



# Theoretical and cyclic voltammetric studies on electrocatalysis of benzethonium chloride at carbon paste electrode for detection of dopamine in presence of ascorbic acid

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## ABSTRACT

In the past decade, many surfactants have been used to modify carbon electrode to sense dopamine (DA). Even though plenty of works are already available on this strategy, still analyzing DA and ascorbic acid (AA) by surfactant modification is exciting and unfortunately, molecular level understanding of these types of electrode is still missing. Here, we have used benzethonium chloride modified carbon paste electrode (BzTCMCPE) to sense DA and AA at physiological conditions (pH7.4) and BzTCMCPE showed high electrocatalytic activity towards the redox activity of DA and AA (BzTCMCPE successfully resolved the anodic peaks of DA and AA). Quantum chemical modeling is helpful to know about the arrangement (adsorption) of benzethonium chloride on the electrode surface. The electrochemical behavior of the BzTCMCPE was explained using frontier molecular orbitals (FMO) and analytical Fukui functions.

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## 1. Introduction

Dihydroxyphenylethylamine also commonly known as Dopamine (DA), released by neurons in a number of regions of the mammalian brain and is thought to be important in the expression of a wide variety of behaviors [1–4]. DA imbalance in the brain is linked to Parkinson's disease, psychiatric disorders such as schizophrenia and attention deficit hyperactivity disorders (ADHD) [5]. Therefore, it is essential to develop simple and rapid methods for the determination of DA [6]. DA in mammalian brain cells exists with ascorbic acid (AA). AA is a water-soluble vitamin, which can be easily oxidizable to L-dehydroascorbic acid [7]. Oxidation of AA is close to DA and their oxidation potentials are overlapped with each other at bare carbon paste electrodes (BCPE). Therefore electrochemical determination of DA in the presence of AA is not possible at BCPE. This problem can be rectified by modifying BCPE surface. The performance of BCPE based electrochemical sensors is strongly dependent

on the surface structure of the electrode. To obtain desired properties like selectivity, considerable efforts had been done to modify BCPE surfaces by surfactants [8,9], nano particles [10–12], carbon nanotubes [13], dyes [14] and amino acids [15]. Especially, the surfactants at the electrode interface can significantly alters the redox potential, diffusion coefficients, charge transfer coefficients of the electrode processes [16–18].

Surfactants are linear molecules with a hydrophilic (attracted to water) head and a hydrophobic (repelled by water) domains [19]. The amphiphilic structure of surfactant molecules makes them adsorb on the electrode interfaces. Surfactant molecules make a layer formation on the surface of electrode [17,20]. Cationic surfactants give positive charge and anionic surfactants give a negative charge on the electrode surface. The formed monolayer affects the charge transfer rates and the oxidation potential in electrochemical measurements [21]. In the past two decades a number of articles had been reported to utilize surfactant as the electrode modifier [19,22–26]. Surfactants like TX-100 [27], CTAB [28], and SDS [29] were commonly used for modification of electrodes. Unfortunately, there are no much reports to utilize benzethonium chloride (BzTC) as the modifier for determination of DA in the presence of AA. BzTC

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is a water-soluble cationic surfactant well known for its antiseptic and anti-infective properties. BzTC is also used in detergents, deodorants, astringents, topical antiseptics, cold sterilization techniques and the food industry as a hard surface disinfectant. The Salazar research group has been utilized BzTC for electrochemical applications [30,31]. Salazar et al. [31] had developed the modified carbon electrodes with BzTC for chlorine sensing applications. Salazar et al. [30] also modified screen printed carbon electrodes by BzTC for  $\text{H}_2\text{O}_2$  sensing applications.

From the past two decades, density functional theory based quantum chemical calculations have been used to solve electrochemical problems. In particular, quantum chemical calculations have been successfully used to understand electron transfer reactions [32], corrosion mechanisms [33], material surface properties [34] and to know the arrangements of analytes at the electrode surface [35]. Quantum chemistry is also helpful to understand electrodes at the molecular level. Molecular level knowledge of electrode interface can be helpful to improve electrode performance like selectivity. Unfortunately, there are only a few reports have been done to understand carbon paste electrode surface in molecular level [35]. In the current work, we report the fabrication of BzTC modified carbon paste electrode (BzTCMCPE) to sense DA in the presence of AA. Sensitivity and selectivity (resolved the overlapped voltammetric responses of DA and AA into two well-defined voltammetric peaks) of the BCPE have been improved after the modification from BzTC.

## 2. Experimentation

### 2.1. Reagents and chemicals

BzTC was purchased from Sigma Aldrich (TM), graphite powder, DA, AA, potassium chloride, perchloric acid were obtained from Himedia, sodium dihydrogen phosphate and disodium hydrogen phosphate were used for the preparation of 0.1 M phosphate buffer solution (PBS) solution. All chemicals and reagents were prepared with distilled water. pH of the solution was monitored by a digital pH meter fabricated by Systronics.

### 2.2. Instrumentation

Cyclic voltammograms were collected using a model CHI-660 C (CH-Instruments, Inc.). All the experiments were carried out in a conventional three electrochemical cell. The electrode system contains a platinum wire as a counter electrode and saturated calomel (SCE) as a reference electrode. The working electrode was BCPE. All the experiments were carried out at room temperature ( $25 \pm 2^\circ\text{C}$ ). The baseline of CV was subtracted, by taking tangents to the  $i$ - $E$  curves far from the current response of the redox couple. For redox reactions baseline of anodic and cathodic peak currents were subtracted separately.

### 2.3. Preparation of BCPE

To prepare a bare carbon paste electrode 70% of graphite powder (particle size of 50 mm and density is 20 mg/100 mL) was mixed with 30% silicone oil in a mortar by hand mixing till the homogeneous paste was achieved. The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothened on a weighing paper until the surface becomes uniform [15,36–39]. The modified carbon paste electrodes were prepared by immobilizing the surfactant on the BCPE surface.

### 2.4. Computational methods and model

Atomic coordinates of all models were constructed using MOLDEN [40] software. Full geometry optimization of the models was carried out using density functional theory (DFT) level of theories

in the deMon2k [41] software with VWN [42] and PBE [43,44] and correlation functions and DZVP [45] and TZVP [45] basis sets. Since energies are more reliable at PBE correlation functional with TZVP basis set [46], we have compared VWN/DZVP energies with PBE/TZVP. CVs are plotted using GNUPLLOT. Reactive orbital space (ROS) of frontier molecular orbitals (FMO) [highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)] and analytical Fukui functions were graphically plotted using Sinapsis [47] software.

## 3. Results and discussion

### 3.1. Electrocatalytic oxidation of DA and AA at BzTCMCPE

#### 3.1.1. Electrochemical studies of DA at BzTCMCPE

Fig. 1 represents a CV of  $10 \mu\text{M}$  DA (0.1 V/s) in PBS at BCPE (purple line with dots) and BzTCMCPE (green line). DA exhibits a weak electrochemical responses at the BCPE in the given potential range with anodic peak potential 0.200 V and cathodic peak potential 0.090 V. However, at the BzTCMCPE oxidation potential of DA was negatively shifted (0.200 V to 0.170 V) and reduction potential was positively shifted (0.090 V to 0.0132 V). Thus, BzTCMCPE is a better electrochemical sensor when compared to BCPE. At the BzTCMCPE background capacitance currents are high; which is due to increased electrolyte transport and decreased surface tension at the electrode interface [48]. Background capacitance current subtracted CV is shown as inset figure in Fig. 1.

#### 3.1.2. Electrochemical studies of AA at BzTCMCPE

Fig. 2 represents a CV of BCPE (purple line with dots) and BzTCMCPE (green line) of 1 mM AA in the 0.1 M PBS at the scan rate of 0.1 V/s. Background current subtracted CV of 1 mM AA at BzTCMCPE is shown in the inset figure in Fig. 2. At the BCPE, oxidation peak of AA occurs at 0.265 V with a broad voltammetric peak. However, BzTCMCPE showed sharp oxidation potential at  $-0.037$  V. The sharpness of the peak in conjunction with the huge negative shift in the oxidation potential of AA clearly tells that BzTCMCPE is good for the detection of AA. The large negative shift in the oxidation potential of AA determines the simultaneous detection of AA in presence of the DA. However, understanding of underlying molecular process is missing.

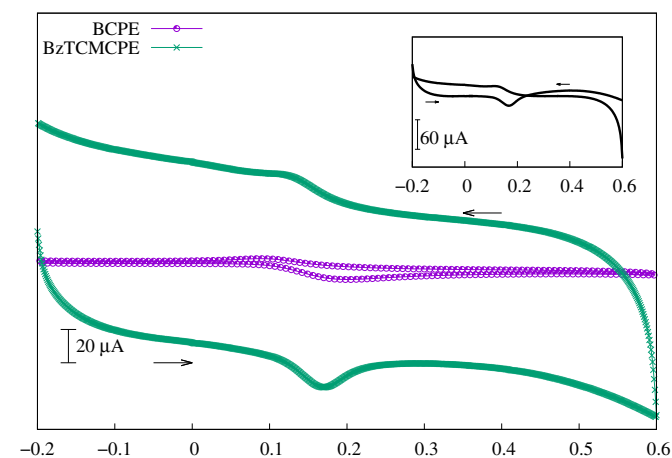


Fig. 1. CV of  $10 \mu\text{M}$  DA at BCPE and BzTCMCPE at 0.1V in PBS (pH7.4). Inset is background capacitance current subtracted CV of  $10 \mu\text{M}$  DA at BzTCMCPE. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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