

Sodium Alpha Olefin Sulfonate Modified Carbon Paste Electrode Sensor for Dopamine: A Voltammetric Study

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Abstract

Sodium alpha olefin sulfonate, an anionic surfactant was modified in carbon paste electrode by immobilization technique. The surfactant modified carbon paste electrode (SAOS/MCPE) was applied for the electrochemical determination of dopamine. The modified electrode shows excellent electrocatalytic property towards DA at pH 7.2 in Phosphate Buffer solution (PBS). The effects of scan rate and concentration of dopamine was studied and the electrode process was adsorption-controlled processes. The modified electrode resolves the well-defined two peaks for dopamine and ascorbic acid which is absent for bare carbon paste electrode and simultaneous studies was studied by cyclic and differential pulse voltammetric techniques. The detection limit was found to be 1.051×10^{-6} M respectively and the modified electrode shows good sensitivity and selectivity for dopamine.

Keywords: Sodium alpha olefin sulfonate; Dopamine; Ascorbic acid; Modified carbon paste electrode; Bare carbon paste electrode; Cyclic voltammetry

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Introduction

The Sodium alpha olefin sulfonate (SAOS) surfactants are produced by the direct reaction of olefins with strong sulfonating agents, such as sulfur trioxide. This leads to the formation of surface active anionic mixtures containing both alkenes sulfonates and hydroxylalkene sulfonates. These surfactants may be used in place linear alkyl benzene sulfonate in many formulas with resulting improvements in biodegradability, mildness to skin, foaming and detergency. In addition, SAOS surfactants are stable over a much broader pH range than alkyl sulfates alkyl ethers sulfates and esters type surfactants. They also exhibit excellent foaming and detergency in hard water. The INCL name of the primary SAOS of commerce is sodium C14-16 olefin sulfonate. Irritation studies on SAOS have been conducted on the backs of ten human volunteers using the closed patch technique with daily applications of 2.5% aqueous solutions, It was shown that irritation was comparable to that produced by soap. The SAOS surfactants have been used successfully in the formulation of a variety of skin cleaning products including toilet bars and bubbles bath compositions, a suggested liquid bubble bath formulation containing SAOS. The trend in the cosmetic market to use liquid hand cleansers in place of bar soap continues to be strong. As a

result of their relative mildness, cleansing efficiency outstanding lathering properties and favorable cost SAOS surfactants have gained popularity for this use [1-4].

The surfactants play very important role especially in electrochemistry and these are the active ingredients in personal hygiene products. These are helpful in detergents for industrial and household cleaning. There are four classes (cationic, anionic, amphoteric and non-ionic) based on the ionic charge (if present) of the hydrophilic portion of the surfactant in an aqueous solution [5,6]. These surfactants have an inherent tendency to accumulate at interfaces depending upon the nature of the interface and that of the surfactants. Accordingly, the properties which depend on the interfacial character of a system exhibit alteration in the presence of such surfactants [7-9]. Therefore the surfactants are frequently used in a variety of textile technology and biotechnology. The use of enzymes in detergents (primarily protease and amylase) needs biotechnological skills to solve problems like enzyme production and isolation, enzyme storage stability and preserving the activity, thermostability, pH stability etc., [10,11]. Hu's group has introduced surfactants to electro analytical chemistry to improve the detection limits of some important biomolecules. The results

showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactant types [12-16].

Dopamine (DA) was discovered by Arvid Carlsson's in 1958 and it plays very important role in the mammalian brain [17]. It is also an important neurotransmitter widely distributed in the mammalian central nervous systems. It has been discovered that, the lack of DA is associated with the debilitating ailment i.e., Parkinson's disease [18,19], HIV infection and Huntington's diseases. In the past 30 years, a variety of approaches, including spectrophotometry, colorimetry, chromatography, have been developed for the DA detection by different techniques. The DA can be detected using electrochemical techniques due to its good electro active nature. Therefore, the electrochemical methods for quantifying the amount of DA in human body fluids have attracted more attentions due to its high accuracy, fast response and bulk modification with simple instruments [20-30].

Ascorbic acid is a water soluble vitamin and it is a compound that takes part in many important life processes. It is one of the most important vitamins, due to its antioxidant and pH regulator properties often being added to various food products and pharmaceuticals [31,32]. Ascorbic acid (AA) prevents scurvy and is known to take part in several biological reactions. It has been widely used in foods and drinks as an antioxidant and also for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [33,34]. Now-a-days this compound has been the subject of many electrochemical investigations and on the basis of such studies; several methods have been developed for its determination in various samples [35-42].

In the present work, the SAOS anionic surfactant was modified and applied for the electrochemical detection of DA and AA at pH 7.2 PBS solution. The modified electrode shows good electro catalytic activity and enhancement in current signals with the decreasing over potential for DA. After the modification of the electrode, the adsorption of SAOS on the surface of carbon paste electrode interface and the redox reactions in solution leads to acts as electrochemical sensor. These results might be able to explain the enhancement effects of surfactants in electro analytical chemistry [43].

Experimental Part

Reagents and chemicals

Dopamine (DA), Ascorbic Acid (AA) and Uric Acid (UA) were obtained from Himedia chemical company and of analytical grade used without further purification. 25×10^{-4} M DA stock solution was prepared in 0.1 M perchloric acid, 25×10^{-4} M AA was prepared in double-distilled water and 25×10^{-4} M UA was prepared in 1 M NaOH. Graphite powder of 50 mm size was purchased from Loba, silicon oil was purchased from Himedia and Sodium alpha olefin sulfonate anionic surfactant was purchased

from Himedia chemical company. The chemicals for preparation of buffer solution were purchased from Merck. Phosphate buffer (0.2 M pH 7.2) was used as supporting electrolyte.

Apparatus

Cyclic voltammetry (CV) was performed in a model CHI-660c (CH Instrument-660 electrochemical workstation). All experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire as counter electrode and saturated calomel as reference electrode for the electrochemical measurements. The carbon paste electrode was prepared by using 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. In the same way, the sodium alpha olefin sulfonate modified carbon paste electrode (SAOS MCPE) was prepared by immobilizing 10 μ L of SAOS on the surface of the carbon paste electrode for 5 min and then applied for the electrochemical analysis.

Results and Discussion

Electrochemical response of potassium ferrocyanide at sodium alpha olefin sulfonate modified carbon paste electrode

Due to the simple and well defined response at carbon materials the $\text{Fe}(\text{CN})_6^{-3}/\text{Fe}(\text{CN})_6^{4-}$ redox couple has been widely used to characterize the surface properties of all kinds of carbon electrodes [44-48]. Potassium ferrocyanide was selected to evaluate the performance of the modified CPE electrode. **Figure 1** shows the electrochemical response of 1mM $\text{K}_4\text{Fe}(\text{CN})_6$ bare (dashed line) and SAOS/MCPE (solid line) in supporting electrolyte 1 M KCl at the scan rate 50 mVs⁻¹.

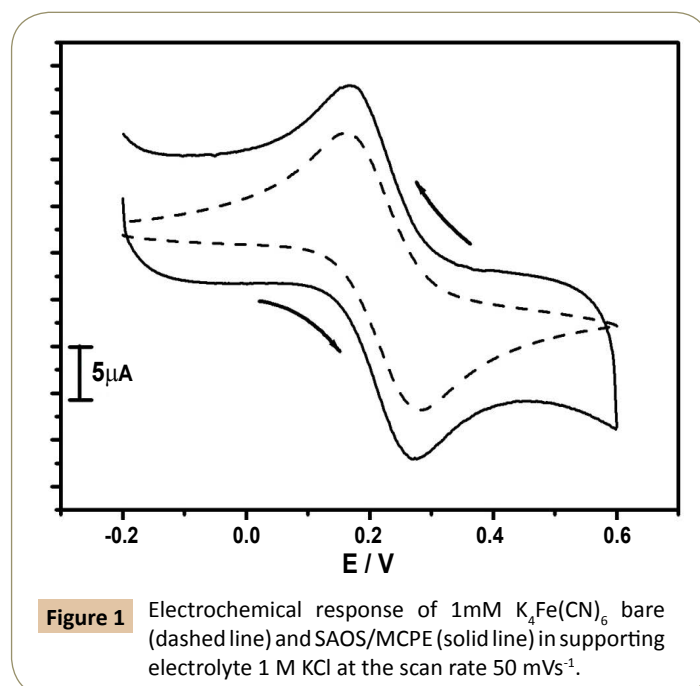


Figure 1 Electrochemical response of 1mM $\text{K}_4\text{Fe}(\text{CN})_6$ bare (dashed line) and SAOS/MCPE (solid line) in supporting electrolyte 1 M KCl at the scan rate 50 mVs⁻¹.

electrolyte 1 M KCl at the scan rate 50 mVs⁻¹. The modified carbon paste electrode peak current increases when compared to bare carbon paste electrode. This may be due to SAOS surfactant plays an important role in the electro active surface area and provides the conducting bridges for the electro transfer of ferrocyanide [49-53].

Effect of scan rate of potassium ferrocyanide

Figure 2a explains the SAOS/MCPE was recorded at the different scan rates for potassium ferrocyanide with 1M KCl as a supporting electrolyte. The peak currents of K₄Fe(CN)₆ at SAOS/MCPE increased linearly with increasing the scan rate from 50-500 mVs⁻¹. The I_{pa} versus v^{1/2} shows linear with the correlation coefficient R²=0.9978 (**Figure 2b**) respectively. This indicates that SAOS/MCPE shows diffusion -controlled process [54].

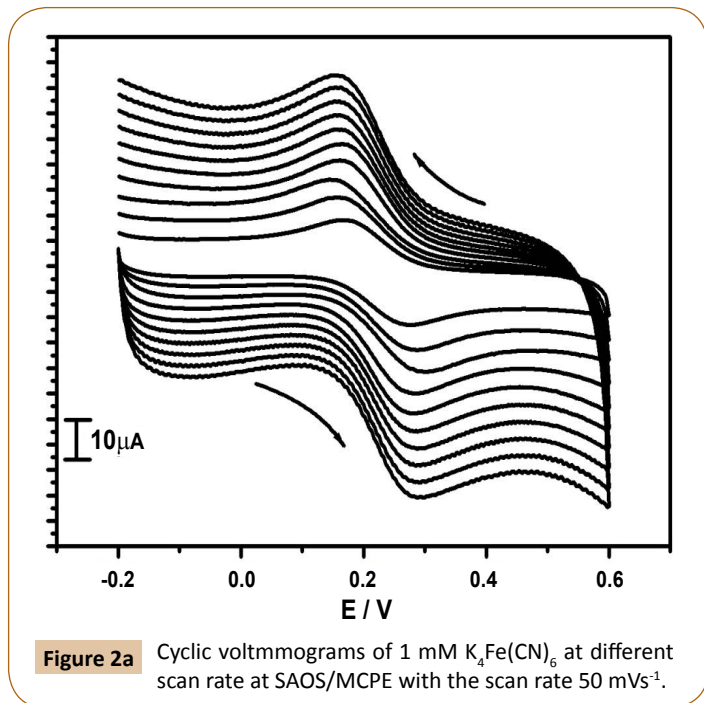


Figure 2a Cyclic voltammograms of 1 mM K₄Fe(CN)₆ at different scan rate at SAOS/MCPE with the scan rate 50 mVs⁻¹.

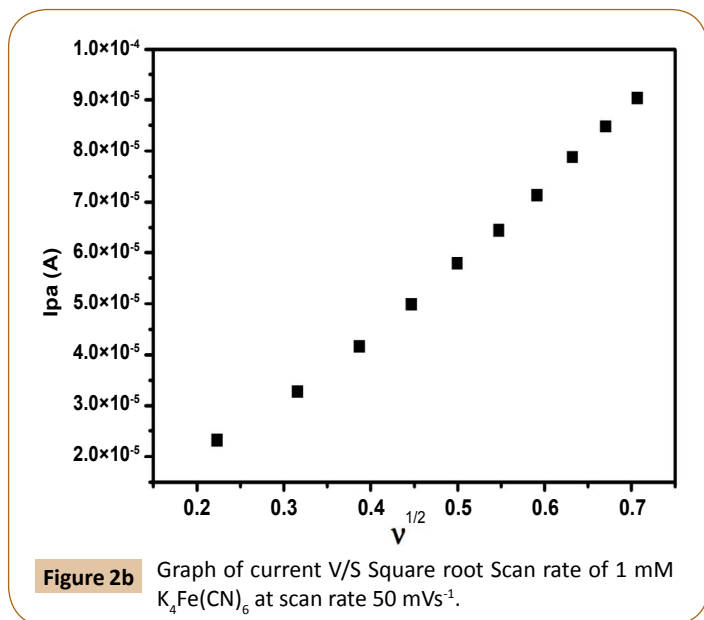


Figure 2b Graph of current V/S Square root Scan rate of 1 mM K₄Fe(CN)₆ at scan rate 50 mVs⁻¹.

Electrochemical response of dopamine at SAOS/MCPE

Figure 3 shows the cyclic voltammograms for the bare CPE (dashed line) and SAOS MCPE (solid line) in the presence of 0.1 × 10⁻⁴ M DA at pH 7.2 PBS solution with the scan rate 50 mVs⁻¹. At bare CPE shows difference in peak potential (ΔE_p=47 mV) with low current signal. However at SAOS/MCPE the peak current was strongly increases (I_p) with peak potential difference (ΔE_p=35 mV). This indicates the SAOS/MCPE shows good electro catalytic properties.

Effect of scan rate

The cyclic voltammograms of 0.1 × 10⁻⁴ M DA at SAOS/MCPE was studied at different scan rates at pH 7.2 PBS solution as shown in the **Figure 4a** and the observations was made to investigate the kinetics of the modified electrode reaction [55]. With the increase in the scan rate from 10-300 mVs⁻¹ the anodic and cathodic peak currents goes on increasing. The plot of I_{pa} versus v shows linear regression equation I_{pa} = -5.608 × 10⁻⁷ + 0.1311 (v) R²=0.9996 (**Figure 4b**) respectively. This indicates that electron transfer process was adsorption-controlled process for DA.

Effect of dopamine concentration

The effect of dopamine concentration was studied at SAOS/MCPE in the range (0.1-0.8 × 10⁻⁴ M) at pH 7.2 as shown in the **Figure 5a**. As the concentration of DA was increased, the anodic and cathodic peak currents also increases and the plot of I_{pa} versus DA concentration shows increase in electrochemical peak currents with linear regression equation I_{pa} (μA) = 2.840 × 10⁻⁵ (C) M/L + 5.3776 (μA) (R²=0.9913) as shown in the **Figure 5b**. The detection limit was calculated by using the formula (1) [56], where S is the standard deviation and M is the slope obtained from the calibration plots. The detection limit for dopamine was found to be 1.05 × 10⁻⁶ M.

$$\text{LOD} = 3S/M \dots \dots \dots (1)$$

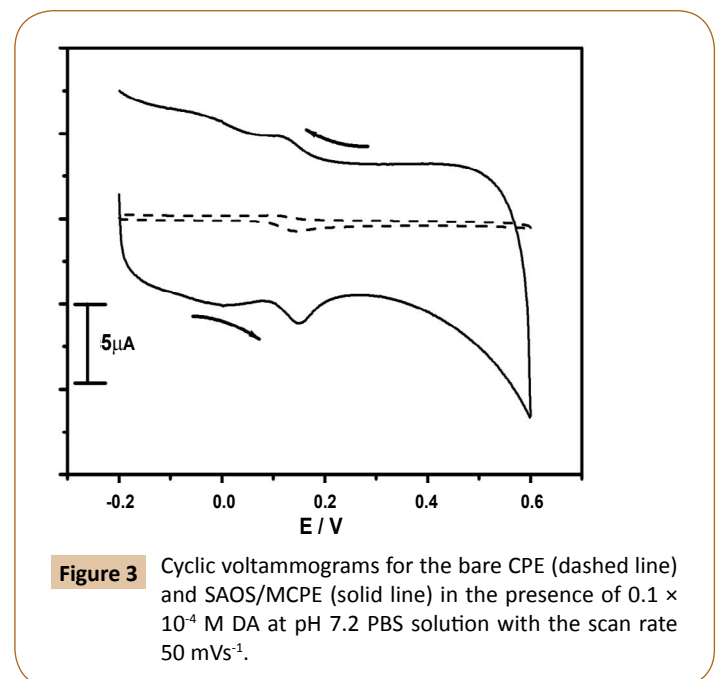


Figure 3 Cyclic voltammograms for the bare CPE (dashed line) and SAOS/MCPE (solid line) in the presence of 0.1 × 10⁻⁴ M DA at pH 7.2 PBS solution with the scan rate 50 mVs⁻¹.

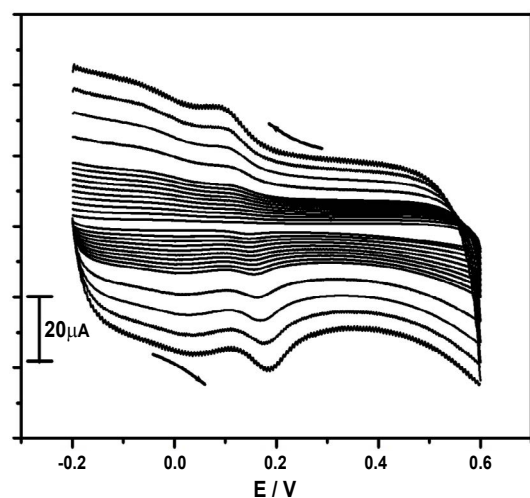


Figure 4a Cyclic voltammograms of 0.1×10^{-4} M DA at SAOS/MCPE was studied at different scan rates at pH 7.2 PBS.

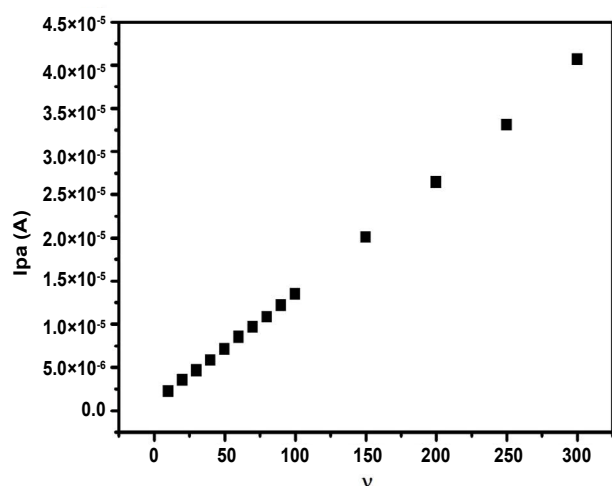


Figure 4b Graph of current V/S Scan rate of at scan rate 0.1×10^{-4} M DA 50 mVs^{-1} .

Simultaneous determination of DA and AA by cyclic voltammetry

The main objective of the work is to determine the 0.5×10^{-4} M DA and 2×10^{-4} M AA simultaneous at SAOS/MCPE in 0.2 M PBS of pH 7.2 system as shown in the **Figure 6**. The bare CPE (dashed line) shows one broad peak for both the analysts and it indicates that the bare CPE fails to separate the voltammetric signals for DA and AA. This is due to the electrode fouling effect and the fact that their oxidation potential is indeed quite close. The oxidized DA product, dopamine-o-quinone, can also be catalytically reduced to DA by AA again becoming available for oxidation [57-59]. On the other hand, SAOS/MCPE (solid line) exhibits two well oxidation peaks of DA and AA at 151 mV and 24 mV with the enhancement in the I_{pa} current of DA and AA respectively. This indicates that the modified electrode acts as a electrochemical sensor for the dopamine.

Simultaneous determination of DA and AA by DPV technique

The simultaneous determination of DA and AA was carried out in the potential range of -0.4 to 0.6 V at pH 7.2 as shown in the **Figure 7**. The modified carbon paste electrode is able to separate two well-defined peaks of DA and AA on 0.067 and 0.139 mV respectively [60]. The **Figure 8a** shows that the concentration of DA was varied from (10×10^{-6} to 90×10^{-6} M) by keeping AA remains constant at SAOS MCPE. The plot of I_{pa} versus DA (**Figure 8b**) indicates that, the concentration of DA was increasing linearly and the corresponding DA linear regression equation is $I_{pa} (\mu\text{A}) = 0.812(C) \mu\text{M/L} + 11.60 (\mu\text{A})$ $R^2 = 0.9973$. The detection limit (LOD) was calculated by using the formula (1) [61-66] and obtained results was shown in the **Table 1**.

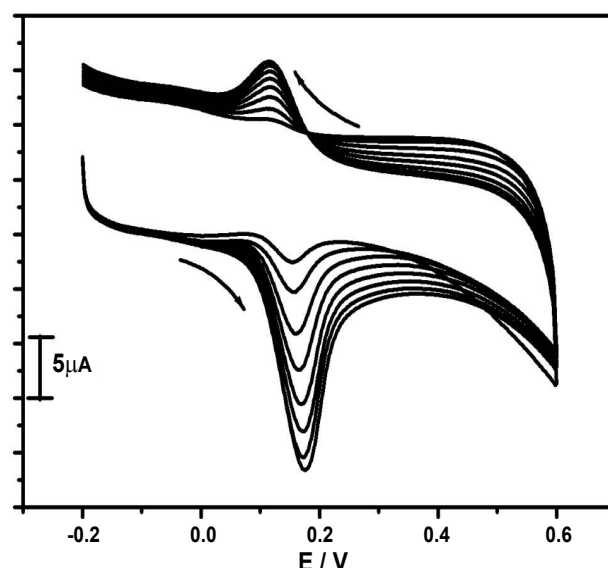


Figure 5a Cyclic voltammograms of dopamine concentration was studied at SAOS/MCPE in the range $(0.1-0.8 \times 10^{-4}$ M) at pH 7.2.

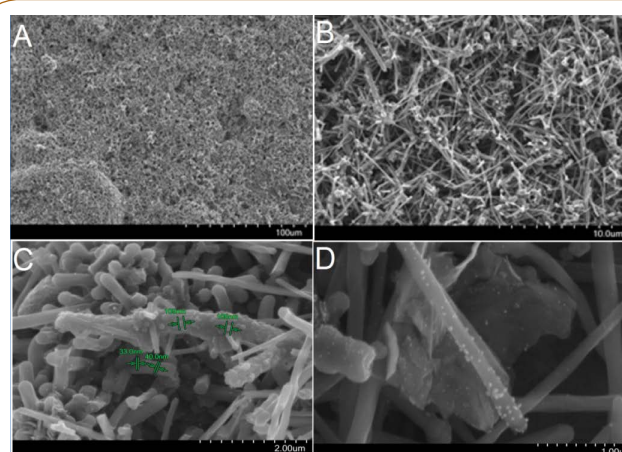


Figure 5b Graph of current V/S concentration of DA at scan rate 100 mVs^{-1} of pH 7.2.

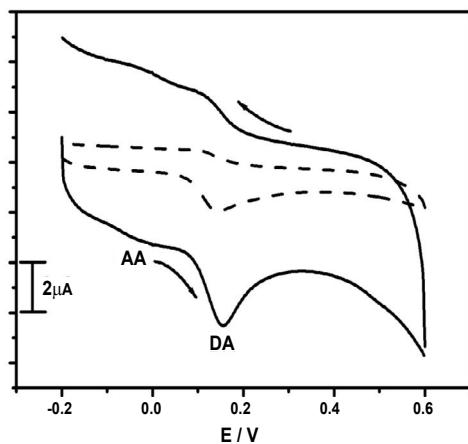


Figure 6 Cyclic voltammograms obtained for oxidation of 0.5×10^{-4} M DA and 2×10^{-4} M AA at bare (dashed line) and SAOS/MCPE (Solid line) at scan rate of 50 mVs^{-1} 0.2 M PBS (pH 7.2).

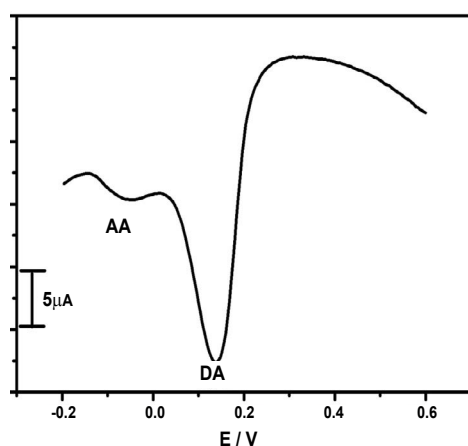


Figure 7 Differential pulse voltammogram for 0.5×10^{-4} M DA and 2×10^{-4} M AA at SAOS/MCPE modified carbon paste electrode at 50 mVs^{-1} .

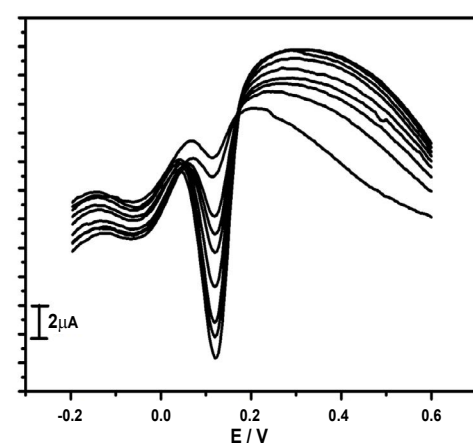


Figure 8a Differential pulse voltammograms of 2×10^{-4} M AA keeping constant by varying concentration of DA (10×10^{-6} to 90×10^{-6} M) at SAOS/MCPE modified carbon paste electrode at 50 mVs^{-1} .

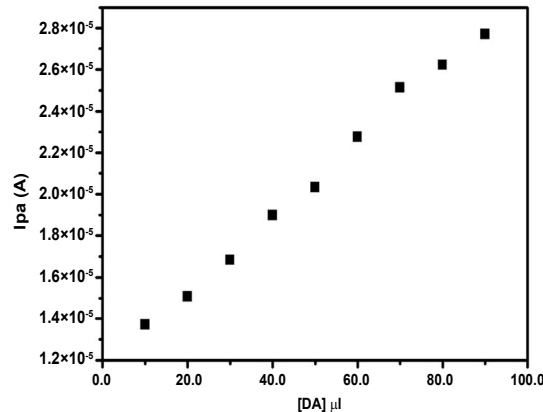


Figure 8b Graph of current V/S concentration of DA at scan rate 50 mVs^{-1} of pH 7.2.

Table 1 Detection limit (LOD) values.

Electrode	Detection Limit (μM)	Method	Reference
Au-CA SAMs	2.34	DPV	[61]
α -CD/CNT/PGE	1.0	DPV	[62]
Metallothioneins self-assembled gold electrode	6.0	CV	[63]
Hydrogenated cylindrical Carbon electrodes	7.0	CV	[64]
Lignin Modified Carbon Paste Electrode	14.0	CV	[65]
Long-Length Carbon Nanotube	0.02	DPV	[66]
GNS-CNTs/MoS ₂	0.05	DPV	[66]
SAOS MCPE	0.64	DPV	This work

Conclusion

In this work, the sodium alpha olefin sulfonate MCPE shows good electro catalytic properties towards electrochemical determination of dopamine in PBS solution at pH 7.2. The effects of scan rate and the concentration were found to be adsorption-controlled process. The SAOS/MCPE was able to determine AA and DA simultaneously in both the CV and DPV techniques in their sample mixtures and the detection limit of DA was found to 1.05×10^{-6} M. This indicates that the modified electrode act as good sensors for DA and this method can also be applied for other neurotransmitters.

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