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# Combination of a poly(3,4-ethylene-dioxythiophene) electrode in the presence of sodium dodecyl sulfate with centri-voltammetry

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A poly(3,4-ethylene-dioxythiophene) (PEDOT) electrode was prepared by electropolymerization of 3,4-ethylene-dioxythiophene (EDOT) in the presence of sodium dodecyl sulfate (SDS). The electrode was combined with centri-voltammetry for the first time and applied for dopamine (DA) detection. Under the experimental conditions, SDS provides a high density of negative charges to the PEDOT electrode and by this way the electrode attracts the positively charged DA. Also by applying centrifugation, effective accumulation of DA onto the electrode surface was achieved. Two linear ranges  $1 \times 10^{-9}$  M to  $1 \times 10^{-5}$  M and  $2 \times 10^{-5}$  M to  $1 \times 10^{-1}$  M with two LOD values of 5.9 nM and 3.1 nM were found for the developed system. Sample application and interference study were also conducted.

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## Introduction

Electroanalytical methods have been extensively used for the determination of dopamine (DA) which is an important neurotransmitter in brain tissue.<sup>1–6</sup> The usage of conducting polymers (CPs) for the detection of DA provides immense development in chemical and biological sensor areas.<sup>7–11</sup>

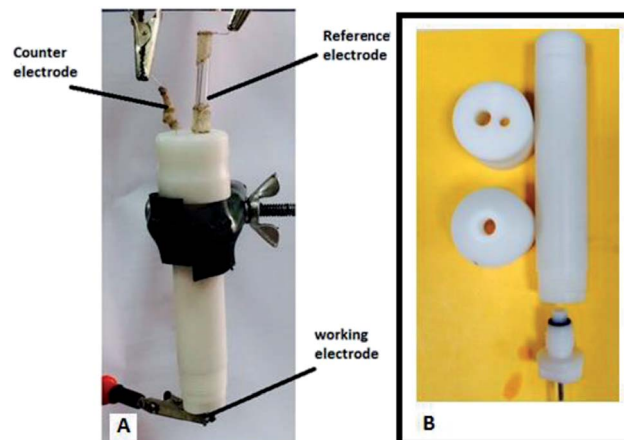
Among these CPs, poly(3,4-ethylenedioxythiophene) (PEDOT) is a class of polythiophenes with very high electrochemical stability in oxidized states and a low band-gap<sup>12,13</sup> due to the presence of the two electron donating oxygen atoms coupled to the thiophene ring.<sup>14,15</sup> With the usage of oxidants like ferric chloride, PEDOT can be produced chemically<sup>13,16</sup> or in the presence of appropriate solvents, it can be produced electrochemically.<sup>13</sup> PEDOT has some advantages compared to unsubstituted polythiophene and other polythiophene derivatives. One of them is caused by the ethylenedioxy substituent. This substituent lowers the oxidative doping potential of the polymer and stabilizes its conducting form.<sup>17</sup> Recently, PEDOT modified electrodes have been extensively reported and showed an excellent electrocatalytic effect on phenolic compounds.<sup>18–21</sup>

On the other hand sodium dodecyl sulfate (SDS) is a surfactant. Surfactants can be described as a type of amphiphilic molecule with a hydrophilic head on one side and a long hydrophobic tail on the other. These substances have been widely applied in electrochemistry to improve the properties of the electrode/solution interface.<sup>22,23</sup> Also it has been demonstrated that surfactants are important in the electroanalysis of

biological compounds and drugs.<sup>24,25</sup> Considering SDS, there are many studies that cover selective determination of DA in the presence of SDS in the literature.<sup>26–29</sup>

Centri-voltammetry and biocentri-voltammetry were developed by our group. These methods include the combination of the centrifugal force with direct voltammetric scan afterwards without applying any filtration, decantation or any other separation methods.<sup>30–39</sup> For the application of this method, a specially designed centri-voltammetric cell is used where the working electrode is at the bottom of the centri-voltammetric cell (Scheme 1). Recently we managed to apply centri-voltammetry for the detection of DA and very promising results were obtained.<sup>39</sup>

In this work, PEDOT was electrochemically formed on the Pt electrode of the centri-voltammetric cell by means of



Scheme 1 Illustration of the centri-voltammetric cell, (A) on the stand and (B) the parts of the centri-voltammetric cell.

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electropolymerization of 3,4-ethylenedioxythiophene (EDOT). Then SDS was added and centrifugation was applied. In this way, centri-voltammetry was combined for the first time with a conductive polymer where DA was chosen as a model analyte. After the optimization of experimental parameters, analytical characteristics were examined. Then the developed system was applied for detection of DA in synthetically prepared plasma samples and DA ampoules. The interference effects of ascorbic acid (AA) and uric acid (UA) were also examined.

## Experimental section

### Chemicals and reagents

All chemicals were of analytical grade. DA, EDOT, UA, urea, Trizma hydrochloride (Tris-HCl), SDS, potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), sodium phosphate dibasic ( $\text{NaH}_2\text{PO}_4$ ), potassium chloride (KCl), calcium chloride ( $\text{CaCl}_2$ ) and lithium perchlorate ( $\text{LiClO}_4$ ) were purchased from Sigma-Aldrich. Sodium chloride (NaCl), D+ glucose monohydrate, magnesium chloride ( $\text{MgCl}_2$ ), acetonitrile, acetone, PC and hydrochloric acid (HCl) were purchased from Merck. Finally, AA was obtained from Scharlau and isopropyl alcohol was purchased from Pan-reac. Ultrapure water was used in all solutions. DN ampoules were purchased from a local pharmacy.

All experiments except electrochemical polymerization of EDOT were performed in PBS at room temperature.

PBS of pH 7 was prepared by mixing 60 mL of a  $1/15 \text{ mol dm}^{-3}$  solution of  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  with 40 mL of a  $1/15 \text{ mol dm}^{-3}$  solution  $\text{KH}_2\text{PO}_4$  and adjusting the pH to 7 by adding either  $\text{KH}_2\text{PO}_4$  or  $\text{Na}_2\text{HPO}_4$ .<sup>40,41</sup>

### Instrumentation

Voltammetric measurements were carried out with a  $\mu$ -AUTO-LAB Type III electrochemical measurement system from Metrohm B.V. controlled using NOVA 1.10 software. The experiments were conducted in a 5.0 mL centri-voltammetric cell, at room temperature (25 °C), using a three-electrode cell configuration. A Pt disk was used as the working electrode and Pt wire was used as reference and also counter electrodes.

A Sigma 3-16 PK was used for centrifugation and pH measurements were carried out with Thermo Electron Corporation.

### Preparation of the PEDOT modified Pt electrode

The Pt disk that was used as a working electrode was polished by hand using 0.3 and 0.5  $\mu\text{L}$  alumina slurry on a felt pad. Then the electrode was sonicated in water and acetone for 5 minutes. Before starting each experiment, the Pt electrode was washed with isopropyl alcohol, and dried by using a blow drier. Potentiodynamic electrodeposition was performed in a solution consisting of 0.1 M  $\text{LiClO}_4$  in PC solution containing 5 mM EDOT.

The electrodes were polarized in the range of  $-0.7$ – $1.85 \text{ V}$  (vs. Ag/AgCl) by applying six cycles at a scan rate of  $50 \text{ mV s}^{-1}$ . Then the PEDOT films were replaced in monomer free 0.1 M  $\text{LiClO}_4$  in PC solution and further 4 cycles were applied at 50

$\text{mV s}^{-1}$  scan rate in the potential range of  $-0.5 \text{ V}$  to  $+1.0 \text{ V}$  to obtain a stable film. Finally, the PEDOT films obtained on the surface of the working electrode were washed with acetonitrile and dried by using a blow drier before being used in buffer solution. For every set of the measurements, the freshly prepared PEDOT film was used.

### Electrochemical measurements

After the formation of PEDOT, DA detection was performed by monitoring cyclic voltammetry (CV) and square wave voltammetry (SWV) signals of DA oxidation in the presence of SDS. For this purpose, a PEDOT coated working electrode was mounted at the end of the centri-voltammetric cell. DA solution which contains  $6.7 \times 10^{-5} \text{ M}$  150  $\mu\text{L}$  SDS was stirred for 5 minutes and then was transferred into the centri-voltammetric cell (Scheme 1). After that, centrifugation was applied for a particular amount of time and at an appropriate speed. Finally, the cell was carefully placed on the voltammetric stand and reference and counter electrodes were immersed into working solution. CV was performed with  $100 \text{ mV s}^{-1}$  scan rate and from potential  $-0.5 \text{ V}$  to  $+0.7 \text{ V}$ . The parameters for SWV experiments were as follows: potential was scanned from  $-0.5 \text{ V}$  to  $+0.7 \text{ V}$  with 0.02 V amplitude and 0.005 V step potential. On the other hand, for electrochemical impedance spectroscopy (EIS), 250 mV applied potential, 5 mV amplitude, and 0.1–100.000 Hz frequency range were applied. All experiments of DA detection were performed in pH: 7,  $6.7 \times 10^{-2} \text{ M}$  PBS containing DA in the presence of  $6.7 \times 10^{-5} \text{ M}$  150  $\mu\text{L}$  SDS unless it is mentioned differently.

### Preparation of sample solution

The developed system was applied for DA detection in synthetically prepared plasma samples. For this purpose, a synthetic plasma sample was prepared by incorporating the reagents into the 10 mM Tris-HCl including 140 mM NaCl, 4.7 mM D+ glucose monohydrate, 0.8 mM  $\text{MgCl}_2$ , 4.5 mM KCl, 2.5 mM  $\text{CaCl}_2$  and 2.5 mM urea.<sup>39</sup> Also, the developed system was applied for DA detection in real samples. For this purpose, DA ampoule which is a type of medicine was used. For this procedure, a necessary DA amount was taken directly from the ampoule and spiked into the centri-voltammetric cell at  $5 \times 10^{-5} \text{ M}$ . The measurements were repeated three times.

## Results and discussion

Introducing SDS onto the PEDOT electrode results in a high density of negative charges covered on the electrode surface. For this reason, it is expected to achieve sensitive and selective positively charged (at pH 7) DA detection with this electrode.<sup>29,43</sup> On the other hand, centri-voltammetry provides a centrifugal force meaning more effective accumulation of the analyte on the electrode surface.<sup>39</sup>

### Electrochemical polymerization and characterization of the Pt/PEDOT electrode

Electrochemical polymerization was conducted *via* CV. Cyclic voltammograms that were obtained during the polymer growth

at 6 cycles are shown in Fig. 1A. As the polymer grows on the bare Pt disc electrode, by applying successive CVs, the background current increases demonstrating that the electrode is covered with PEDOT. In order to strengthen the formation process, an EIS diagram is also provided (Fig. 1B). The formation of PEDOT on the Pt electrode is clearly seen just by comparing the diameters of semicircles. As can be seen from the Figure, formation of PEDOT on the Pt electrode decreases the diameter of semicircles together with electron transfer resistance.

### Optimization of experimental conditions

Optimizations of experimental parameters are important in order to achieve high sensitivity and better reproducibility. Thus the amount of SDS, centrifugation speed and centrifugation time were optimized.

**Optimization of SDS amount.** SDS forms a monolayer on the PEDOT surface and the electrochemical response of DA is improved in the presence of SDS due to the enhanced

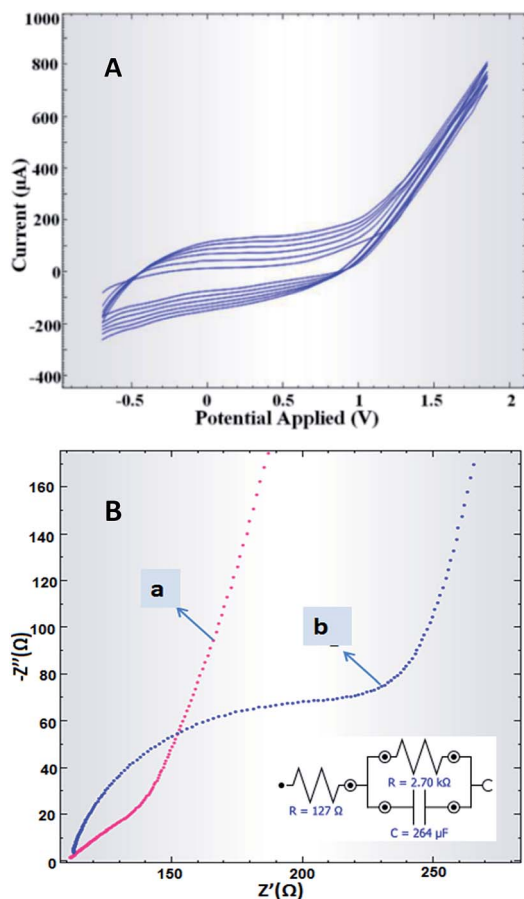


Fig. 1 (A) CV voltammograms of electrochemical polymerization of EDOT. Conditions: 5 mM EDOT in PC solution containing 0.1 M LiClO<sub>4</sub>, working potential:  $-0.7$  V to  $+1.85$  V and scan rate  $50$  mV s<sup>-1</sup>. (B) Nyquist diagrams for the EIS measurements at (a). Pt/PEDOT electrode (b). Pt electrode and equivalent circuit of the Pt/PEDOT electrode. Working conditions: in  $6.7 \times 10^{-2}$  M pH 7.0 PBS including  $5.0 \times 10^{-5}$  M DA and  $6.7 \times 10^{-5}$  M 150  $\mu$ L SDS at potential 250 mV, amplitude: 5 mV, and frequency range: 0.1–100.000 Hz.

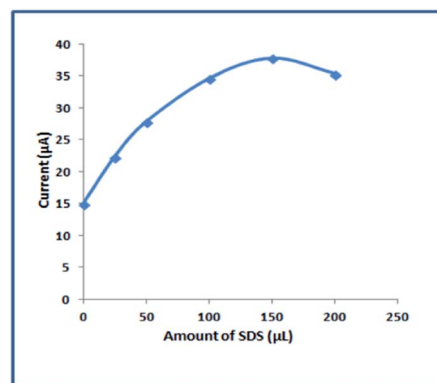


Fig. 2 The effects of different amounts of SDS on the sensor response for  $5.0 \times 10^{-5}$  M DA. Conditions: in  $6.7 \times 10^{-2}$  M phosphate buffer solution (PBS) (pH 7.0), working potential:  $-0.5$  V to  $+0.7$  V and scan rate  $100$  mV s<sup>-1</sup>.

accumulation of protonated DA *via* electrostatic interactions. For this reason, the SDS amount was optimized. The response signals of DA ( $5.0 \times 10^{-5}$  M) oxidation in the presence of 0  $\mu$ L, 25  $\mu$ L, 50  $\mu$ L, 75  $\mu$ L, 100  $\mu$ L, 150  $\mu$ L and 200  $\mu$ L of  $6.70 \times 10^{-5}$  M SDS were recorded, respectively (Fig. 2). As can be seen from Fig. 2, the current value increases up to 150  $\mu$ L and then a decrease was observed. Following these findings, 150  $\mu$ L SDS was selected as the optimum SDS amount and used for further studies.

The current increment in the presence of SDS is explained by the aggregation of this surfactant on the electrode surface in the form of bilayers, cylinders, or surface micelles.<sup>25</sup> The electron transfer process will take place when the electroactive species approaches the vicinity of the electrode surface. There are three suggestions for explaining the charge transfer: the first one is the displacement of the adsorbed surfactant by the analyte, the second one is the approach of the analyte to the surface of the electrode within the space of one to two head groups of adsorbed surfactant moieties and the third one includes the formation of an ion-pair that anchors onto the surface of the electrode that should possess some hydrophobic character.<sup>42,43</sup> As mentioned before due to electrostatic attraction and by following the second suggested mechanism we believe that current increases up to some point of increased SDS concentration. Then since increment of SDS amount may block the electrode surface, up to some point, DA cannot reach the electrode surface and as a result a decrease in the current value is observed. At this point it is not possible to suggest the exact mechanism, but the above explanation could be an alternative for that behaviour.

**Optimization of centrifugal parameters.** The centrifugation parameters are very important in centri-voltammetry.<sup>30–39</sup> In this study, SDS molecules should be deposited onto the electrode surface in order to obtain electrostatic interactions with DA. For this purpose, the centrifugation speed and centrifugation time were optimized. Firstly, centrifugation speeds of 0 rpm, 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm, 5000 rpm and 6000 rpm were applied on the centri-voltammetric cell for 5 minutes. The

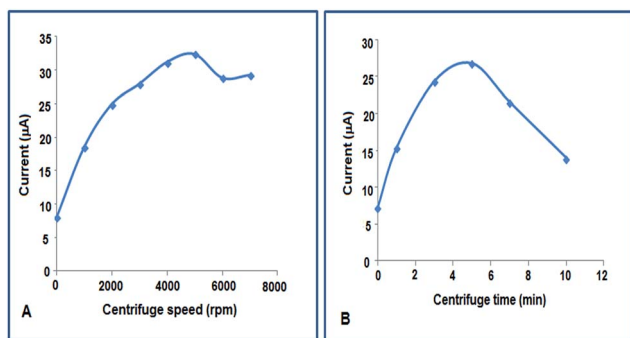


Fig. 3 The effects of centrifugation parameters on the sensor response, (A) centrifugation speed, (B) centrifugation time for  $5.0 \times 10^{-5}$  M DA. Conditions: in  $6.70 \times 10^{-2}$  M PBS (pH 7.0) in the presence of  $6.70 \times 10^{-5}$  M  $150 \mu\text{L}$  SDS, working potential:  $-0.5$  V to  $+0.7$  V and scan rate  $100 \text{ mV s}^{-1}$ .

best current value was obtained at 5000 rpm (Fig. 3A). For optimization of centrifugation times, 0 min, 1 min, 3 min, 5 min and 7 min were applied on the centri-voltammetric cell at 5000 rpm. As a result, the best result current value was obtained at 5 minutes (Fig. 3B).

The increase in current values that were obtained due to the increased centrifugation time and speed can be attributed to the accumulation of the analyte layer onto the electrode surface.<sup>30–39</sup> On the other hand the decrease that was obtained when the centrifugation time was increased can be due to the desorption of the analyte from the electrode surface due to the long centrifugation period.<sup>30–32,36,38,39</sup> The other possible explanation for this phenomenon could be the accumulation of supporting electrolyte ions onto the electrode surface instead of DA. At this point, it is not possible to state the exact reason but these two explanations seem reasonable to us. On the other hand, the current decrease at the higher speeds might be due to the destruction of the analyte layer that was on the electrode surface.<sup>30–32,36,38,39</sup> All optimizations of centrifugal parameter experiments were performed in the presence of  $5.0 \times 10^{-5}$  M DA in  $6.7 \times 10^{-2}$  M pH: 7 PBS.

#### Effect of scan rate on the voltammetric response of DA

Fig. 4A shows the CV of  $5.0 \times 10^{-5}$  M DA in  $6.7 \times 10^{-2}$  M pH: 7 PBS containing  $6.7 \times 10^{-5}$  M  $150 \mu\text{L}$  SDS at the Pt/PEDOT electrode at different scan rates (from  $10 \text{ mV s}^{-1}$  to  $250 \text{ mV s}^{-1}$ ). Fig. 4B also shows a comparison of the linear relationship for DA at Pt/PEDOT in  $6.7 \times 10^{-2}$  M, pH: 7 PBS containing  $150 \mu\text{L}$  SDS and  $6.7 \times 10^{-2}$  M, pH: 7 PBS without SDS versus square root of scan rate.

As it is expected with SDS, higher current values were obtained compared with the plain PEDOT electrode. Examination of data in terms of the effect of scan rate reveals that the linearity of the relationship is observed up to a square root of the scan rate of  $100 \text{ mV s}^{-1}$  in the presence and absence of SDS. A deviation from the linearity is obtained for at higher scan rates. This demonstrates a partial diffusion control process for the charge transfer process for both situations. However, as can

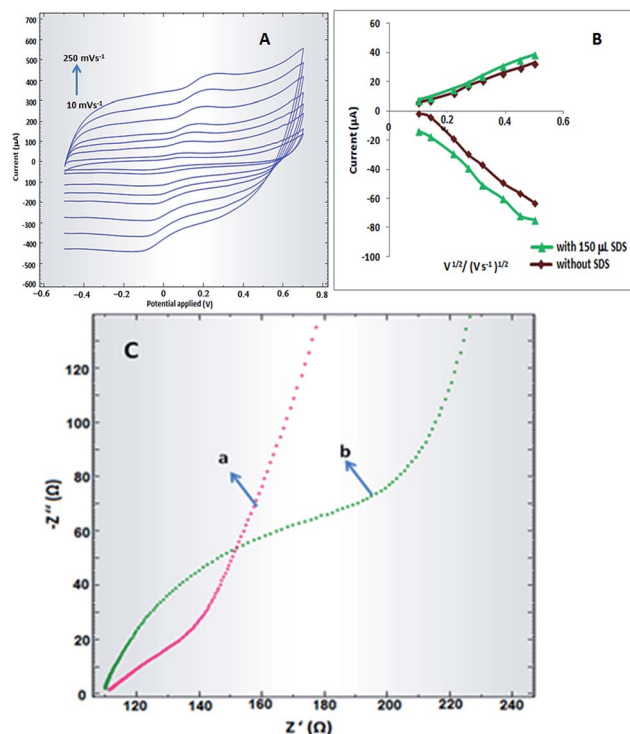


Fig. 4 (A) CVs of  $5.0 \times 10^{-5}$  M DA in  $6.7 \times 10^{-2}$  M PBS (pH 7.0) in the presence of  $6.7 \times 10^{-5}$  M  $150 \mu\text{L}$  SDS at different scan rates ( $10$ – $250 \text{ mV s}^{-1}$ ). (B) Linear relationship between anodic and cathodic currents vs. square roots of scan rate, in the presence of SDS and in the absence of SDS. (C) Nyquist diagrams for the EIS measurements at the Pt/PEDOT electrode in  $6.7 \times 10^{-2}$  M pH 7.0 PBS including  $5.0 \times 10^{-5}$  M DA (a). In the presence of SDS (b). In the absence of SDS. For the EIS measurements, working conditions: at potential  $250 \text{ mV}$ , amplitude:  $5 \text{ mV}$ , and frequency range:  $0.1$ – $100,000 \text{ Hz}$ .

be seen from the Figure, more deviations are observed for scan rates higher than  $100 \text{ mV s}^{-1}$  in the presence of SDS. This could be accepted as a confirmation of aggregation of SDS in the vicinity of the electrode hence the higher flux of DA *via* SDS through the electrode surface.

In order to observe a more clear effect of addition of SDS, dependence of the anodic peak current density on the scan rate has been used to calculate the “apparent” diffusion coefficient ( $D_{\text{app}}$ ).  $D_{\text{app}}$  is calculated from the Randles–Sevcik equation as follows.

$$I_p = 0.4463(F^3/RT)^{1/2}n^{3/2}v^{1/2}D_0^{1/2}AC_0$$

In these equations:  $I_p$  is the peak current density ( $\text{A cm}^{-2}$ ),  $n$  is the number of electrons appearing in half-reaction for the redox couple,  $v$  is the rate at which the potential is swept ( $\text{V s}^{-1}$ ),  $F$  is Faraday’s constant ( $96,485 \text{ C mol}^{-1}$ ),  $C_0$  is the analyte concentration ( $5 \times 10^{-5} \text{ mol cm}^{-3}$ ),  $A$  is the electrode area ( $0.126 \text{ cm}^2$ ),  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature ( $K = 298$ ), and  $D$  is the electroactive species diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ).

The  $D_{\text{app}}$  value was calculated to be  $1.05 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  in the absence of SDS and  $1.62 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  in the presence of

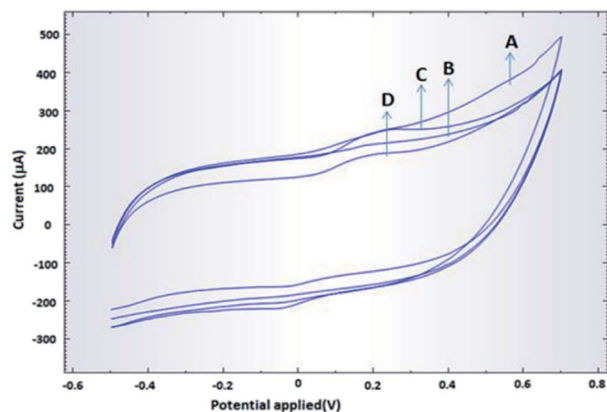


Fig. 5 CV voltammograms show the effects of SDS and centri-voltammetry for electrochemical detection of  $5.0 \times 10^{-5}$  M DA. (A) Without SDS and centrifugation, (B) with SDS and without centrifugation, (C) with SDS and centrifugation and (D) without SDS and with centrifugation.

SDS. The anionic surfactant SDS affects positively the diffusion component of the charge transfer at the electrode surface as indicated by the  $D_{app}$  values.

Also an EIS diagram is provided to enlighten the charge transfer process in the presence of SDS (Fig. 4C). The difference in Nyquist diagrams in the presence and absence of SDS is pretty obvious. The addition of SDS definitely decreases the semicircle diameter hence increases the charge transfer rate.

#### Comparison of obtained voltammograms under different conditions

The effects of SDS together with centrifugation for electrochemical detection of  $5.0 \times 10^{-5}$  M DA were investigated. For this purpose, the experiments were performed in the presence of SDS, in the absence of SDS, with centri-voltammetry and without centri-voltammetry. When the experiments were performed in the presence of SDS, with centri-voltammetry and without centri-voltammetry, the current values were obtained to be  $28.2 \mu\text{A}$  (with SDS and centri-voltammetry) and  $15.3 \mu\text{A}$  (with SDS and without centri-voltammetry), respectively. When the experiments were performed in the absence of SDS, with centri-voltammetry and without centri-voltammetry, the current values were obtained to be  $16.6 \mu\text{A}$  (without SDS, with centri-

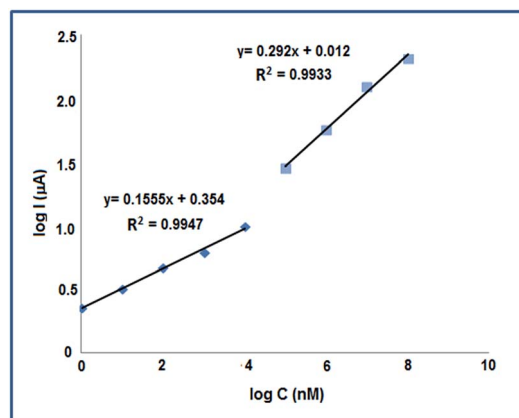


Fig. 6 Calibration graph for DA concentrations between  $1.0 \times 10^{-9}$  M to  $1.0 \times 10^{-5}$  M and  $2.0 \times 10^{-5}$  M to  $1.0 \times 10^{-1}$  M. Centrifugation speed 5000 rpm and centrifugation time 5 min.

voltammetry) and  $4.3 \mu\text{A}$  (without SDS and centri-voltammetry), respectively.

As can clearly be seen from Fig. 5, the best current value was obtained under the working conditions when SDS was added and when centri-voltammetry was applied to the system (Fig. 5C).

#### Analytical characteristics

After the optimization of experimental conditions, analytical characteristics were investigated. As can be seen from Fig. 6, two linear ranges of  $1.0 \times 10^{-9}$  M to  $1.0 \times 10^{-5}$  M and  $2.0 \times 10^{-5}$  M to  $1.0 \times 10^{-1}$  M DA with the correlation coefficients of 0.995 and 0.993 were obtained. Following these data, the detection limits were calculated to be  $5.9 \text{ nM}$  and  $3.1 \text{ nM}$ , respectively. For two linear ranges, LOQ values were also calculated and found to be  $1.9 \times 10^{-8}$  M and  $1.0 \times 10^{-8}$  M. Finally, RSD values were calculated for  $5.0 \times 10^{-5}$  M DA ( $n = 3$ ) and found to be 1.6%. The comparison of the developed system was carried out with similar systems and presented in Table 1. From the table it is clear that the developed system has one of the largest linear ranges with higher sensitivity. The introduction of PEDOT and SDS to centri-voltammetry definitely improves the linear range and sensitivity in terms of DA detection.

Table 1 Comparison of the same studies about DA detection<sup>a</sup>

Electrode	LOD	Linear range	References
GCE/PEDOT/Pd	500 nM	0.5–1 $\mu\text{M}$	44
Pt/PEDOT	61–86 nM	5–25 $\mu\text{M}$ and 30 $\mu\text{M}$ –0.1 mM	29
Pt/PMPy/Pd <sub>nano</sub>	12 nM	0.1–10 $\mu\text{M}$	45
Au/PEDOT/Au <sub>nano</sub>	0.39 nM and 1.55 nM	0.5–20 $\mu\text{M}$ and 25–140 $\mu\text{M}$	21
GCPE (centri-voltammetry)	1 nM	$5 \times 10^{-9}$ M to $5 \times 10^{-6}$ M	39
Pt/PEDOT (centri-voltammetry)	5.9 nM and 3.12 nM	$1 \times 10^{-9}$ M to $10^{-5}$ M and $2 \times 10^{-5}$ M to $1 \times 10^{-1}$ M	This work

<sup>a</sup> GCE: glassy carbon electrode, GCPE: glassy carbon paste electrode, Pt: platinum electrode, Pd<sub>nano</sub>: palladium nanoparticles, PMPy: poly(*N*-methylpyrrole), and Au<sub>nano</sub>: gold nanoparticles.

### Sample application and interference studies

For the sample application, standard addition of DA into the synthetic plasma sample solution, the preparation procedure of which is described in the Experimental part, was conducted.  $5.0 \times 10^{-5}$  M DA was added into synthetic plasma solution that contains  $6.7 \times 10^{-5}$  M 150  $\mu$ L SDS. This experiment was repeated for three times. The recovery value was calculated by dividing obtained standard addition current values with the DA concentration current value and multiplying the result by 100. As a result,  $96\% \pm 1.2$  was calculated as the recovery value.

Also centri-voltammetric DA detection was realized in real samples, here in DA ampoules as stated in the Experimental part. Three measurements were conducted by spiking  $5 \times 10^{-5}$  M DA (from ampoules) into the centri-voltammetric cell. The obtained current values were evaluated and  $4.96 \times 10^{-5} \pm 1.61$  M DA was detected.

It is well known that DA, UA and AA coexist in the extracellular fluid of the central nervous system and serum. Therefore, eliminating AA and UA is important for any DA analytical method. For this purpose, the electrochemical behaviors of DA, UA and AA in a mixture solution were studied by using CV. Two studies were conducted for this purpose. In the first study,  $5.0 \times 10^{-5}$  M AA and UA were added into  $5.0 \times 10^{-5}$  M DA. In the second study, tenfold more AA and UA were added to the  $5.0 \times 10^{-5}$  M DA solution. For the same concentration of AA, UA and DA and in the presence of tenfold more AA and UA, recovery values were calculated to be % 105.3 and % 94.2, respectively. These recovery values demonstrate that the developed system can detect DA in the presence of tenfold more AA and UA.

### Conclusions

Combination of PEDOT in the presence of SDS with centri-voltammetry yields very sensitive results for DA detection. The negative charge that SDS provides to the PEDOT electrode and enhanced accumulation of the analyte on this electrode by means of centrifugation are responsible for that. The interference studies stated that DA can be easily detected in the presence of 10 fold more AA and UA. Also the recovery value that was obtained from sample application work demonstrates that the developed system is suitable for DA detection in complex matrices like plasma samples. On the other hand, DA detection in real samples was conducted by using medicinal DA ampoules. As can be seen above, very accurate results were obtained demonstrating the usage of the developed system for DA detection in real samples. From the insight of these findings it can be concluded that a sensitive, selective and practical system has been developed for DA detection.

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