

## Electrochemical sensing of dopamine in the presence of ascorbic acid using carbon paste electrode modified with molybdenum Schiff base complex/1-butyl-3-methylimidazolium tetrafluoroborate

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### Abstract

In this paper, the carbon paste electrode (CPE) is modified using an ionic liquid (1-Butyl-3-methylimidazolium tetrafluoroborate, [BMIM]BF<sub>4</sub>) and the *cis*-dioxo-bis[3-methoxy-2,2-dimethylpropanediamine] molybdenum(VI) complex (*cis*-[Mo(O)<sub>2</sub>L]). In order to study the electrochemical behavior of ascorbic acid (AA) and dopamine (DA) at the surface of the prepared CPEs, the differential pulse and cyclic voltammetric methods (DPV and CV) were used. The presence of the [BMIM]BF<sub>4</sub> in the matrix of the modified CPE is optimized, and then the effect of the pH of the buffered solution on the electrode response and the resolution between the anodic peaks of AA and DA is studied by CV and DPV. These results reveal that by application of the modified CPE a peak resolution about 325mV is obtained for AA and DA and the linear range for AA and DA in buffered solutions of pH 5.0 is acquired in the range from  $5.0 \times 10^{-7}$  to  $1.0 \times 10^{-3}$  M. The respective limits of detection (S/N = 3) were  $1 \times 10^{-7}$  M and  $2 \times 10^{-7}$  M for DA and AA, respectively. Surface regeneration and the very easy preparation of the modified CPE together with the very good peak resolution and sub-micromolar detection limits designate the prepared CPE in this work appropriate for simultaneous voltammetric determination of DA and AA.

**Keywords:** Molybdenum Schiff base complex; [BMIM]BF<sub>4</sub>; dopamine; ascorbic acid; voltammetry.

### Introduction

Recently, the manufacture and design of modified sensors have been of notable interest [1,2]. Specially, detection of secretion neurotransmitters, e.g. ascorbic acid and dopamine as a vital nutritional factor, through the improvement of the electrochemical sensors received many interests. DA, a significant

neurotransmitter, exists in mammalian central nervous system and its primary content of DA is very low [3,4]. Both of the plant and animal kingdoms contain AA. Among animal organs, anterior pituitary lobe, leukocytes and the liver represent the highest content of AA. AA or vitamin C is also used in multivitamin preparations and various biological systems [5]. A serious

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problem in detection of DA or AA is the overlapping of the anodic peaks of AA and coexisting DA. The anodic oxidation potential of DA is close to that of AA at common solid electrodes and results in the lack of good resolution between their anodic peaks. Several methods have been applied in order to overcome this problem. For instance, the electrochemical behavior of DA was investigated at a glassy carbon electrode modified with graphene-zinc oxide composite [6], organic polymers-modified electrodes [7–9], nanoparticles [10] and complexes of metal [11] and so on. Recently, application of carbon nanotubes in modification of electrodes has performed for detection of DA [12–14]. In recent years, in order to determine these biologically important compounds chemically modified electrodes (CMEs) have extensively been applied. Application of functionalized carbon nanotubes [15–17], nanomaterials [18–20], complexes of transition metal [21–23] and organic electron mediators [24–26] in preparation of CMEs have attracted most consideration in this regard. Using the electron mediators in modification of the electrodes decrease in the overpotential of the electrochemical process of the interested analyte and of course improve the selectivity and sensitivity of the electrode response.

Previous works showed that Schiff base complexes are efficient electron mediators and the oxidation process of different biological compounds, such as AA can be catalyzed using them [23,27,28]. The major drawback in using redox mediators in the modification of the electrodes is the lack of good resolution for simultaneous determination of different analytes in the mixed samples. In other

words, the application of an electron mediator together with [BMIM]BF<sub>4</sub> can separate the voltammetric peaks of different compounds and improve the selectivity for their simultaneous detection. With Respect to the charge sign of various analytes and [BMIM]BF<sub>4</sub>, the electrostatic interactions can be exclusive or inclusive that is important for the improvement of the voltammetric resolution between the analytes peak. A nafion/reduced graphene oxide prepared film on the surface of carbon electrode has been applied in electrocatalytic oxidation of ascorbic acid [29]. Modification of carbon paste electrode using an ion pair (thionine/nafion) has been reported [18]. This electrode has been effective in simultaneous voltammetric determination of AA and DA by DPV. Triton X-100 (as a neutral surfactant) has been applied in preparation of the modified glassy carbon electrode [30]. Results of this work revealed that the hydrophobicity of the surfactant at the surface of the electrode is effective in promoting the electrochemical response of the studied heme proteins.

In the present work, the electrochemical oxidation of AA and DA at the surface of the modified carbon paste electrode containing the *cis*-[Mo(O)<sub>2</sub>L]/[BMIM]BF<sub>4</sub> is studied. Modification of the carbon paste electrode using the [BMIM]BF<sub>4</sub> results in increasing the anodic overpotential for DA oxidation. In order to obtain a higher sensitivity and selectivity in the voltammetric response of the modified electrode the effect of the [BMIM]BF<sub>4</sub> percent on the separation of the anodic peaks DA and AA is studied. Noteworthy, advantages of the modified-CPE in this paper such as ease of surface regeneration and fabrication, excellent resolution

between the anodic peaks of DA and AA and high stability of the *cis*-[Mo(O)<sub>2</sub>L] and [BMIM]BF<sub>4</sub> in its matrix designate it very useful for the sensitive and selective simultaneous detection of DA and AA.

## Experimental

### Materials

For the synthesis of the complex *cis*-dioxo-bis[3-methoxy-2,2-dimethylpropanediamine] molybdenum(VI), to a solution of 1 mmol [MoO<sub>2</sub>(acac)<sub>2</sub>] in 50 mL methanol was added a solution of 1 mmol 3-methoxy-2,2-dimethylpropanediamine (Schiff base ligand) in 10 mL methanol and the reaction mixture was stirred for 120 min at reflux condition. Then, the precipitated orange complexes were filtered and washed with methanol [31]. Spectroscopic mineral oil (Nujol), 1-Butyl-3-methylimidazolium tetrafluoroborate as an ionic liquid, and Graphite powder (20 μm) were purchased from Merck. All the other chemicals were purchased from Merck. Using doubly distilled deionized water, all aqueous solutions were made up. Stock solutions of DA and AA were freshly made up in a buffered solution and, before voltammetric experiments, purged with pure nitrogen gas (99.999%) for 120 s. The buffered solutions of DA and AA was deoxygenated by purging the pure nitrogen (99.999% from Roham Gas Company), and then was used for voltammetric studies. Nitrogen gas was passed over the surface of the test solutions during the measurements in order to avoid the influx of oxygen into the solution.

For the detection of the recovery in spiking of dopamine, the sample of fresh human serum, prepared from Razi Institute of Vaccine and Serum Co.

(Tehran, Iran), was filtered and diluted using a 0.1 M acetate buffer solution of pH 5.0. Each tablet was grounded with a mortar and pestle to detect AA in commercial vitamin preparations then 100 mg of the powdered sample was dissolved in 100 mL of the buffered solution.

### Apparatus

In order to make up the buffered solutions, a digital pH/mV/ion meter (CyberScan model 2500) was used. A common three-electrode system was applied with a platinum wire as a counter electrode, a saturated Calomel reference electrode, and modified or unmodified carbon paste working electrode. Voltammetric measurements were performed using a computerized potentiostat/galvanostat Autolab model 302 (Eco Chemie Utrecht) controlled with General Purpose Electrochemical System (GPES) software.

### Preparation of modified electrode

To prepare the unmodified CPE, a suitable amount of mineral oil with powder of graphite (~25:75, w/w) was mixed by hand mixing in a mortar and pestle, then a portion of the resulted mixture was packed into the end of a polyamide tube (ca. 2.5 mm i.d.). A copper pin makes the electrical contact into the back of the composite in the polyamide tube. The *cis*-[Mo(O)<sub>2</sub>L]-modified carbon paste electrode was fabricated by mixing the *cis*-[Mo(O)<sub>2</sub>L] (3%, w/w) with powder of graphite and a suitable amount of mineral oil, and then the resulted composite was dissolved in dichloromethane in order to reach better homogeneity and reproducibility by polishing the electrode surface. For fabrication of the *cis*-[Mo(O)<sub>2</sub>L]-modified carbon paste electrode containing [BMIM]BF<sub>4</sub>,

various percents of [BMIM]BF<sub>4</sub> together with 3 wt.% *cis*-[Mo(O)<sub>2</sub>L], powder of graphite and a suitable amount of mineral oil were mixed in an appropriate amount of dichloromethane. The solvent of the resulted mixture has been evaporated completely by stirring, and then air dried for one day and packed into the end of a polyamide tube.

## Results and discussion

### *Voltammetric experiments of AA and DA at the prepared electrodes*

Our previous work revealed that anodic overpotential for ascorbic acid oxidation is reduced and its oxidation process is catalyzed by Schiff base complexes [17]. The electrochemical behavior of 1 mM AA in a buffered solution of pH 5.0 at the surface of the unmodified CPE and the *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing various wt.% of [BMIM]BF<sub>4</sub> is studied by cyclic voltammetry. Results of this study are shown in Figure 1A. As can be observed, at the surface of the unmodified carbon paste electrode, a relatively broad wave in 480 mV is appeared for the anodic oxidation of AA. But, by introducing the *cis*-[Mo(O)<sub>2</sub>L] in the matrix of the carbon paste electrode (*cis*-[Mo(O)<sub>2</sub>L]/CPE), the anodic oxidation potential of AA is decreased to about 430 mV. At the surface of modified electrodes including *cis*-[Mo(O)<sub>2</sub>L] and different wt.% of [BMIM]BF<sub>4</sub>, this overpotential is slightly decreased with increasing the amount of [BMIM]BF<sub>4</sub> in the matrix of the electrode. A comprehensive explanation of the electrocatalytic oxidation of AA using the *cis*-[Mo(O)<sub>2</sub>L]/CPE is presented. AA, with a pK<sub>a</sub> of 4.17, mainly exists as an anionic form (ascorbate) under the experimental condition (buffered solution with pH 5.0). Therefore, there

is an electrostatic interaction between the anionic form of AA and the [BMIM]BF<sub>4</sub> on the surface of the modified-CPE including [BMIM]BF<sub>4</sub> (*cis*-[Mo(O)<sub>2</sub>L]/[BMIM]BF<sub>4</sub>/CPE). Results of this investigation reveal that the higher percents of [BMIM]BF<sub>4</sub>, because of decreasing the electrical conductivity of the electrode and unsuitable mechanical properties, result in worsening the voltammetric response of the modified-CPE, e.g. enlargement of the capacitive background current, broadening the wave shape and lowering the anodic peak. Hence, the percent of [BMIM]BF<sub>4</sub> in the matrix of the modified-CPE is optimized to obtain the excellent resolution between the voltammetric responses of DA and AA and also, higher sensitivity in voltammetric peaks (lower background current and greater anodic peak current).

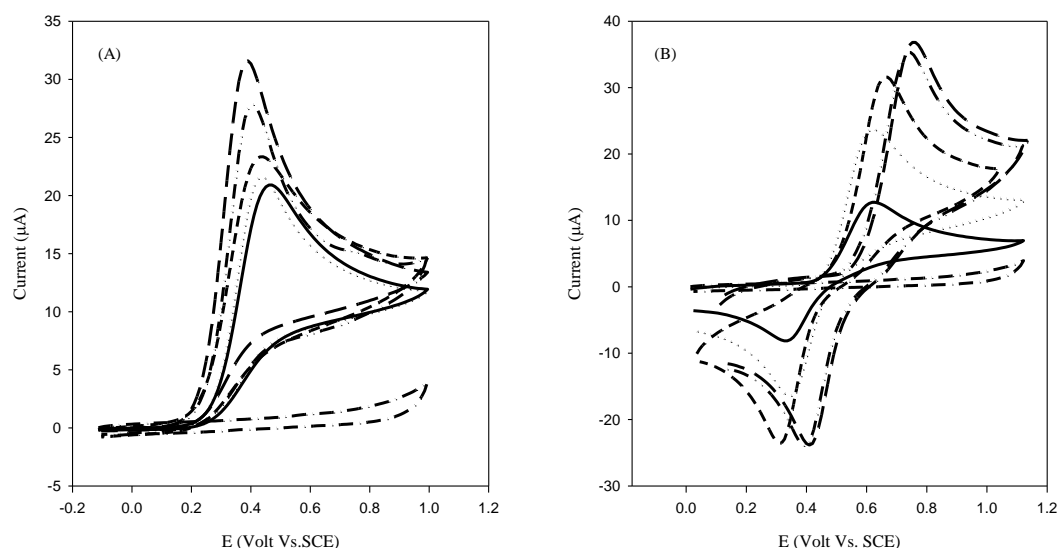
The electrochemical behavior of 1 mM DA in a buffered solution of pH 5.0 at the surface of the unmodified CPE and the *cis*-[Mo(O)<sub>2</sub>L]-modified carbon paste electrode containing various wt.% of [BMIM]BF<sub>4</sub> is studied by cyclic voltammetric method. The results of this study are shown in Fig. 1B. A pair of redox peaks with anodic and cathodic peak potentials respectively, 608 and 332 mV ( $\Delta E_p = 276$  mV) and the ratio of cathodic to anodic peak current ( $I_{p,c}/I_{p,a}$ ) nearly 0.88 were acquired for DA at unmodified carbon paste electrode (CPE). As a result, at the surface of CPE, the electrochemical process of DA is quasi-reversible and the oxidation product of DA under the empirical conditions (pH 5.0) is relative stable.

Previous studies revealed that oxidation product of DA (dopaminequinone) performed an intramolecular 1,4-Michael addition in

solutions of higher pHs [32]. In this reaction, a nucleophilic attack of external amine group on dopaminequinone leads to leucodopaminochrome. Thus buffered solution of pH 5.0 was selected for all experiments of DA in order to obtain a simple electron transfer and prevent the following reactions for DA. In fact, in solutions of  $\text{pH} \leq 5$ , DA contains protonated amine group and mostly exists in cationic form. Hence, the product of anodic oxidation of DA in acidic solutions will be almost stable and can be obtained about 1.0 for ratio of  $I_{p,c}/I_{p,a}$ .

Application of the [BMIM]BF<sub>4</sub> in the preparation of the modified-CPE causes

an increase in anodic overpotential of DA oxidation, because of the electrostatic interaction at the surface of the modified electrode between the positive charge of [BMIM]BF<sub>4</sub> and the cationic form of DA. As a result, the reversibility of the electrochemical process of DA at the surface of the electrode is decreased ( $\Delta E_p$  is increases) and its overpotential for oxidation is increased. As can be seen in Figure 1B by increasing the percent of [BMIM]BF<sub>4</sub> in the modified carbon paste electrode, this effect is intensified. The result of this effect is excellent resolution between the anodic peaks of AA and DA.



**Figure 1.** CV responses of blank buffered solution of pH 5.0 using *cis*-[Mo(O)<sub>2</sub>L]/modified CPE containing 1.5% [BMIM]BF<sub>4</sub> (-.-) and of 1 mM AA (A) and 1 mM DA (B) in the same buffer at the surface of unmodified CPE (—), CoL/modified CPE containing 0% (.....), 1% (---), 1.5% (-.-) and 2% [BMIM]BF<sub>4</sub> (---). Sweep rate: 100 mVs<sup>-1</sup>; pulse amplitude: 50 mV.

### Voltammetric experiments in the mixed solutions of DA and AA

Making an approach for separation of anodic peaks and simultaneous detection of AA and DA is very significant in clinical and analytical chemistry. At the traditional solid electrodes, the anodic overpotential for

oxidation of AA is the same as that of DA; furthermore, both of AA and DA are present simultaneously in mammalian brain which will cause to overlap the voltammetric responses of these species [33]. Many efforts have been made on the fabrication of the modified electrodes that are capable to

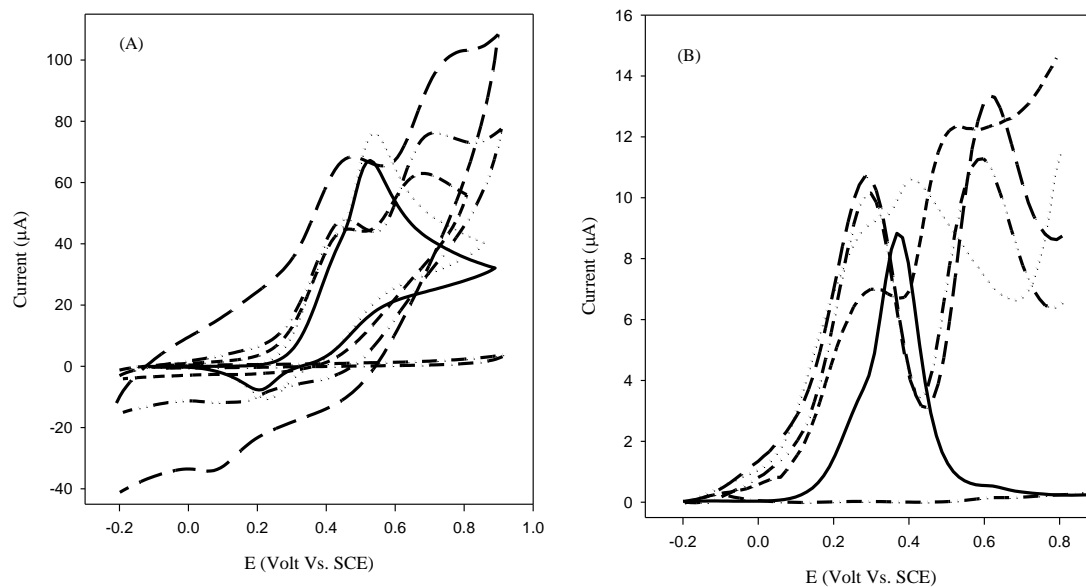


separate their anodic peaks and make the feasibility of simultaneous determination of DA and AA [21-26]. In this work, in order to simultaneous voltammetric detection of these compounds, the *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing [BMIM]BF<sub>4</sub> was used. The electrochemical behavior of 1 mM of both DA and AA in a buffered solution of pH 5.0 at the surface of the unmodified CPE and the *cis*-[Mo(O)<sub>2</sub>L]-modified carbon paste electrode containing various wt.% of [BMIM]BF<sub>4</sub> is studied by cyclic voltammetric method. The results of this study are shown in Fig. 2A. Fig. 2B shows the differential pulse voltammograms (DPVs) of five prepared electrodes in this solution. These figures revealed that at the surface of the unmodified CPE, only a quasi-reversible wave can be observed for DA and a distinguished wave cannot be obtained for AA, therefore this electrode (unmodified-CPE) isn't suitable for the simultaneous voltammetric detection of DA and AA. By introducing the *cis*-[Mo(O)<sub>2</sub>L] in the matrix of carbon paste electrode (*cis*-[Mo(O)<sub>2</sub>L]/CPE), a little resolution between anodic peaks of DA and AA is obtained but the detection of each compound in the presence of the other isn't possible because of the overlapping of their anodic peaks. Application of *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing [BMIM]BF<sub>4</sub>, results in more resolution of anodic peaks for DA and AA, because of positive shift of DA anodic peak. As can be seen in Figure 2, at the modified-CPE including 1.5 wt.% of [BMIM]BF<sub>4</sub>, the complete resolution between anodic peaks of DA and AA is obtained. The positive shift in anodic peak potentials of DA under the experimental condition (buffered solution of pH 5.0) is a result of the electrostatic repulsion effects

between the [BMIM]BF<sub>4</sub> and cationic form of dopamine. A better resolution does not obtained by using higher percents of [BMIM]BF<sub>4</sub>, whereas the sensitivity of electrode response to DA is decreased because of the resulted anodic overpotential and kinetic limitation for DA. Moreover, this investigation revealed that using of higher percents of [BMIM]BF<sub>4</sub> in modification of the electrode caused to limit the voltammetric detection limit for DA and AA (increase the capacitive background current). These efficacies can be obviously seen by comparing of the CVs or DPVs for the different modified CPEs in Figure 2. As a result, the *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing 1.5 wt.% [BMIM]BF<sub>4</sub> was selected for simultaneous detection of DA and AA. The resulting resolution between the anodic peaks of DA and AA in this investigation (325mV) is significantly more desirable than other reported voltammetric sensors. The modified electrode with nanocomposite of carbon dots/ferrocene derivative functional Au NPs and graphene obtained a peak resolution for DA and AA about 180 mV using differential pulse voltammetry [34]. Application of a nanocomposite containing polypyrrole/Cu<sub>x</sub>O-ZnO in modification of the electrode for voltammetric detection of AA and DA resulted in a peak separation of 150 mV [35]. The electrode modified with nanoparticles of  $\gamma$ -WO<sub>3</sub> is applied using DPV for simultaneous detection of AA and DA and a peak resolution of 133 mV is obtained [36]. In comparison to the previous works, the decay of anodic current between the anodic peaks of DA and AA is taken place close to the capacitive background by using the *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing [BMIM]BF<sub>4</sub>. The resulted decay of current significantly causes to decrease

the overlapping of the anodic waves of DA and AA, and simultaneous detection of these compounds in mixture samples possesses a more desirable accuracy. Moreover the

reproducibility of the detections is improved due to more stability of DA and AA in slightly acidic condition (pH 5.0).



**Figure 2.** (A) CV and (B) DPV responses of blank buffered solution of pH 5.0 using *cis*-[Mo(O)<sub>2</sub>L]/modified CPE containing 1.5% [BMIM]BF<sub>4</sub> (-.-) and of a mixture of 1 mM DA and 1 mM AA in the same buffer at the surface of unmodified CPE (—), CoL/modified CPE containing 0% (.....), 1% (---), 1.5% (-.-) and 2% [BMIM]BF<sub>4</sub> (---). Sweep rate: 100 mVs<sup>-1</sup>; pulse amplitude: 50 mV.

### The effect of pH and sweep rate

Voltammetric studies of the buffered solutions with different pHs containing AA and DA were carried out to find out the optimized pH for acquiring the good sensitivity and an excellent resolution between their anodic peaks. In these experiments, 0.1 M phosphate was applied in preparation of buffered solutions of pH 3.0, 6.0 and 7.0, and 0.1 M acetate for pHs 4.0 and 5.0. Table 1 shows the peak potentials and peak currents of cyclic voltamograms obtained at the surface modified CPE in the mixture solutions of DA and AA with different pHs. These results reveal that the best peak separation is resulted in pH 5.0. Therefore in all voltammetric studies, the buffered solution with pH

5.0 was applied as supporting electrolyte.

In order to investigate the effect of the potential scan rate, cyclic voltammetric experiments were carried out in the buffered solution with pH 5.0. The results revealed that the anodic peak currents ( $I_{p,a}$ ) of DA and AA increase linearly with increasing the square root of the scan rate ( $v^{1/2}$ ) in the range of 25–200 mVs<sup>-1</sup>. These results corroborate the diffusion-controlled anodic oxidation of DA and AA at the prepared CPE surface. The current function ( $I_p/v^{1/2}$ ) for AA decreased with  $v^{1/2}$ , which corroborates a catalytic manner for AA at the surface of the modified CPE, whereas for DA can't be seen this effect.

**Table 1.** Variation of peak potential and peak current of cyclic voltammograms for mixture solutions of DA and AA with pH using *cis*-[Mo(O)<sub>2</sub>L]/modified CPE containing 1.5 wt.% of [BMIM]BF<sub>4</sub>

pH	AA		DA		
	I <sub>p,a</sub> (μA)	E <sub>p,a</sub> (mV)	I <sub>p,a</sub> (μA)	E <sub>p,a</sub> (mV)	ΔE <sub>p</sub> (mV)
3	24.2	458	23.6	731	273
4	19.9	421	22.5	722	301
5	22.5	395	25.3	710	315
6	18.8	391	23.8	679	288
7	16.5	387	23.3	668	281

### Analytical characterization

The differential pulse voltammetric method using the *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing 1.5 wt.% of [BMIM]BF<sub>4</sub> was applied as a useful method with low limits of detection for detections of DA and AA in a wide range of their concentrations. Supporting electrolyte for these experiments was buffered solutions of pH 5.0. Figure 3 shows some obtained DPV waves in these experiments. By drawing the anodic current signal versus the concentration (the calibration curves), a linear range is obtained that is  $5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$  M for DA and AA (Figure 4). A slope of 9355.75 μA/M ( $R^2 = 0.9991$ ) is resulted for AA, and a slope of 6534.37 μA/M ( $R^2 = 0.9988$ ) for DA. The relative standard deviations (R.S.D.) for these slopes on the basis of five replicates were 3.2 and 3.6% for DA and AA, respectively and were less than 3.5% for both DA and AA, based on seven measurements in a period of two months. So the prepared modified CPE in this work revealed to be very stable.

The differential pulse voltammograms obtained in solutions containing  $5 \times 10^{-4}$  M AA and five various amounts of DA from  $4 \times 10^{-4}$  to  $1 \times 10^{-3}$  M are shown in Fig. 5A. The waves obtained in solutions including  $5 \times 10^{-5}$  M DA and various amounts of AA in the range of  $5 \times 10^{-5}$  to  $9 \times 10^{-4}$  M is represented in Figure 5B. Using the modified CPE in

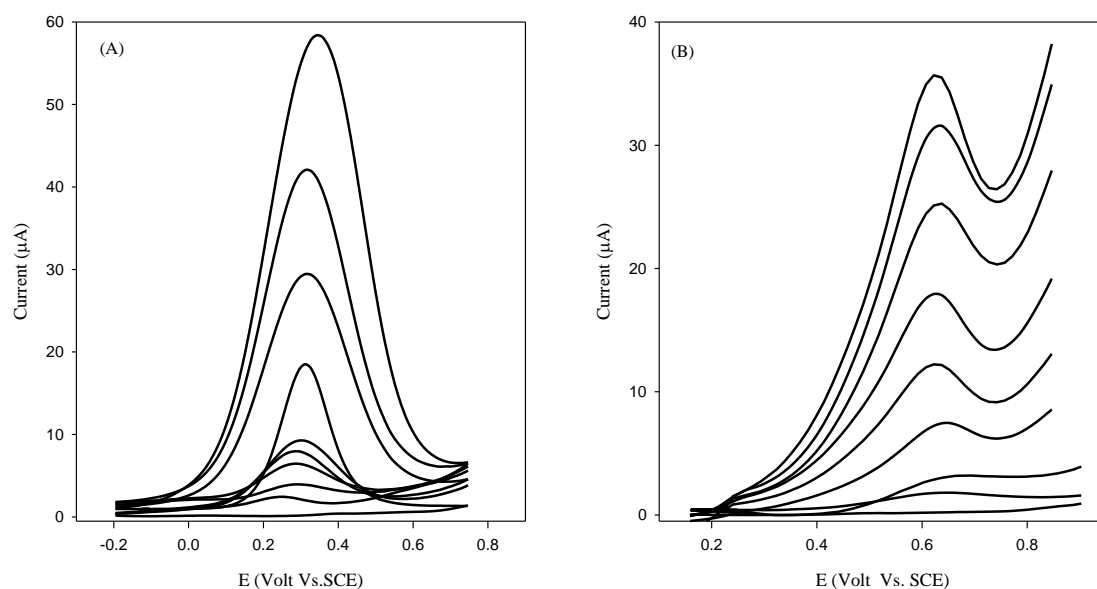
this work, a linear range for AA in buffered solutions of pH 5.0 is acquired in the range from  $6.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$  M and for DA from  $7.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$  M. The respective limits of detection ( $S/N = 3$ ) were  $4 \times 10^{-7}$  M and  $3 \times 10^{-7}$  M for DA and AA, respectively. The resulted limits of detection and linear ranges were very similar to the detections in solutions containing only one of DA or AA. In the presence of  $5 \times 10^{-4}$  M AA, the calibration curve slope for DA was 6402.99 μA/M ( $R^2 = 0.9989$ ), which was about 98% of the resulted slope value for the separate DA solutions. This slope for AA, in the presence of  $5 \times 10^{-5}$  M DA was 9074.58 μA/M ( $R^2 = 0.9984$ ).

To evaluate the validity of the proposed method, the *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing 1.5 wt.% of [BMIM]BF<sub>4</sub> was applied for simultaneous determination of AA and DA in human urine samples. In order to avoid the interferences of the real samples matrix and fit into the linear ranges of AA and DA only diluted urine samples were added into the electrochemical cell. The urine samples were diluted with solutions of pH 5.0 before detection. To ascertain the correctness of the results, real samples were analyzed by the standard addition method and the diluted samples mentioned above were spiked with certain amounts of AA and DA and then detected. The recovery of the

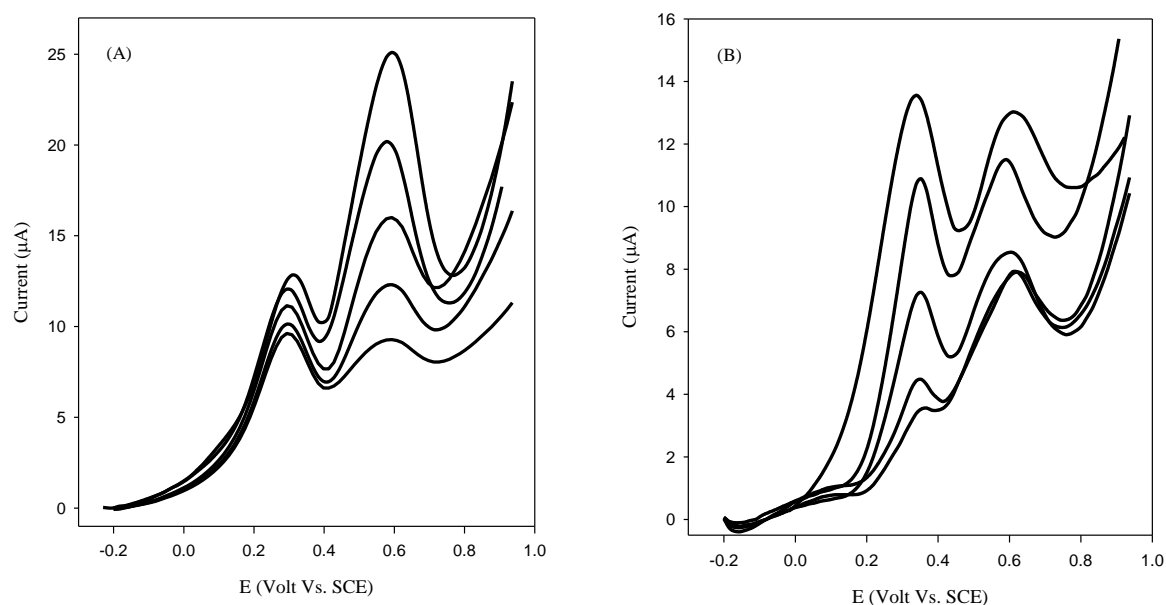


spiked samples ranged from 97.1% to 103.4% (Table 2), indicating that the *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing 1.5 wt.% of [BMIM]BF<sub>4</sub>

was reliable and sensitive enough for the determination of AA and DA in real samples.



**Figure 3.** Differential pulse voltammograms of buffered solution of pH 5.0 containing (A) 0.0, 0.005, 0.05, 0.08, 0.1, 0.3, 0.5, 0.7, 0.9, 0.8 and 1.0 mM AA and (B) 0.0, 0.005, 0.02, 0.04, 0.05, 0.08, 0.1, 0.4, 0.8 and 1.0 mM DA (down to up). Pulse amplitude: 50 mV.



**Figure 5.** Differential pulse voltammograms for buffered solution of pH 5.0 containing (A) 0.5 mM AA (constant) and various concentrations of DA: 0.3, 0.5, 0.7, 0.9, 1.0 mM. (B) 0.5 mM DA (constant) and various concentrations of AA: 0.05, 0.1, 0.5, 0.7, 0.8 and 0.9 mM. Pulse amplitude: 50 mV.

**Table 2.** Determination of AA and DA in human urine samples (n = 6) using *cis*-[Mo(O)<sub>2</sub>L]/modified CPE containing 1.5wt.% of [BMIM]BF<sub>4</sub>

Sample	Spicies	Detected (μM)	Added (μM)	Found (μM)	Recovery (%)
Urine 1	AA	-	200.0	204.4	102.2
	DA	-	30.0	30.4	101.3
Urine 2	AA	-	210.0	206.5	98.3
	DA	-	50.0	51.7	103.4
Urine 3	AA	-	205.0	209.9	102.3
	DA	-	40.0	39.0	97.5
Urine 4	AA	-	180.0	185.2	102.9
	DA	-	45.0	43.7	97.1

### Conclusion

The *cis*-[Mo(O)<sub>2</sub>L]-modified CPE containing [BMIM]BF<sub>4</sub> prepared in the present work can enhance the selectivity and resolution of voltammetric responses of DA and AA. This modified CPE has been revealed to be capable to separate the anodic peaks of DA and AA. The detection limits for determination of AA and DA is higher than some previous works but the linear range and the resolution between the anodic peaks for

determination of AA and DA is much better than the previous reported works,. Table 3 shows a comparison of analytical properties for the detection of DA and AA at the prepared electrode in this work and various electrodes. Application of the modified CPE in differential pulse voltammetric method in this work results in a good resolution more than 320 mV for anodic peaks of AA and for six replicates in the spiked range of DA and AA concentration, R.S.D. was less than 3.2%.

**Table 3.** Various modified electrodes: DA and AA analytical properties

Electrode	Experimental condition	Method	$\Delta E_p$ (mV)	Linear range (μA)		DL (μA)		Ref.
				DA	AA	DA	AA	
Carbon Paste-modified GCE	pH 7.0 PBS	DPV	187	3.84 - 27.0	19.2 - 135	1.5	8.3	[6]
CPE modified with [Cu(bp)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	pH 5.0 PBS	DPV	200	0.05 - 30.0	0.05 - 30.0	0.04	0.02	[18]
GCE modified with CuNP/p-TA <sub>ox</sub>	pH 4.0 PBS	DPV	205	0.6 - 21.6	240 - 750	0.03	5.0	[20]
Polyethylene oxide-modified GCE	pH 5.0 PBS	DPV	216	5.0 - 40	300 - 1700	0.25	50	[25]
CCE modified MWCNTs-MIP	pH 4.5 PBS	DPV	300	1.72-11.58	16.83-226	0.21	2.24	[26]
GCE modified with ZnO-Cu <sub>x</sub> O-PPy	pH 4.0 BR solution	DPV	150	0.1-130	0.2-1.0	0.04	25.0	[38]
GCE modified	pH 7.0	DPV	133	0.1-600	-	0.024	-	[39]

with $\gamma$ -WO <sub>3</sub>	PBS								
<i>cis</i> - [Mo(O) <sub>2</sub> L]/[BM IM]BF <sub>4</sub> /CPE	pH 5.0 0.1M acetate buffer	DPV	325	5.0-1000	5.0-1000	0.4	0.3	This work	

Note: CP, carbon paste; GCE, glassy carbon electrode; [Cu(bp)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>, polymer of 4,4'-dicyanamidobiphenyl Cu(II) complex; CuNP, Copper nanoparticles; p-TAox, overoxidized poly(3-amino-5-mercapto-1,2,4-triazole); MWCNTs, multiwalled carbon nanotubes ; MIP, molecularly imprinted polymer; PPy, polypyrrole;  $\gamma$ -WO<sub>3</sub>, monoclinic structure of Tungsten trioxide nanoparticles.

DA making it very appropriate and efficient for simultaneous detection of these compounds. Surface regeneration and very easy preparation of the modified electrode together with the acceptable selectivity and sensitivity, sub-micomolar detection limit and good reproducibility of the voltammetric response represent the prepared modified system is very effective in the fabrication of accessible tools for the simultaneous detection of DA and AA in pharmaceutical and clinical preparations.

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