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Study on coordination of selenoamino acids with Ag^+ at silver nitrate-modified carbon paste electrode

Yan Bai [a,*], Yu-dong Wang [a], Wen-jie Zheng [a], Ya-sheng Chen [a,b]

[a] *Chemistry Department of Jinan University, Guangzhou 510632, PR China*
[b] *Science Institute of Zhanjiang Ocean University, Zhanjiang 524088, PR China*

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Abstract

Surface Ag^+ ions forming complexes with the amino (selenoamino) acids compounds have been studied at a silver nitrate-modified carbon paste electrode ($AgNO_3$/CPE). The carboxyl, amidogen and selenium of selenoamino acids could coordinate with Ag^+. The coordinating sites of Ag^+-SeCys and Ag^+-SeMet on electrode surface have been studied in the range of pH value from 1.0 to 12.0. The coordinating sites of Ag^+-SeCys and Ag^+-SeMet are due to the different configuration and electronegative charge of amino acids in different acidity. Increase of the coordination number of adsorbed species increases the average lifetime of these species on the surface, and hence causes that stronger bonded molecules more effectively prevent the depletion of the surface layer from the Ag^+ ions. The voltammetric signals of Ag^+-selenoamino acid and Ag^+-sulfur-containing amino acid are stronger than those of Ag^+-alanine due to the coordinating sites of Ag—S and Ag—Se bonds. Moreover, the adsorption of Ag^+-selenoamino acid on electrode surface relates to different acidity.

Keywords: Selenocystine; Selenomethine; Carboxyl; Amidogen; Selenium

1. Introduction

Selenium (Se) is an essential trace element for living organisms. Selenocystine (SeCys) and selenomethionine (SeMet) are the major selenoamino acids. The coordination between selenoamino acids and metal ions demonstrates the biological behavior and specific chemical derivative transformation of natural process. There are many researches done to demonstrate the coordination between amino and Ag^+. Castro and co-workers indicated that g-aminobutyric acid (GABA) adsorbed on silver colloids and was characterized by the formation of Ag–OCO bonds [1]. Some researches focused on sulfur-containing amino acids. Brolo and co-workers indicated that L-cysteine strongly adsorbed on silver surface and was characterized by the formation of Ag–S and Ag–OCO bonds at alkaline pH [2]. A lot of works showed that sulfur, amino and carboxyl groups could coordinate with silver. Michota and co-workers demonstrated that the $–SCH_2CH_2NH_2$ group was characterized by the formation of Ag–S and Ag–N bonds on silver electrode surface [3,4]. Kudelski and co-workers indicated that the $–SCH_2CH_2COOH$ adsorbed on silver electrode surface and was characterized by the formation of Ag–S and Ag–OCO bonds [5]. In addition, they pointed out that thiols terminal of HS $(CH_2)_2$-X adsorbed very strongly on silver surface, and cysteine layers performed double bonding on the metal surface via the sulfur moiety and the terminal amino or the carboxyl group [6]. The chemical behavior of selenium is similar to that of sulfur. Moreover, there were stripping voltammetric signals of selenoamino acids on silver electrode [7].

Now we focus on the coordinating sites of Ag^+ ions with selenoamino acids adsorbed on the surface of the silver nitrate-modified carbon paste electrode ($AgNO_3$/CPE).

2. Experimental

2.1. Reagents and apparatus

All reagents used were of AR grade unless otherwise mentioned. Amino acid such as SeCys, SeMet, cysteine (Cys), methine (Met) and alanine (Ala) solutions were stored at 4 °C or

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* Corresponding author. Tel.: +86 2085220223.
E-mail addresses: tbaiyan@jnu.edu.cn, baiyemail@tom.com (Y. Bai).

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were prepared freshly. Double distilled water was used throughout the experiment to prepare the solutions. The BAS-100B electrochemical system (BAS Co., USA) was used for the voltammetric determination at 25 ± 1 °C.

2.2. Preparation of silver nitrate-modified carbon paste electrode

Carbon powder mixed with saturated silver nitrate solution with ethanol, the appropriate ratio is about 1 g/2 mL. After the mixture of ethanol volatilized completely, liquid paraffin was filled in by the appropriate ratio of 3 g powder/2 g liquid paraffin. The silver nitrate-modified carbon paste was putted in a PVC pipe electrode, filled 5-mm length each time. Before determination, the silver nitrate-modified carbon paste electrode ($AgNO_3$/CPE) was polished to smooth on filter paper firstly, weighing paper lastly.

2.3. Voltammetric procedure

The working electrode was the $AgNO_3$/CPE. A Pt wire and an Ag/AgCl/KCl (sat.) were the counter and the reference electrode, respectively. All potentials reported are referred to Ag/AgCl/KCl (sat.). The supporting electrolytes were of 0.10 mol/L KNO_3/0.10 mol/L NaAc-Hac (pH 6.40) or 0.10 mol/L phosphate buffer solution. Voltammetric characteristics were studied at the scan rate (ν) 100 mV/s by cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronocoulometry (CC).

3. Results and discussion

3.1. Voltammetric behavior of Ag^+-selenoamino acid

3.1.1. Voltammetric characters in SeCys and SeMet solution

Only residual current at the carbon paste electrode was observed in blank solutions [8] and selenoamino acid solutions. As shown in Fig. 1a, the cathodic peak (curve A) was attributed to the reduction of Ag^+ ions on the surface of $AgNO_3$/CPE in blank solution. The current of cathodic peaks (curves B and C) increased obviously in selenoamino acids solution. The cathodic peak current increased when the concentration of selenoamino acids increased (Fig. 1b). These experimental results indicate that the Ag^+-selenoamino acid was formed on the $AgNO_3$/CPE surface. Immersion of the $AgNO_3$/CPE electrode in the KNO_3 solution caused the depletion of the surface layer of the electrode from the Ag^+ ions. When the $AgNO_3$/CPE electrode was immersed in the solution containing selenoamino acids, the complexes between surface Ag^+ ions and the selenoamino acids were formed. Surface Ag^+ ions forming complexes with the selenoamino acids compounds were significantly slower and were removed from the surface. In other words, immersion into the selenoamino acid solution caused smaller decrease in the amount of Ag^+ ions that were removed from the surface than immersion into the blank solution. Hence, increase of the reduction current was observed. The addition of the selenoamino acids caused the appearance of the cathodic current at more negative potential (Fig. 1b). In reality, the formation of complexes almost always causes change is the reduction potential to the more negative potential region.

3.1.2. Research of adsorption

As shown in Fig. 2, there is the linearity between the cathodic peak currents (I_P) and scan rate (ν), as well as I_P and $\nu^{1/2}$. When $\nu < 150$ mV/s, $I_P = 1.42\nu^{1/2} - 2.92$, $R^2 = 0.996$ (Fig. 2a). When $\nu > 200$ mV/s, $I_P = 0.07\nu + 4.07$, $R^2 = 0.990$ (Fig. 2b). These indicate that when $\nu < 150$ mV/s, the electrode reaction is under diffusion control, when $\nu > 200$ mV/s, the electrode reaction is the adsorbing process, when at the middle rage of the scan rate, diffusion and adsorbing process coexist.

As shown in Fig. 3, adsorption peaks appeared after $AgNO_3$/CPE electrode dipped in SeCys and SeMet solutions for 3 min. The pair of postpeaks, which appeared after the redox peaks, indicated that the reactants are strongly adsorbed. The pair of prepeaks, which appeared before the redox peaks, indicated the products are strongly adsorbed. In SeCys solution (Fig. 3a and c), reactants are strongly adsorbed in acid solution, and products are strongly adsorbed in alkaline solution. In SeMet solution (Fig. 3b and d), products are strongly adsorbed in acid solution, and reactants are strongly adsorbed in alkaline solution.

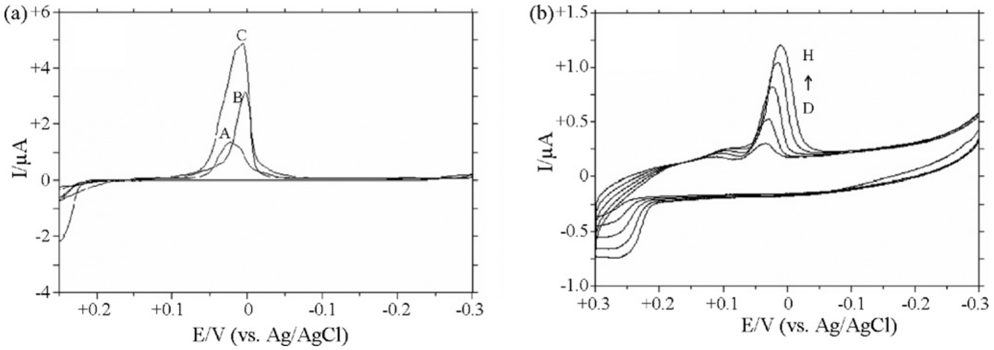

Fig. 1. Cyclic voltammograms on $AgNO_3$/CPE electrode. (a) Curve A: 0.10 mol/L KNO_3/0.10 mol/L HAc-NaAc (pH 6.40). Curve B: 1.0×10^{-4} mol/L SeMet with blank solution. Curve C: 1.0×10^{-4} mol/L SeCys with blank solution. (b) Curve D–H: concentration of SeCys is 2.0×10^{-5}, 3.0×10^{-5}, 4.0×10^{-5}, 5.0×10^{-5} and 6.0×10^{-5} mol/L, respectively. The voltammetric behavior in SeMet solution was similar.