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Electrochemical Response of Dopamine at Phthalic acid and Triton X-100 Modified Carbon Paste Electrode: A cyclic voltammetry study

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The influence of Phthalic acid and TritonX-100 (TX-100) modified carbon paste electrode (MCPE) on the electrochemical behavior of dopamine was investigated. The electrochemical response of dopamine confirming from the remarkable oxidation and reduction peak current enhancement. The electrode process of dopamine was examined and then all the experimental parameters which affect the electrochemical response of dopamine, such as pH, scan rate, concentration and the immobilization of surfactant were studied. Finally a sensitive and simple voltammetric method was developed for the determination of dopamine.

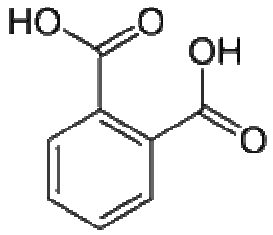
Keywords: Phthalic acid, Dopamine, TX-100, Cyclic voltammetry, Carbon Paste Electrode

1. INTRODUCTION

Phthalic acid (benzene-1, 2-dicarboxylic acid) is an aromatic dicarboxylic acid, (scheme.1) with formula $C_6H_4(COOH)_2$. It is an isomer of isophthalic acid and terephthalic acid. Phthalic acid was obtained by French chemist Auguste Laurent in 1836 by oxidizing naphthalene tetrachloride and the resulting substance to be a naphthalene derivative, he named it naphthalenic acid.

Dopamine is a neurotransmitter associated with proper functioning of several organs such as the heart, brain, and suprarenal glands. The determination of dopamine is a subject of great significance for investigating its physiological functions and diagnosing nervous diseases resulting from dopamine abnormal metabolism, such as epilepsy, Parkinsonism and senile dementia [1]. The fact that dopamine and other catecholamines are easily oxidizable compounds makes their detection

possible by electrochemical methods based on anodic oxidation [2]. Dopamine has been determined using various electrochemical methods [3-5].



Scheme 1. Structure of phthalic acid

One of the most common routes is to use the modified carbon paste electrode which has the ability to eliminate the interfering substances from DA determination. The study of electrochemical determination of DA with different modified electrode for sensitive and selective. The modification can be done by adding different types of modifiers [6-11]. One of the modifiers chosen for the determination of electrochemical response of DA is phthalic acid and it was immobilized with TX-100 surfactant. Surfactant is a linear molecule with a hydrophilic (attracted to water) head and a hydrophobic (repelled by water) end. Due to its unique molecular structure, surfactant has been extensively used in the fields of electrochemistry [12,13] and electroanalytical chemistry [14,15] for various purposes. Surfactants, containing hydrophobic and hydrophilic groups, can change the properties of the electrode /solution interface and subsequently influence the electrochemical processes of other substances. Adsorption of surfactant aggregates on the electron transfer, gently enhance the peak current, change the redox potential or charge transfer coefficients or diffusion coefficients, as well as alter the stability of electrogenerated intermediates or electrochemical products.

The aim of the work is to establish a simple and sensitive electrochemical method for the determination of dopamine in the presence of phthalic acid and TX-100 surfactant the oxidation peak current of dopamine remarkably increases at the CPE suggesting significant improvement of determining sensitivity. Related works have been done by our research group [16-22].

The newly proposed work some obvious advantages including high sensitivity, extreme simplicity, rapid response and low cost.

2. EXPERIMENTAL PART

2.1. Reagents and chemicals

Phthalic acid was received from G.S. chemicals, India, Bombay, 10^{-5}M TX-100, Potassium ferricyanide was prepared in double distilled water, and 25mM dopamine stock solution was prepared

in 0.1 M perchloric acid. All other chemicals were of analytical grade quality and were used without further purification.

2.2. Apparatus and procedure

Cyclic voltammetry (CV) was performed in a model EA-201 Electroanalyser (EA-201 Chemilink system). All experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0mm in diameter) a platinum wire as counter electrode and saturated calomel as reference electrode.

2.3. Preparation of carbon paste electrode

The carbon paste electrode was prepared as fallows 70% graphite powder and 30% silicone oil were mixed by hand to produce a homogeneous carbon paste .The paste was then packed into the cavity of a homemade carbon paste electrode and smoothed on a weighing paper. Similarly the modified carbon paste electrode was prepared by grinding different concentration of phthalic acid along with graphite powder.

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of $K_3Fe(CN_6)$ at a modified phthalic acid carbon paste electrode

Fig .1 shows the electrochemical response of Bare Carbon Paste Electrode (BCPE) and Phthalic acid Modified Carbon Paste Electrode in the presence of 1mM potassium ferricyanide in 1M KCl solution. The dashed line shows the electrochemical response of BCPE having the cathodic peak current (Ipc) 17μA and anodic peak current (Ipa) –21.3μA. The electrochemical cathodic peak potential (Epc) 187mV and anodic peak potential (Epa) 260mV. After modification with 5mg Phthalic acid MCPE shows in solid line the current enhancement of both electrochemical anodic peak current (Ipa) –27.6μA and cathodic peak current (Ipc) 25.3μA The anodic peak potential is 265mV and cathodic peak potential is 192mV.

3.2. Electrochemical response of dopamine at phthalic acid modified carbon paste electrode

Dopamine being as easily oxidizable catecholamine. Fig.2 shows quasireversible voltammogram in 0.2M phosphate buffer solution at pH 7 at 100 mV/s scan rate for BCPE (solid line). At BCPE the E_{Pa} was found to be 186mV and E_{pc} 74mV (vs. SCE). The ΔE_p 112mV and the I_{pa}/I_{pc} was 2.96. The formal peak potential (E^0) was obtained as 130mV. However at Phthalic acid MCPE, a pair of redox peak is obtained with strong increase in both anodic cathodic peak current. The anodic peak potential at 188mV and cathodic peak potential (E_{pc}) at 112mV. The separation of redox potential

peaks (ΔE_p) was found to be 76 mV and the ratio of peak current (I_{pa}/I_{pc}) was 1.90 and E^0 was 150mV. So the voltammogram obtained for phthalic acid MCPE shows good electrocatalytic properties at CPE.

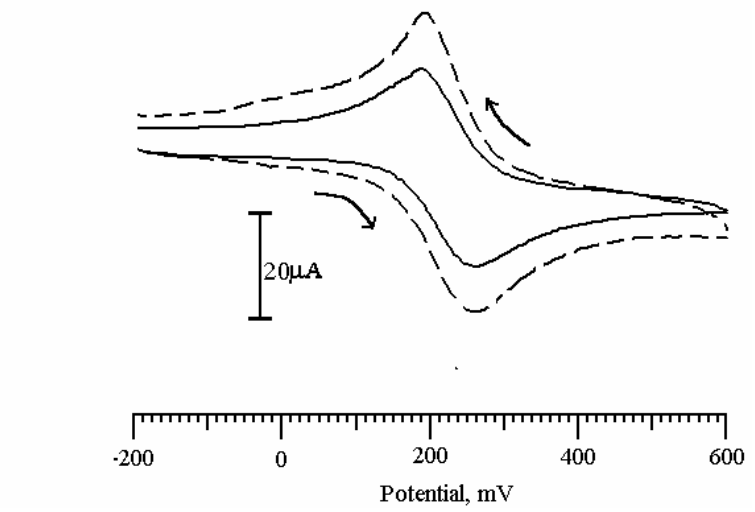


Figure 1. Electrochemical response of $K_3Fe(CN_6)$ at Phthalic acid modified carbon paste electrode and bare carbon paste electrode.

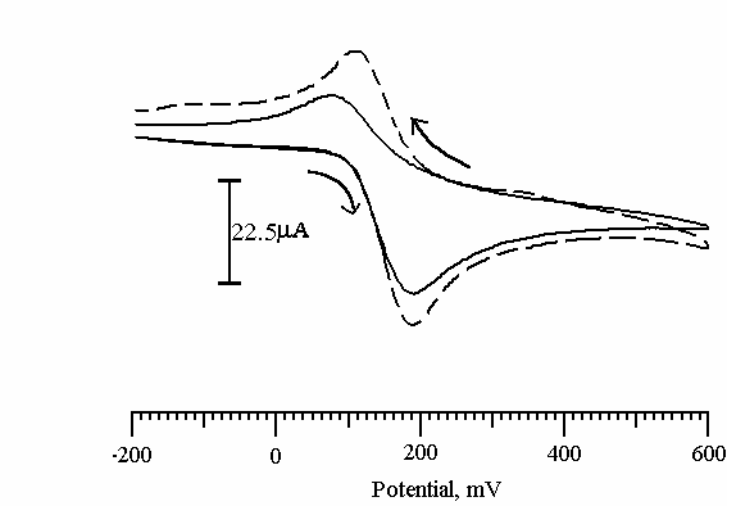


Figure 2. Cyclic voltammogram of $1X10^{-3}$ M DA in 0.2 M phosphate buffer solution of pH 7.0 at bare CPE (solid line) and Phthalic acid MCPE (dashed line).

3.3. Effect of scan rate

Fig.3a.shows the effect of varying the potential scan rate of dopamine was studied. The cyclic voltammograms were recorded in 0.2M phosphate buffer of pH 7.0 as a supporting electrolyte. The

peak current increased linearly with square root of the scan rate over the range 100 to 500 mVs^{-1} with a correlation coefficient of 0.97695(fig.3b). The overall electrode process is diffusion- controlled

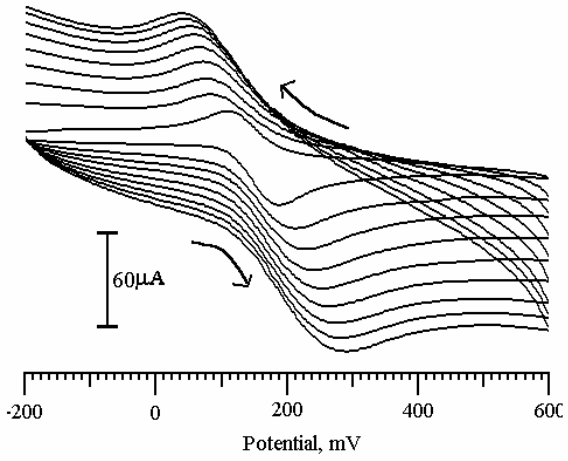


Figure 3a. Variation of scan rate for DA at Phthalic acid MCPE ($100mVs^{-1}$ to $500mVs^{-1}$).

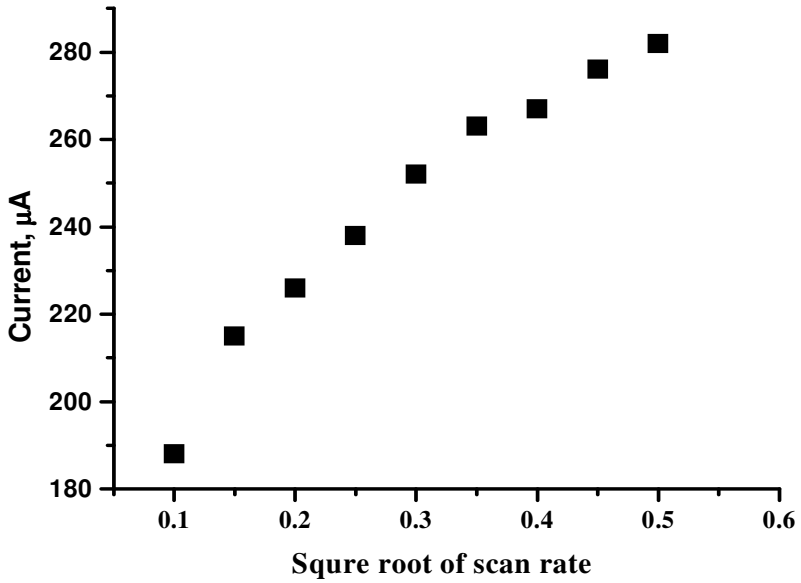


Figure 3b. Graph of current vs. square root of scan rate.

3.4. Effect of dopamine concentration

The concentration of dopamine was increased from 1 mM to 3.5 mM in phosphate buffer as a supporting electrolyte at a sweep rate of 100 mVs^{-1}. The cathodic peak current increases linearly with

the concentration of dopamine and hence obeys Randles-Sevic equation, which implies that the process is diffusion controlled (Fig. 4a and 4b.).

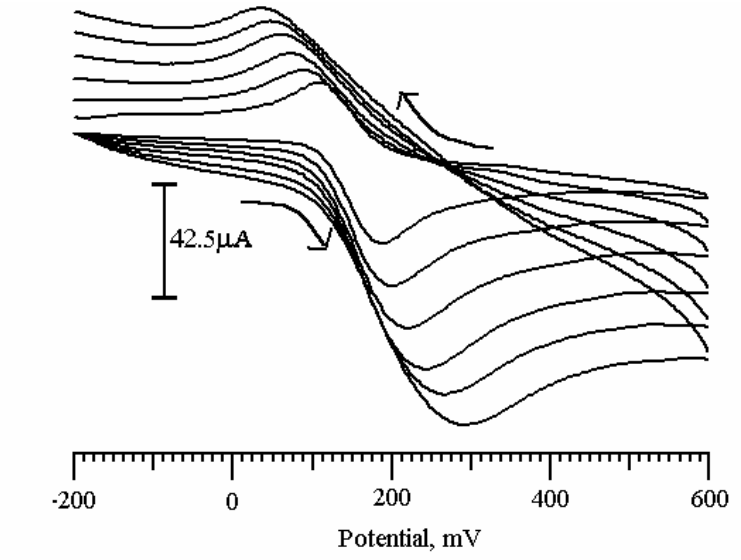


Figure 4a. Cyclic voltammogram of DA at different concentration ($0.1X10^{-3}$ M, $1.5X10^{-3}$ M, $2X10^{-3}$ M, $2.5X10^{-3}$ M, $3\ X10^{-3}$ M, $3.5X10^{-3}$ M,).

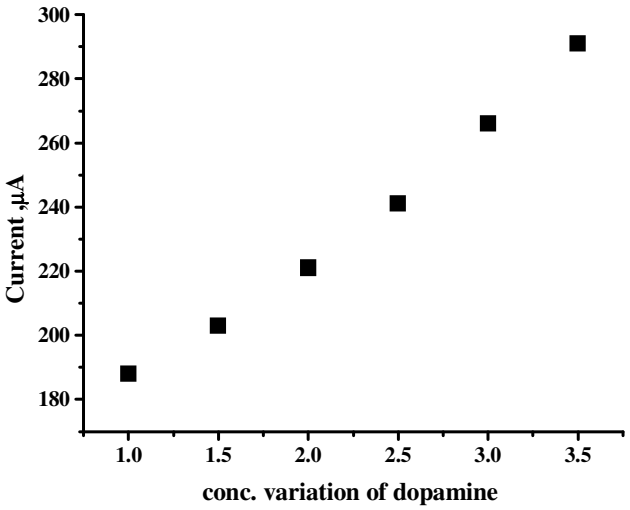


Figure 4b. Graph of current vs. concentration of DA.

3.5. Effect of surfactant

The electrochemical response of dopamine at carbon paste electrode was shown in Fig.5a owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram

of dopamine in the absence of TX-100 Phthalic acid MCPE is low current signal. The TX-100 surfactant showed great influence on cyclic voltammogram of DA in Phthalic acid MCPE. In Fig. 5a the solid line shows cyclic voltammogram of BCPE, dotted line is Phthalic acid MCPE and dashed line is TX-100 and Phthalic acid MCPE (40uL) showed the electrochemical response of dopamine at TX-100 immobilized Phthalic acid MCPE.

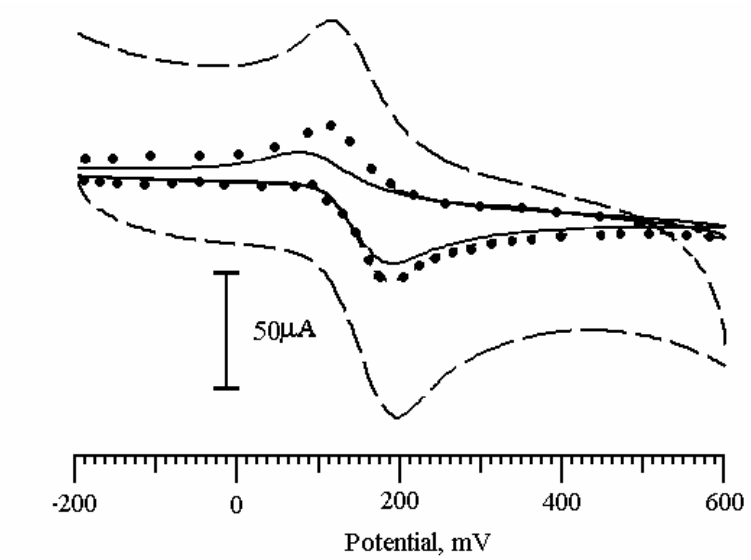


Figure 5a. Cyclic voltammogram of DA for BCPE (solid line) Phthalic acid MCPE(dotted line) and40µL TX-100dashed line

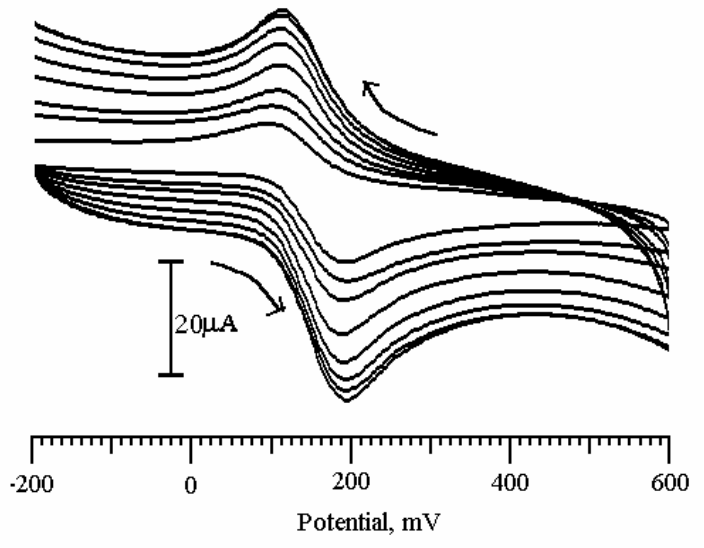


Figure 5b. Cyclic voltammogram of TX-100 different concentration (5uL-40uL)

3.6. The influence of concentration of TX-100 surfactant on voltammetric response for dopamine on Phthalic acid MCPE

To study the effect of addition of surfactants the experiments were carried out using non-ionic surfactant TX-100 . Initially, cyclic voltammogram were recorded for Phthalic acid MCPE a solution containing dopamine (2mM) in Phosphate buffer solution at pH 7 .Keeping the concentration of Dopamine constant, the concentration of the surfactant was increased from 5µM to 40µM by immobilization method. Fig.5b shows the effect of surfactant concentration by immobilized method both the i_{pa} and i_{pc} increases rapidly with the increases of surfactant concentration. As mentioned above TX-100, might form a monolayer in this concentration range and hence increase in the signals.

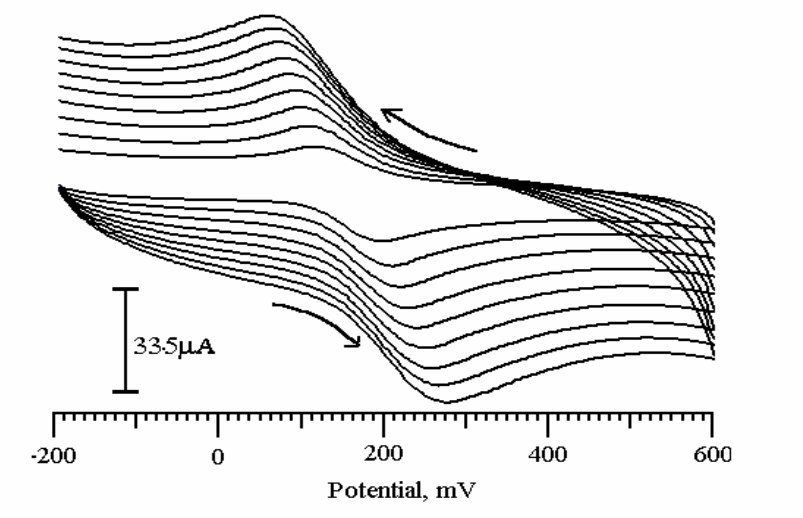


Figure 6a. The effect of scan rate of dopamine at surfactant immobilized Phthalic acid MCPE

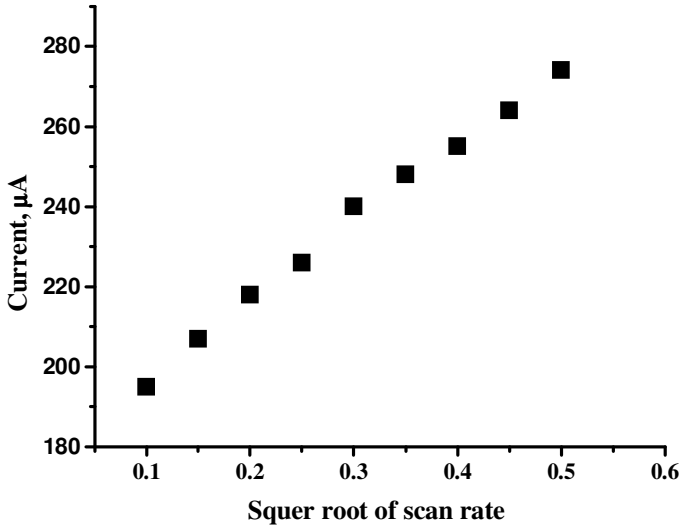


Figure 6b. Graph of the peak potential (Ep) vs. log of scan rate.

3.7 Effect of scan rate at 40μL TX-100 immobilization of Phthalic acid MCPE

According to Randles Sevick's equation, increases in the scan rate increase the peak current.40μL TX-100 surfactant on to the surface of Phthalic acid MCPE showed increase in the peak current with increase in scan rate from 100 to 500mV/s in the presence of 1mM DA and 0.2M Phosphate buffer solution pH 7.0 as shown in Fig.6a.The plot of anodic peak current against square root of scan rate shows linear straight line as shown in Fig.6b.

4. CONCLUSIONS

In this work, chemically modified phthalic acid carbon paste electrode acts as a good sensor exhibited strong promoting effect and stability towards the electrochemical oxidation of potassium ferrocyanide in KCl solution and dopamine at pH 7 in phosphate buffer solution (PBS). Nonionic surfactant TX-100 showed very good electrocatalytic effect on the phthalic acid modified carbon paste electrode. With its low cost and easy of preparation, the phthalic acid modified carbon paste electrode seems to be great utility for further sensor development.

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