1}, 5 mL per injection, from Shanghai Harvest Pharmaceutical Co.) were injected into a 25-mL volume flask and made up to volume with 0.10 mol·L^{-1} (pH 5.0), respectively. Then, this test solution was placed in an electrochemical cell for the determination of DA and AA using the above DPV method. The results are listed in Tables 1 and 2.

Table 2 Determination of AA in hydrochloride injection solutions (n=5)

Labeled (10^{-4}M)	Spiked (10^{-4}M)	Found (10^{-4}M)	RSD (%)	Recovery
3.18	1.00	3.93	2.1	94
3.18	1.00	4.68	1.9	112
3.18	1.00	4.48	2.2	107

Conclusion

The DCTMACl/GCE was developed and applied for the simultaneous determination of AA and DA, which resolved the merged voltammetric signals of AA and DA into two well-defined peaks with a peak separation of 200 mV. The electrocatalytic oxidation of AA occurred due to the favorable electrostatic interaction, whereas DA oxidation took place through the repulsive interaction between the DCTMACl film and DA. The study provides a feasible approach to fabricate surfactant-modified electrode for the simultaneous determination of AA and DA with good sensitivity, stability and selectivity. The proposed methods can be applied to the determination of DA and AA in real samples with satisfactory results.

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