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Resolution of dopamine and ascorbic acid using nickel(II) complex polymer-modified electrodes

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Abstract

A glassy carbon (GC) electrode was modified with electropolymerized macrocyclic Ni(II) complex, at which dopamine (DA) and ascorbic acid (AA) were clearly resolved below pH 6.0 by cyclic voltammetry. Their charge transfer reaction was examined to elucidate their resolution and the oxidation reaction. DA had two charge transfer reactions below pH 6.0, allowing resolution of DA and AA. DA increased the peak separation between DA and AA, and the GC surface exposed to DA was involved in the DA oxidation that occurred at the Ni(II) complex-modified electrode. DA was determined selectively using the Ni(II) complex-modified electrode and the selective DA accumulation improved the DA response. The linear range was 0.5–50 μM ($R = 0.9989$) and the limit of detection (S/N = 3) was 0.15 μM. A Ni(II) complex-modified electrode can be used for selective DA detection in an acidic sample, such as urinary DA.

Keywords: Ni(II) complex; Resolution; Dopamine; Electron transfer; Accumulation

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1. Introduction

Dopamine (DA) is a catecholamine neurotransmitter. Abnormal DA concentrations can result from the loss of dopaminergic neurons in the brain and can precipitate neurodegenerative disorders, such as Parkinson's disease [1]. L-DOPA, the metabolic precursor of DA, is used to treat Parkinson's disease and is converted into DA in the brain. The levels of L-DOPA and catecholamine metabolites are monitored in urine samples in Parkinson patients, such as urinary DA. DA is readily oxidized chemically and electrochemically; and this property has been used to grow nanoparticles [2]. Oxidized DA species can polymerize into granules or films according to the oxidation method. DA polymer granules have been used as a model compound for neuromelanin, which is synthesized in the DA neurons of the human brain [3–5]. The DA polymer film formed on an electrode surface has been used in selective DA determination [6].

In biological samples, DA often occurs with ascorbic acid (AA) in relatively high concentrations. AA is oxidized at similar potentials to DA at conventional electrodes and has much larger signals in the brain than DA [7]. Consequently, the AA peak can overlap that of DA. To improve DA selectivity, electrochemical resolution of DA and AA has been achieved by modifying conventional electrodes with positively or negatively charged materials, and DA and AA are usually resolved at a pH of 7.4. Not only does this pH correspond to the physiological value but also DA is oppositely charged to AA at this pH. At a pH of 7.4, DA ($\mathrm{p}K_a = 8.75$) is cationic and AA ($\mathrm{p}K_a = 4.17$) exists as the anionic ascorbate species. Their opposing charges are used for a charge effect between the charged electrodes and DA and AA.

A charge can be introduced to electrode surfaces using electropolymerization [8–13], drop-coating [14–16],

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self-assembly [17,18], and pasting [19] techniques. With electropolymerization, the charged polymer-modified electrodes enable simultaneous detection of DA and AA. The electropolymerization process involves either a potential-cycling or controlled-potential method, which produces highly modified electrode surfaces with charged polymers. Using this technique, the potential can be cycled more than 10 times [8,9,11,13] or applied for 60 min [10]. DA and AA are oxidized mostly on these highly modified electrode surfaces, via interactions with the charged polymer. If DA and AA were resolved at an electrode modified using a few potential cycles or a potential applied for a relatively short period, other factors, including the interaction with the bare electrode surface, might be involved in their resolution.

In this study, an asymmetrical macrocyclic nickel(II) complex, 2,4,9,11-tetramethyl-1,5,8,12-(benzo)tetraaza-cyclotetradecinatonickel(II), was used to modify a glassy carbon (GC) electrode. The Ni(II) complex (NC) readily forms a stable polymer film on a GC surface through electrochemical oxidation using potential-cycling and controlled-potential methods [20–22]. An NC-modified electrode has an electrocatalytic effect on the oxidation of AA and DA [20,22,23], although further modification is needed to increase the DA selectivity over that of AA at neutral pH. Further modification using a negatively charged material enhances the DA selectivity and decreases the DA sensitivity [23,24]. For the Ni(II) complex used here, a single modification was more desirable in terms of both sensitivity and selectivity. However, when the solution pH was decreased to below 6.0, DA and AA were clearly resolved by cyclic voltammetry (CV). The NC-modified electrode was prepared by electropolymerization by cycling the potential once. The electrochemical resolution of DA and AA does not seem to be caused by a simple charge effect. This study examined how DA and AA are resolved at a pH below 6.0 at an NC-modified electrode and what reactions occur. The oxidation potential and current of DA and AA were compared with the pH and NC polymer modification of the electrode, and the oxidation mechanisms are discussed. The NC-modified electrode was also used to determine DA selectively using differential pulse voltammetry. The NC-modified electrode surface was analyzed using atomic force microscopy (AFM).

2. Experimental

2.1. Reagents and solutions

An asymmetric, macrocyclic Ni(II) complex, 2,4,9,11-tetramethyl-1,5,8,12-(benzo)tetraaza-cyclotetradecinatonickel(II), was synthesized, as described elsewhere [20]. Briefly, 1,2-phenylenediamine and ethylenediamine were added to a mixture of 2,4-pentanedione and nickel(II) acetate tetrahydrate in methanol and this mixture was refluxed and recrystallized. Tetraethylammonium perchlorate (TEAP) was prepared and recrystallized; acetonitrile was purified by distillation and stored in a desiccator until use. The Ni(II) complex was dissolved in acetonitrile to a concentration of 0.50 mM.

Dopamine and ascorbic acid were used as received from Sigma (St. Louis, MO, USA). The other reagents were of guaranteed analytical grade and were used without further purification. Solutions were prepared in a 0.1 M phosphate buffer before use. The pH was adjusted using NaH_2PO_4 and Na_2HPO_4, which were purchased from Merck (Darmstadt, Germany). All aqueous solutions were prepared with deionized water using a Milli-Q water system (Millipore, Bedford, MA, USA).

2.2. Electrochemical measurements

A three-electrode system was used in all the electrochemical measurements, as well as in the NC modification procedure. The working electrodes were GC and NC-modified electrodes and the reference electrodes were $Ag|Ag^+$ (0.01 M $AgNO_3$ in acetonitrile) and a saturated calomel electrode (SCE). Pt wire was used as an auxiliary electrode. Electrochemical measurements were carried out in a 0.1 M phosphate buffer (pH 7.4) at 35 °C, using a BAS 100 W electrochemical analyzer (Bioanalytical Systems, USA). All solutions were deaerated with purified nitrogen before measuring. The accumulation effect was examined using fresh DA and AA solutions for each preconcentration time. Differential pulse voltammograms of DA were obtained after preconcentrating for 90 s without applying a potential. After the measurements, the NC-modified electrodes were stored in air.

Amperometry was used to examine the stability of the NC-modified GC electrodes using a thin-layer flow cell (BAS). The flow cell consisted of dual GC working, Ag|AgCl (3 M NaCl) reference, and stainless steel auxiliary electrodes. The current was measured at +0.80 V; the NC-modified electrode showed the best DA response in the hydrodynamic voltammogram at this potential.

2.3. NC polymer-modified electrodes

A GC surface (0.07 cm^2) was polished with aqueous slurries of 1.0-, 0.3-, and 0.05-μm alumina and cleaned by repeated flushing with water. The polished surface was sonicated in acetonitrile for 2 min and rinsed in acetonitrile. The polished GC electrode was dipped in a 0.50 mM NC solution containing 50 mM TEAP in acetonitrile as a supporting electrolyte under a nitrogen atmosphere. The potential was cycled once between −2.0 and +1.8 V vs. $Ag|Ag^+$ (0.01 M $AgNO_3$ in acetonitrile) at 25 °C and a scan rate of 0.2 V s^{-1}. After cycling the potential, the GC electrode modified with NC polymer was removed and dried at room temperature. The NC-modified GC electrode was washed with acetonitrile and water before use. An NC-modified electrode used for amperometry with flow injection was prepared in a similar way, except that the NC