Asian Journal of Chemistry Vol. 21, No. 4 (2009), 2577-2582

Determination of Dopamine in Hypoxanthine System with Glassy Carbon Mercury Film Electrode

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The electrochemical behaviour of glassy carbon mercury film electrode in hypoxanthine solution and its electrocatalytic oxidation for dopamine in this solution were studied. It indicated, by adding certain amount of hypoxanthine in electrolyte solution, it had good inhibition on the stripping peak of Hg at higher potentials and the electrode showed a better stability in the solution. In pH 1.81 buffer solution, the reduction peak of dopamine was almost unchanged when ascorbic acid coexisted, the reduction peak current of dopamine was proportional to its concentration in the range of 1.5×10^{-5}–5.6×10^{-4} mol L^{-1} and the detection limit could reach 2×10^{-6} mol L^{-1}. The method could obtain better result when it applied to the determination dopamine in synthetic sample.

Key Words: Glassy carbon mercury film Electrode, Hypoxanthine, Dopamine, Ascorbic acid.

INTRODUCTION

Dopamine, the most significant catecholamine, belongs to the family of excitatory chemical and plays an important role in the functioning of central nervous, renal, hormonal and cardiovascular system. Extreme abnormalities of dopamine concentration levels may lead to several diseases such as Pakinson's[1]. Thus determination of dopamine is important in the field of neurochemistry and biomedical chemistry. Electrochemical sensors attracted wide attention due to their advantages of simple, inexpensive and fast analysis in combination with high sensi-tivity and selectivity. But a major obstacle in monitoring of dopamine with electrochemical methods is the interference of ascorbic acid, which can be oxidized at the potential close to that of dopamine on the solid electrode. Generally, for alleviating this problem is the use of chemically modified electrodes (CMEs)[2-6].

Glassy carbon mercury film electrode (GCMFE) is frequently used in electrochemical stripping analysis of trace metals[7-9]. For deposition of the mercury a different type of glassy carbon electrodes, are commonly used in environmental detection[10,11] and drug analysis[12,13] applications. But in acidic solutions, the positive potential of the GCMFE is limited, the mercury will be stripped by oxidation when the working potentials is above 0.2 V. Herein, a method to increase the available potential range of mercury film and the electrocatalytic oxidation of dopamine is described. Present

results showed that adding certain amount of hypoxanthine in electrolyte solution, it had good inhibition on the stripping peak of mercury at higher potentials and the GCMFE showed a better stability in the solution. Furthermore, the electrochemical behavior of dopamine in hypoxanthine system with the GCMFE was examined. Thus, dopamine concentration can be determined simultaneously when ascorbic acid coexist with dopamine. And the proposed method has been applied to the determination of dopamine in synthetic sample with satisfactory result.

EXPERIMENTAL

Cyclic voltammetry (CV) measurements were carried out using a MEC-12B multi-function electrochemical analyzer (Jiangsu Jiangfen Instrument Int., China). All the cyclic voltammograms were made using a three-electrode system with a glassy carbon electrode as a working electrode, an Ag/AgCl (saturated with KCl) as a reference electrode and a platinum wire electrode as a counter electrode. The KQ218 ultrasonic instrument (Kunshan Ultrasonic Instrument Factory, China) was used.

Dopamine hydrochloride (Shanghai Hefeng Chemicals, China) and ascorbic acid (Tianjin Chemicals, China) were used as received. Hypoxanthine was analytical grade and purchased from Sigma (USA). They and all other chemical reagents were used without further purification. All other chemicals used in this investigation were of analytical grade. 0.05 mol L^{-1} H_3PO_4 + 0.05 mol L^{-1} CH_3COOH + 0.05 mol L^{-1} H_3BO_3-0.2 mol L^{-1} NaOH buffer solutions of various pHs were prepared by mixing 2 stock solutions, ascorbic acid and dopamine were prepared daily. All solutions were prepared with double-distilled water.

Preparation of the glassy carbon mercury film electrode (GCMFE): The glassy carbon electrodes (GCE) surface was polished on a piece of velvet with alumina slurry, rinsed with distilled water and then sonicated for 10 min. The electrodes were placed in a voltammetric cell containing 10 mL of distilled water and 10 mL of mercury plating solution (200 mg L^{-1} $HgCl_2$ in 2 M HCl). Nitrogen gas was bubbled through the cell for 5 min and then the electrode was conditioned by scanning the potential between -1.2 V and -0.1 for three times. Mercury deposition was maintained by applying a potential of -1.0 V for 1 min.

Procedure: The electrochemical behavior of GCMFE in hypoxanthine solution cycled in pH 1.81 buffer solution in the potential range between -0.3 and +0.7 V. Application of the electrode for the determination of ascorbic acid and dopamine was evaluated by running the CVs in pH 1.81 buffer solution (containing 0.1 g L^{-1} hypoxanthine in order to prevent the stripping of the mercury film). The potential range between -0.3 and +0.7V and the scan rate was 100 mV s^{-1}. The effect of pH can be studied by running the experiments in electrolytes of different pH values. At the same time, note down the cyclic voltammograms for investigating the cyclic voltammetric behaviours of ascorbic acid and dopamine on GCMFE. The experimental results were obtained at room temperature.

RESULTS AND DISCUSSION

Electrochemical behavior of GCMFE in hypoxanthine solution: In acidic solutions, the positive potential of the GCMFE is limited, the mercury will be stripped by oxidation when the working potentials is above 0.2 V, a large peak of Hg appeared at the CV. It is found that adding certain amount of hypoxanthine in electrolyte solution, it had good inhibition on the stripping of mercury at higher potentials. Furthermore, the CVs of different hypoxanthine concentrations at GCMFE had been investigated.

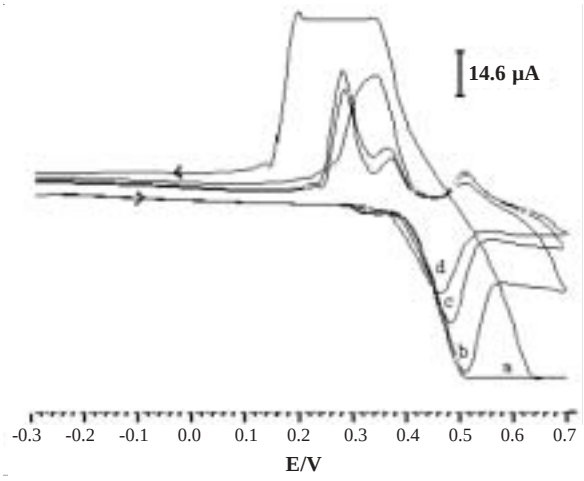

Fig. 1. Cyclic voltammograms of glassy carbon mercury film electrode in different concentrations of hypoxanthine (pH 1.81). Concentrations of hypoxanthine: a. 0.005 g L^{-1}; b. 0.015 g L^{-1}; c. 0.05 g L^{-1}; d. 0.1 g L^{-1}

Fig. 1 showed the cyclic voltammograms of GCMFE in the 0.05 mol L^{-1} H_3PO_4 + 0.05 mol L^{-1} CH_3COOH + 0.05 mol L^{-1} H_3BO_3 buffer solution with pH 1.81 (containing different concentration hypoxanthine). A large peak of Hg appeared at the CV When the GCMFE in buffer solution without hypoxanthine; 0.005 g L^{-1} hypoxanthine were added, then the peak of Hg rapidly reduced (Fig. 1a), the peak of Hg reduced with increasing the hypoxanthine concentration (Fig. 1b-d), the peak of Hg reduced little when the hypoxanthine concentration was above 0.1 g L^{-1}, the product had stable curves of clyclic voltmmogram (Fig. 2) with a oxidation peak (1) and three reduction peak (2, 3, 4) in 0.1 g L^{-1} hypoxanthine (pH 1.81). The mechanism may be that a new electro active substances due to hypoxanthine in the solution react to Hg, the new electro active substances had good inhibition on the stripping peak of Hg at higher potentials. After the GCMFE in 0.1 g L^{-1}, hypoxanthine cycle scaned 15 times, then immersed in the blank solution, the large peak of Hg would presented at once at the CV because of the mercury stripped by oxidation, it indicated that the hypoxanthine interacted with Hg of mercury film, but the surface of electrode was not coated with a stable modified layer.

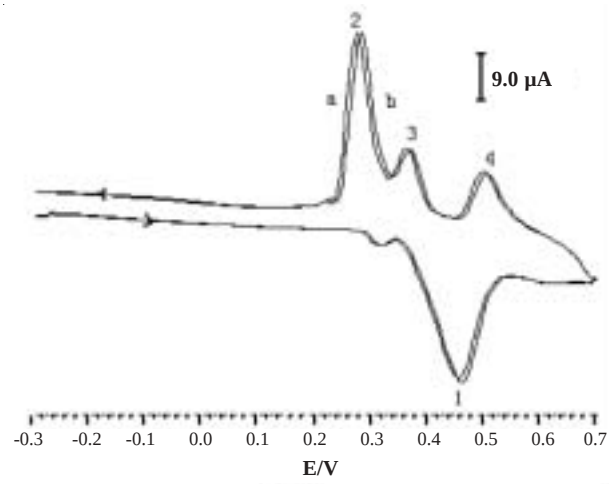

Fig. 2. Cyclic voltammograms of glassy carbon mercury film electrode in 0.1 g L^{-1} hypoxanthine (pH 1.81)

In addition, the stability of the GCMFE in the hypoxanthine solution (pH 1.81) was investigated. Fig. 2a showed the GCMFE in the first using, Fig. 2b showed the CVs of GCMFE after being used 200 times. Two CVs had a little displacement and the size of oxidation or reduction peaks had no change. It indicated that the electrode had a better stability in the solution.

Electrochemical behavior of DA at the GCMFE:

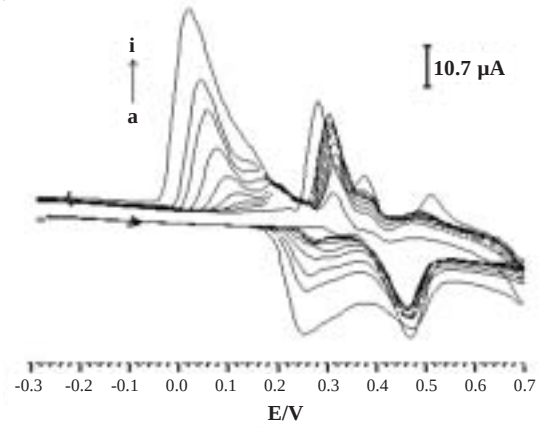

Fig. 3. Cyclic voltammograms of different concentrations of dopamine (pH 1.81) Concentrations of dopamine (10^{-5} mol L^{-1}): a, 0; b, 15; c, 25; d, 50; e, 100; f, 180; g, 280; h, 360; i, 560

Cyclic voltammograms: Fig. 3 showed the CVs of different concentration of dopamine at the GCMFE in the pH 1.81 buffer solution (containing 0.1g L^{-1} hypoxanthine). As can be seen, the sensitive oxidation peaks of dopamine were observed

at 0.28V and more sensitive reduction peaks were observed at 0.07 V, The reduction peak of dopamine was linear with its concentration from 1.5×10^{-5} mol L^{-1} to 5.6×10^{-4} mol L^{-1} with the linear regression equation was i_{Pc} (μA) = 0.2403 + 0.0983c (R = 0.9994). Detection limit of it reached at 2×10^{-6} mol L^{-1}.

The effect of the scan rate on the electrochemical behavior of DA were investigated. the reduction peak potential of dopamine negative shifted with increasing scan rate and the reduction peak current of dopamine (i_{Pc}) was proportional to the square root of the scan rate over the range of 25-400 mV s^{-1}. The linear regression equation was i_{Pc} (μA) = -0.4695 + 1.0262$v^{1/2}$, with a correlation coefficient of R = 0.9948. It indicated that the electrode process was controlled by the mass diffusion, showing a diffusion-controlled process in the solution.

In addition, the effect of the background solution and it's pH value on the response of dopamine were studied in KHPh-NaOH, HOAc-NaOAc, HCl, KCl and H_3PO_4 + CH_3COOH + H_3BO_3 – NaOH buffer solutions. The experiment indicated that the reduction peak was the most sensitive in pH 1.81 (0.05 mol/L H_3PO_4 + 0.05 mol/L CH_3COOH + 0.05 mol/L H_3BO_3) buffer solution.

Cyclic voltammograms when ascorbic acid coexists with dopamine: In the mixture solution of 1×10^{-3} mol L^{-3} ascorbic acid and 2×10^{-4} mol L^{-3} dopamine, the oxidation peak potential difference between dopamine and AA ($E_{Pc \cdot DA} - E_{Pc \cdot AA}$) was small at pH 1.81, there would exist a overlapped peak due to the oxidation peak of dopamine overlapped the oxidation peak of ascorbic acid. But the reduction peak current and potential were almost unchanged compared to when dopamine existed alone at pH 1.81 (Fig. 4), the determination of dopamine reduction peak was not influenced by ascorbic acid in this case. With discussing above, no matter whether existed singly or jointly coexisted with ascorbic acid, the determination of dopamine could be carry out in pH 1.81 buffer solution, because in this condition, the determi-

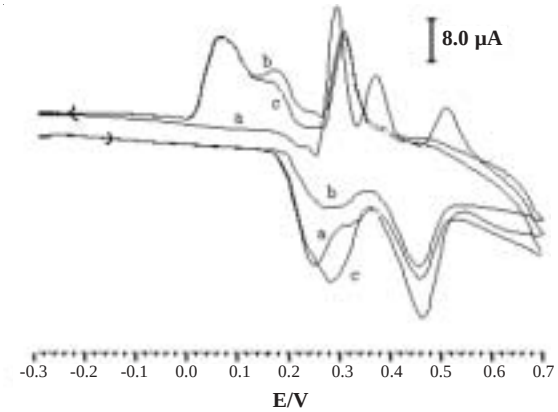

Fig. 4. Cyclic voltammograms of ascorbic acid and dopamine at glassy carbon mercury film electrode (pH 1.81). a. 1×10^{-3} mol L^{-1} ascorbic acid; b. 2×10^{-4} mol L^{-1} dopamine; c. 1×10^{-3} mol L^{-1} dopamine + 2×10^{-4} mol L^{-1} ascorbic acid

nation of dopamine reduction peak was not influenced by ascorbic acid and the peak urgent was more sensitive, the quantification of dopamine were estimated by the work curve of the relationship between dopamine reduction peak current and concentration.

Determination of sample: The mixture of ascorbic acid and dopamine had been prepared with pH 1.81 buffer solution (containing 0.1 g L^{-1} hypoxanthine). With discussing above, the determination of dopamine carried out under the selection conditions. The determination results were shown in Table-1.

TABLE-1
DETERMINATION RESULTS OF DOPAMINE (DA) IN SYNTHETIC SAMPLE

No.	Quantity of ascorbic acid in sample ($\times 10^{-3}$ mol L^{-1})	Quantity of DA in sample ($\times 10^{-4}$ mol L^{-1})	Detect quantity of DA ($\times 10^{-4}$ mol L^{-1})
1	2.00	5.00	5.02
2	2.00	5.00	4.95
3	2.00	5.00	4.98
4	2.00	5.00	4.97
5	2.00	5.00	5.01
Average	2.00	5.00	4.98
Recovery (%)	–	–	99.6
RSD (%)	–	–	0.5

Conclusion

The development of a new method to increase the available potential range of mercury film and an improved technique for determination of dopamine have been described. The results indicated that the hypoxanthine has good inhibition on the stripping peak of Hg at higher potentials and the electrode showed a better stability in the solution. Dopamine concentration could be determined in hypoxanthine system with the GCMFE. The proposed method has wider linear range, low detection limit, good reproducibility and stability. The mechanism of hypoxanthine prevents the stripping of the Hg should be studied further.

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(*Received*: 8 November 2007; *Accepted*: 7 January 2009) AJC-7094