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Simultaneous voltammetric detection of dopamine and ascorbic acid using didodecyldimethylammonium bromide (DDAB) film-modified electrodes

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Abstract

A voltammetric method using a surfactant didodecyldimethylammonium bromide (DDAB) film-modified electrode was developed for simultaneous measurement of various combinations of neurotransmitters and ascorbic acid. The DDAB-modified film has the positive charge and neurotransmitters (dopamine, norepinephrine, and epinephrine) existed as the positively-charged species in the neutral solution whereas AA (ascorbic acid) as a negatively-charged one. Both the cyclic voltammetry (CV) and square-wave voltammetry were used for the measurement of neurotransmitters by means of the DDAB/GC-modified electrode in phosphate buffer solution of pH 6.5. Well-separated voltammetric peaks were observed for dopamine and ascorbic acid at the DDAB/GC-modified electrodes. The oxidation potential of ascorbic acid was shifted to a more positive potential due to a positive electro-catalytic activity of the DDAB/GC-modified electrode while neurotransmitters such as dopamine or norepinephrine or epinephrine were oxidized at a more positive potential due to electrostatic repulsion. The rotating ring disk electrode (RRDE) method was applied to study the redox reaction mechanism of dopamine and ascorbic acid. The DDAB/GC electrode resolved the voltammetric signals of the above analytes successfully.

Keywords: DDAB; Film-modified Electrodes; Dopamine; Ascorbic acid; Electrocatalysis

1. Introduction

Dopamine, epinephrine, and norepinephrine are very important catecholamine neurotransmitters in the mammalian central nervous system, and are often monitored electrochemically in vivo with microfiber electrodes. The oxidation of these compounds is interesting as this process occurs in the human body. Catecholamine drugs are also used to treat hypertension, bronchial asthma, organic heart disease, and used in cardiac surgery and myocardial infarction [1,2].

Surfactants are molecules with non-polar regions and charged or polar head groups. These amphiphilic molecules adsorb strongly at solid/solution interfaces such as electrodes. The film structure was suggested to be a multiple of bilayer molecules composed of DDAB, with sandwiched in between [3,4]. DDAB-modified electrodes form a bilayered film or multi-bilayer films. Dopamine and ascorbic acid can physically diffuse through the DDAB films. The DDAB film forms on and modifies the solid electrode surface.

The development of voltammetric sensors for the detection of neurotransmitters in the extra cellular fluid of the central nervous system has received much attention in the past few decades [5–7]. The electrochemical methods have more advantages over the other because of the advantage of the electrode in sensing the neurotransmitters in living organisms [8]. Electrochemical analysis on the unmodified electrodes, for example glassy carbon has limitations because of the overlapping of oxidation potentials of ascorbic acid

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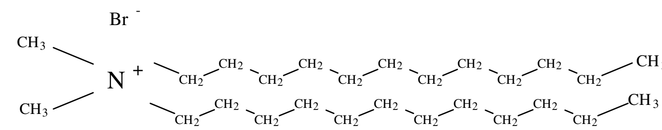
and dopamine and hence often suffers from a pronounced fouling effect that results in rather a poor selectivity and reproducibility [9,10]. Taking the advantage of the opposite micellar effect of dopamine and ascorbic acid, these two bioactive compounds could be simultaneously determined in the ionic micelles, the CTAB or SDS [11]. Modified electrodes from the electrodes surface that could be used for simultaneous determination of dopamine and ascorbic acid have been performed, e.g., 2,4,6-triphenylpyrilium ions encapsulated in to zeolite Y [12,13], carbon-polyvinylchloride composite electrode [14], poly(2-picolinic acid)-modified glassy carbon electrode [15], polymerized luminal film-modified electrodes [16], polymerized film of *N,N*-dimethyl aniline [17] for the sensitive and selective determinations of dopamine and ascorbic acid. Recently, boron doped diamond electrode modified with polymerized film of *N,N*-dimethyl aniline was used for selective determination of dopamine and dopa in the presence of ascorbic acid [18]. The 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane and modified glassy carbon electrode and 4′-mercapto-*N*-phenyl(quinine diimine) self assembled active layer on gold electrode were used for the selective determination of ascorbic acid and dopamine [19,20]. Multilayer films of shortened multi-walled carbon nanotubes (MWNTs) are homogeneously and stably assembled on glassy carbon (GC) electrodes using layer-by-layer (LBL) method based on electrostatic interaction of positively-charged poly(diallyldimethylammonium chloride) (PDDA) and negatively-charged shortened MWNTs [21].

In this paper, we report about the use of the DDAB/GC-modified electrodes for effective separation of ascorbic acid and catecholamine neurotransmitters (dopamine, epinephrine, and norepinephrine) in aqueous solution.

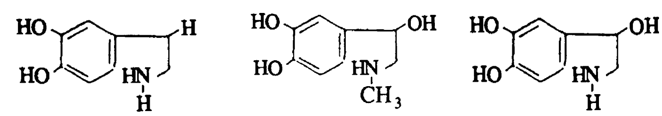
Recently, efforts have been taken for simultaneous determination of ascorbic acid and dopamine [11–21]. The advantages of our modified electrode are high peak potential separation between oxidation peaks of ascorbic acid and dopamine (300 mV) and ease of preparation of film compared to reported systems.

Table 1 shows that comparison of ΔE_{pa} of dopamine and ascorbic acid with earlier report.

The cyclic voltammetry and square-wave voltammetry techniques were used to study the catalytic properties of dopamine (or epinephrine, and norepinephrine) and ascorbic acid. The mechanism of the negative and positive electrocatalysis of dopamine and ascorbic acid were studied through a rotating ring disk electrode coated with the DDAB-modified film.



Didodecyldimethylammonium bromide (DDAB)



dopamine norepinephrine epinephrine

2. Experimental

The electrochemistry was performed using a West Lafayette Model CV-50W bioanalytical system and a CH Instruments CHI-400 potentiostat. The cyclic voltammetry was conducted using a three-electrode cell, and a BAS glassy carbon electrode as the working electrode. The glassy carbon electrode was polished using 0.05 μm alumina on Buehler felt pads and ultrasonicated for 1 min. The auxiliary compartment which contained a platinum wire was separated by a medium-sized glass frit. All the cell potentials were measured with respect to an Ag/AgCl [KCl (saturated solution)] reference electrode or an Hg/Hg_2Cl_2/KCl (saturated solution) reference electrode. UV–Vis absorption spectra were measured by a Hitachi (Japan) Model U-3300 spectrophotometer.

The rotating ring disk electrode (RRDE) experiments were performed by a Pine Instrument Co electrode in conjunction with a CH Instruments CHI-750 potentiostat connected to a Model AFMSRX analytical rotator. The rotating ring disk electrode was consisted of a glassy carbon disk electrode and a glassy carbon (or platinum) ring electrode.

All the chemicals used were of analytical grade. The aqueous solutions were prepared through double-distilled deionized water and deoxygenated by purging with nitrogen gas prior to the start of each experiment.

Table 1
Comparison of ΔE_{pa} between dopamine and ascorbic acid on different modified electrodes with didodecyldimethylammonium bromide (DDAB) film-modified electrode

S. No.	Name of the modified electrode	ΔE_p (V)
1	2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane immobilized glassy carbon	0.2
2	4′-Mercapto-*N*-phenylquinone diimine (MNPD) immobilized Au	0.250
3	Poly(*N,N*-dimethylaniline) (DMA) modified boron-doped diamond	0.2
4	Layer-by-layer assembled carbon nanotubes modified electrode	0.15
5	Gold nanoparticles immobilized on an amine terminated SAM modified electrode	0.165
6	Unmodified exfoliated graphite electrode	0.244
7	Didodecyldimethylammonium bromide (DDAB) film-modified electrodes	0.3