

*Full Paper*

## **Simultaneous Detection of Dopamine and Ascorbic Acid at Cobalt Schiff Base Complex/Surfactant-Modified Carbon Paste Electrode**

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**Abstract-** The complex N,N'-bis(5-Chloro salicylidene) 2,2-dimethyl-1,3-propandiamino cobalt (II) chloride (CoClSal) and 1-octanaminium,N,N,N-trioctyl bromide (as a cationic surfactant) are used for the preparation of the modified carbon paste electrode (CPE). The cyclic and differential pulse voltammetric methods (CV and DPV) used to study of the electrochemical behavior of ascorbic acid (AA) and dopamine (DA) at the surface of the cobalt Schiff base complex-modified CPE containing different percents of cationic surfactant. The effects of the buffered solution pH and potential sweep rate on the electrode response and the resolution between the anodic peaks of AA and DA are studied by CV and DPV. Using the modified electrode, the best peak separation (344 mV) for these compounds is obtained in solutions with pH 5.0. Surface regeneration and the very easy preparation of the modified CPE together with the efficient electrocatalytic property, very good peak resolution and reproducibility of its voltammetric responses designate the modified CPE in this work appropriate for simultaneous voltammetric determination of DA and AA.

**Keywords-** Modified electrode, Surfactant, Dopamine, Differential pulse voltammetry

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### **1. INTRODUCTION**

Recently, the manufacture and design of new voltammetric sensors have been of notable interest [1,2]. Specially, detection of secretion neurotransmitters, e.g. ascorbic acid (AA) and

dopamine (DA) 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 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]. Recently, application of carbon nanotube in modification of electrode has performed for detection of DA [12–14]. In recent years, in order to the determination of these biologically important compounds, chemically modified electrodes (CMEs) have extensively been applied. Application of functionalized carbon nanotubes [15–17], polymeric 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, causes to decrease 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 cobalt Schiff base complexes are efficient electron mediators and can catalyze the oxidation process of different biological compounds, such as AA [23,27,28]. The major drawback in the using of redox mediators in the modification of the electrode is lack of good resolution for simultaneous determination of different analytes in the mixed samples. On the other hand, the application of an electron mediator together with the ionic surfactant in the preparation of modified electrodes, because of the electrostatic repulsion or attraction between the charged analytes and the surfactant, can separate the voltammetric peaks of different compounds and improve the selectivity for their simultaneous detections. Respect to the charge sign of various analytes and the ionic surfactant, the electrostatic interactions can be exclusive or inclusive that is important for the improvement of the voltammetric resolution between the peaks of these analytes. A graphene/ Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-ionic liquid nanocomposite modified carbon paste 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 Schiff base complex of cobalt/cationic surfactant is studied. Modification of the carbon paste electrode using the cationic surfactant 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 cationic surfactant percent on the resolution between the anodic peaks of DA and AA is studied. Noteworthy advantages of the modified-CPE in this paper such as excellent resolution between the anodic peaks of DA and AA, ease of surface regeneration and fabrication, high stability of the Schiff base complex of cobalt and cationic surfactant in its matrix designate it very useful for the sensitive and selective simultaneous detection of DA and AA.

## 2. EXPERIMENTAL

### 2.1. Apparatus and chemicals

In order to make up the buffered solutions, a digital pH/mV/ion meter (CyberScan model 2500, Eutech Instruments) 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, the Netherlands) controlled with General Purpose Electrochemical System (GPES) software.

For the synthesis of the complex N,N'-bis(5-Chloro salicylidene) 2,2-dimethyl-1,3-propandiamino cobalt(II), 2 mmol 5-dichloro-salicylaldehyde-2,2-dimethyl-1,3-propanediamine (Merck, Darmstadt, Germany) was added to the ethanolic solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (2.1 mmol/30 ml, Merck, Darmstadt, Germany) [31]. The mixture was stirred for 30 min with reflux, then resultant was filtered and through slow evaporation of the solvents at room temperature over several days, the complex crystals were obtained [31]. Spectroscopic mineral oil (Nujol), Graphite powder (20 μm), and 1-octanaminium,N,N,N-trioctyl bromide as a cationic surfactant were purchased from Merck (Darmstadt, Germany). All the other chemicals were analytical reagent grade, purchased from Merck (Darmstadt, Germany). 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 the voltammetric experiments, purged with pure nitrogen gas (99.999%) for 120 s. The buffered solutions of DA and AA were deoxygenated by purging the pure nitrogen (99.999% from Roham Gas Company, Tehran, Iran), and then were 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.

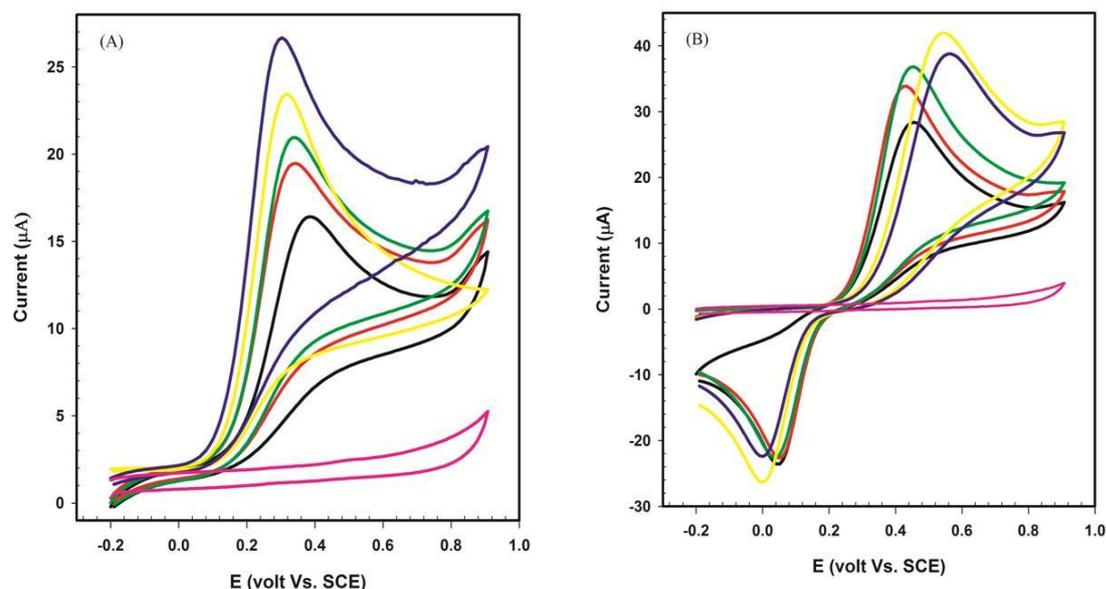
## 2.2. Preparation of modified electrode

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 cobalt Schiff base complex-modified carbon paste electrode was fabricated by mixing the Schiff base complex of cobalt (3%, w/w) with powder of graphite and a suitable amount of mineral oil, and then the resulting composite was dissolved in dichloromethane in order to better homogeneity and reproducibility by polishing the electrode surface. For fabrication of the cobalt Schiff base complex-modified carbon paste electrode containing surfactant, various percents of cationic surfactant together with 3 wt.% of Schiff base complex of cobalt, 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.

## 3. RESULTS AND DISCUSSION

### 3.1. Voltammetric experiments of AA at the prepared electrodes

Our previous work revealed that anodic overpotential for ascorbic acid oxidation is reduced and its oxidation process is catalyzed by cobalt 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 cobalt Schiff base complex-modified CPE containing various wt.% of cationic surfactant is studied by cyclic voltammetry. Results of this study are shown in Fig. 1A. As can be observed, at the surface of the unmodified carbon paste electrode, a relatively broad wave in 382 mV is appeared for the anodic oxidation of AA. But, by introducing the cobalt Schiff base complex in the matrix of the carbon paste electrode (CoClSal/CPE), the anodic oxidation potential of AA is decreased to about 340 mV. At the surface of modified electrodes including Schiff base complex of cobalt and different wt.% of cationic surfactant, this overpotential is slightly decreased with increasing the amount of surfactant in the matrix of the electrode.



**Fig. 1.** CV responses of blank buffered solution of pH 5.0 using CoClSal /modified CPE containing 2% CS (pink) and of 1 mM AA (A) and 1 mM DA; (B) in the same buffer at the surface of unmodified CPE (black), CoL/modified CPE containing 0% (red), 1% (green), 2% (yellow) and 3% CS (dark blue). Sweep rate:  $100 \text{ mVs}^{-1}$ ; pulse amplitude: 50 mV

A comprehensive explanation of the electrocatalytic oxidation of AA using the CoClSal/CPE is presented in the following. AA, with a  $pK_a$  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 cationic surfactant on the surface of the modified-CPE including cationic surfactant (CoClSal/CS/CPE). Results of this investigation revealed that the higher percents of cationic surfactant, 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 cationic surfactant 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).

### 3.2. Voltammetric experiments of DA at the prepared electrodes

The electrochemical behavior of 1 mM DA in a buffered solution of pH 5.0 at the surface of the unmodified CPE and the cobalt Schiff base complex-modified carbon paste electrode containing various wt.% of cationic surfactant 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, 449 and 48 mV ( $\Delta E_p=401$  mV) and the ratio of cathodic to anodic peak current ( $I_{p,c}/I_{p,a}$ ) nearly 0.90 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 the product of DA (dopaminequinone) performed an intramolecular 1,4-Michael addition in solutions of higher pHs [32], that 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  $I_{p,c}/I_{p,a}$ .

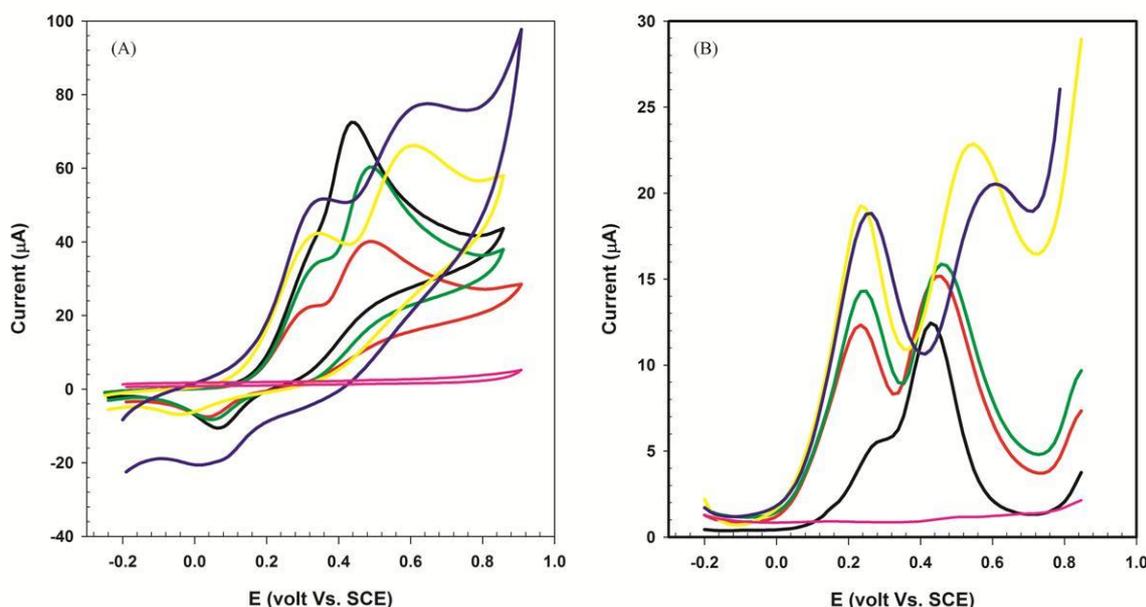
Application of the cationic surfactant in the preparation of the modified-CPE causes an increase in anodic overpotential of DA oxidation, because of the electrostatic interaction at the surface of the modified electrode between the positive charge of cationic surfactant and the cationic form of DA. As 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 Fig. 1B by increasing the percent of cationic surfactant 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.

### 3.3. 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 the present work, for simultaneous voltammetric detection of these compounds, the cobalt Schiff base complex-modified CPE containing cationic surfactant 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 cobalt Schiff base complex-modified carbon paste electrode containing various wt.% of cationic surfactant 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 cobalt Schiff base complex in the matrix of carbon paste electrode (CoClSal/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 cobalt Schiff base complex-modified CPE containing cationic surfactant, results in more resolution of anodic peaks for DA and AA, because of positive shift of DA anodic peak. As can be seen in Fig. 2, at the modified-CPE including 2 wt.% of cationic surfactant, 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 cationic surfactant and cationic form of dopamine. A better resolution does not obtained



**Fig. 2.** (A) CV and (B) DPV responses of blank buffered solution of pH 5.0 using CoClSal/modified CPE containing 2% CS (pink) and of a mixture of 1 mM DA and 1 mM AA in the same buffer at the surface of unmodified CPE (black), CoL/modified CPE containing 0% (red), 1% (green), 2% (yellow) and 3% CS (dark blue). Sweep rate:  $100 \text{ mVs}^{-1}$ ; pulse amplitude: 50 mV

By using higher percent of cationic surfactant, 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 percent of cationic surfactant 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 Fig. 2. As a result, the cobalt Schiff base complex-modified CPE containing 2 wt.% cationic surfactant was selected for simultaneous detection of DA and AA.

The resulting resolution between the anodic peaks of DA and AA in this investigation (314 mV) 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 cobalt Schiff base complex-modified CPE containing cationic surfactant. 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).

### 3.4. 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.

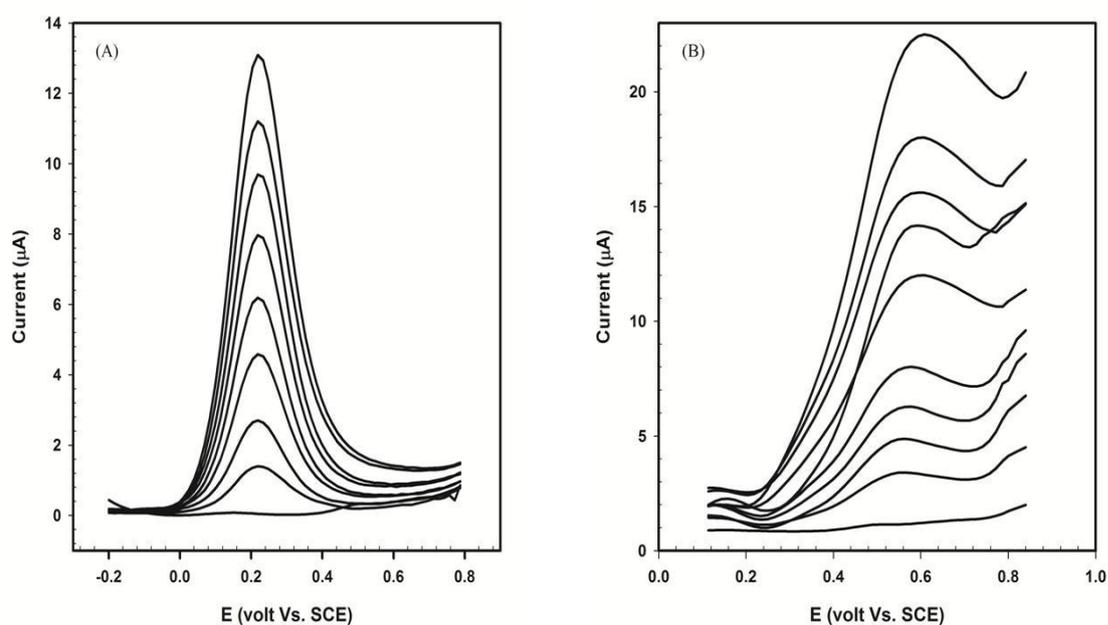
**Table 1.** Variation of peak potential and peak current of cyclic voltammograms for mixture solutions of DA and AA with pH using CoClSal/modified CPE containing 2 wt.% of cationic surfactant

pH	AA		DA		$\Delta E_p$
	$I_{p,a}$ ( $\mu$ A)	$E_{p,a}$ (mV)	$I_{p,a}$ ( $\mu$ A)	$E_{p,a}$ (mV)	
3	18.6	435	18.6	720	285
4	16.4	395	18.5	682	287
5	14.1	299	19.2	615	316
6	16.1	295	18.8	597	302
7	8.8	296	16.3	585	289

Table 1 shows the peak potentials and peak currents of cyclic voltammograms 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 of 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  $\text{mVs}^{-1}$ . 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.

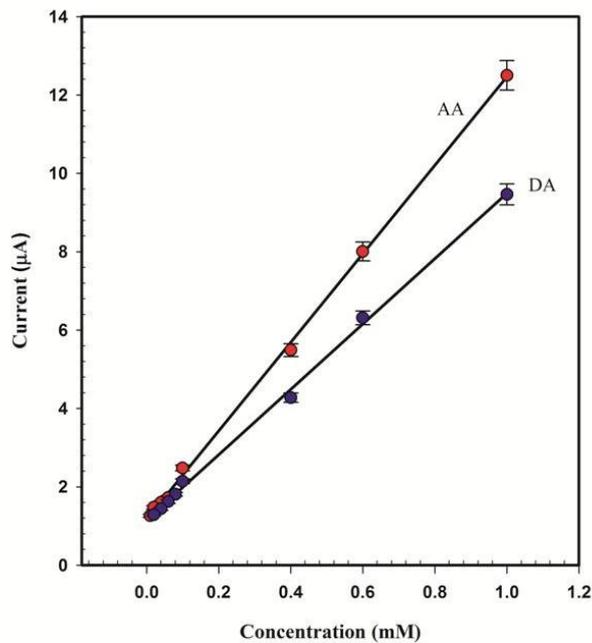
### 3.5. Analytical characterization

The differential pulse voltammetric method using the cobalt Schiff base complex-modified CPE containing 2 wt.% of cationic surfactant 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. Fig. 3 shows some obtained DPV waves in these experiments.

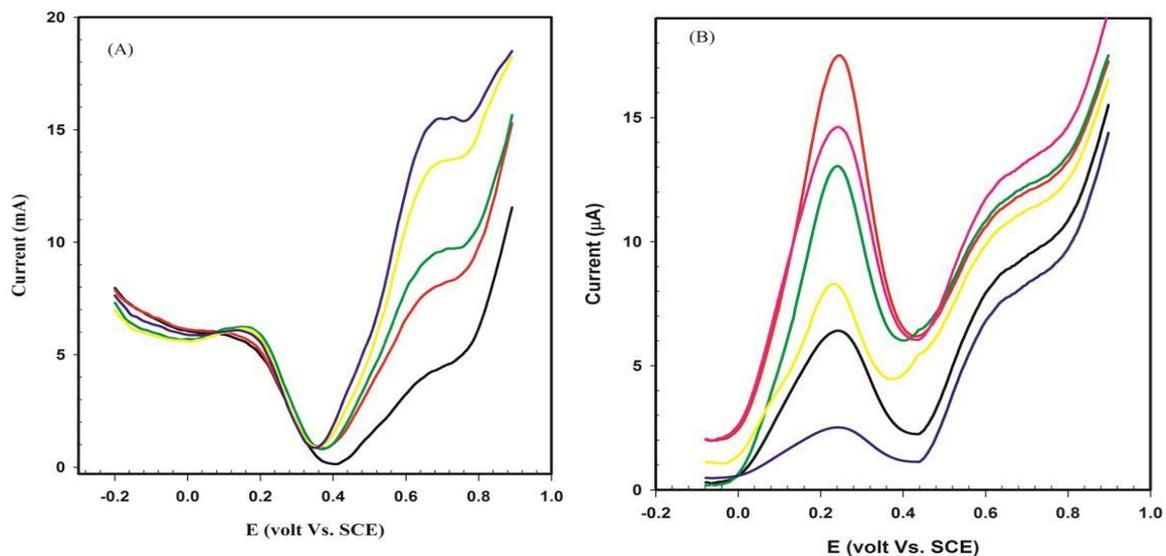


**Fig. 3.** Differential pulse voltammograms of buffered solution of pH 5.0 containing (A) 0.0, 0.01, 0.1, 0.2, 0.4, 0.5, 0.7, 0.8 and 1.0 mM AA and (B) 0.0, 0.01, 0.08, 0.1, 0.2, 0.4, 0.5, 0.6, 0.7 and 1.0 mM DA (down to up). Pulse amplitude: 50 mV

By drawing the anodic current signal versus the concentration (the calibration curves), a linear range is obtained that is  $1.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$  M for AA and DA (Fig. 4). A slope of  $11.2998 \mu\text{A}/\text{mM}$  ( $R^2=0.9991$ ) is resulted for AA, and a slope of  $8.3430 \mu\text{A}/\text{mM}$  ( $R^2=0.9984$ ) for DA.



**Fig. 4.** Linear calibration curves of current signals versus DA and AA concentration in the range 10.0 to 1000.0  $\mu\text{M}$



**Fig. 5.** Differential pulse voltammograms for buffered solution of pH 5.0 containing (A) 0.1 mM AA (constant) and various concentrations of DA: 0.01, 0.02, 0.1, 0.2, 0.3 mM; (B) 0.05 mM DA (constant) and various concentrations of AA: 0.1, 0.3, 0.4, 0.7, 0.8 and 1.0 mM; Pulse amplitude: 50 mV

The relative standard deviations (R.S.D.) for these slopes on the basis of five replicates were 3.2 and 3.3% for DA and AA, respectively and were less than 3.2% 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  $1 \times 10^{-4}$  M AA and five various amounts of DA from  $1 \times 10^{-5}$  to  $3 \times 10^{-4}$  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  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  M is represented in Fig. 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  $1 \times 10^{-6}$  to  $1 \times 10^{-3}$  M and for DA from  $2 \times 10^{-6}$  to  $1 \times 10^{-3}$  M. The respective limits of detection ( $S/N = 3$ ) were  $5 \times 10^{-7}$  M and  $4 \times 10^{-7}$  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  $1 \times 10^{-4}$  M AA, the calibration curve slope for DA was  $8.1761 \mu\text{A}/\text{mM}$  ( $R^2 = 0.9987$ ), 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  $10.9609 \mu\text{A}/\text{mM}$  ( $R^2 = 0.9945$ ).

The cobalt Schiff base complex-modified CPE containing 2 wt.% of cationic surfactant was successfully used in determination of AA in pharmaceutical preparations through the standard addition method.

**Table 2.** AA analysis results in vitamin preparations using CoClSal /modified CPE containing 2 wt.% of cationic surfactant

Sample	Sample preparation	AA found (mg/100 mg powdered sample) <sup>a</sup>		
		Present method	Reference method	Recovery (%)
1	Vitamin C tablet	66.6 ( $\pm 1.9$ )	67.1	-
2	Sample 1 + 10.0 mg AA	75.5 ( $\pm 2.1$ )	-	98.6
3	Sample 1 + 20.0 mg AA	88.7 ( $\pm 2.4$ )	-	102.4
4	Sample 1 + 30.0 mg AA	94.9 ( $\pm 2.2$ )	-	98.2
5	Effervescent tablet	36.0 ( $\pm 1.2$ )	35.2	-
6	Sample 5 + 10.0 mg AA	47.8 ( $\pm 1.1$ )	-	103.9
7	Sample 5 + 20.0 mg AA	54.5 ( $\pm 1.5$ )	-	97.3
8	Sample 5 + 30.0 mg AA	95.1 ( $\pm 0.14$ )	-	99.0
9	Multivitamin drop <sup>b</sup>	36.3 ( $\pm 1.5$ )	37.0	-
10	Sample 9 + 10.0 mg AA	44.5 ( $\pm 2.0$ )	-	96.1
11	Sample 9 + 20.0 mg AA	58.0 ( $\pm 2.0$ )	-	103.0
12	Sample 9 + 30.0 mg AA	67.4 ( $\pm 2.0$ )	-	101.7

<sup>a</sup>Replicates Number was five

<sup>b</sup>Labeled value for AA was 35 mg/ml. Determined values are also in mg/ml

The analyzed vitamin preparations were effervescent tablets (Osvah Co.), multivitamin drops (Shahre Daro Co.) and vitamin C tablets (Osvah Co.). In addition to vitamin C, the multivitamin drops contained sodium saccharin and vitamins such as A, D, E, B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>, B<sub>6</sub>, and B<sub>12</sub>. As a reference method, the method of U.S. Association of Official Analytical Chemists (AOAC) [37] on the basis of using 2,6-dichloro-phenolindophenol was used. Table 2 shows the results of the experiments in different samples of vitamin and the results of the spiked samples with AA standard solutions. These results reveal that the prepared electrode in this work could be successfully used for the detection of AA in pharmaceutical samples because of the good enough precision and recovery. This modified electrode was also used for the recovery measurement in dopamine hydrochloride spiking to human serum samples. The results of these experiments are shown in Table 3.

**Table 3.** Recovery Results of the spiked DA to 10.0 ml of the diluted (10-fold) human serum sample

No.	Amounts of added DA ( $\mu\text{M}$ )	Amounts of found <sup>a</sup> DA ( $\mu\text{M}$ )	Recovery (%)
1	10.0	10.4	104.0
2	25.0	25.6	102.4
3	50.0	48.7	97.4
4	75.0	73.5	98.0
5	100	101.2	101.2

<sup>a</sup>For five replicates in the spiked range of DA concentration, R.S.D. was less than 4.0%

#### 4. CONCLUSION

The cobalt Schiff base complex-modified CPE containing cationic surfactant 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. Resulted resolution is much better than the previous reported works. Application of the modified CPE in differential pulse voltammetric method in this work, results in a good resolution more than 340 mV for anodic peaks of AA and 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-micromolar 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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## **REFERENCES**

- [1] F. Garkani-Nejad, H. Beitollahi, and R. Alizadeh, *Anal. Bioanal. Electrochem.* 9 (2017) 134.
- [2] E. Dasht-Razmi, F. Ebadi-Nejad, S. Y. Kazemi, S. M. Abedirad, R. Alizadeh, S. Jahani, and H. Beitollahi, *Anal. Bioanal. Electrochem.* 8 (2016) 423.
- [3] D. W. Martin Jr., P. A. Mayes, and V. W. Rodwell (Eds.), *Harper's Review of Biochemistry*, 19th ed., Lange, Los Altos, CA (1983) p. 112.
- [4] R. M. Wightman, C. Amatorh, R. C. Engstrom, P. D. Hale, E. W. Kristensen, W. G. Kuhr, and L. J. May, *Neuroscience* 25 (1988) 513.
- [5] A. J. Downard, A. D. Roddick, and A. M. Bond, *Anal. Chim. Acta* 317 (1995) 303.
- [6] X. Zhang, Y. C. Zhang, and L. X. Ma, *Sens. Actuators B* 227 (2016) 488.
- [7] X. Zheng, Y. Guo, J. Zheng, X. Zhou, Q. Li, and R. Lin, *Sens. Actuators B* 213 (2015) 188.
- [8] M. A. Sheikh-Mohseni, and S. Pirsa, *Anal. Bioanal. Electrochem.* 8 (2016) 777.
- [9] B. Mudabuka, A. S. Ogunlaja, Z. R. Tshentu, and N. Torto, *Sens. Actuators B* 222 (2016) 598.
- [10] M. P. Deepak, M. P. Rajeeva, and G. P. Mamatha, *Anal. Bioanal. Electrochem.* 8 (2016) 931.
- [11] J. Oni, P. Westbroek, and T. Nyokong, *Electroanalysis* 15 (2003) 847.
- [12] A. Kutluay, and M. Aslanoglu, *Anal. Chim. Acta* 839 (2014) 59.
- [13] A. A. Abdelwahab, and Y. B. Shim, *Sens. Actuators B* 221 (2015) 659.
- [14] B. Yu, H. Yuan, Y. Y. Yang, H. L. Cong, T. Z. Hao, X. D. Xu, X. L. Zhang, Sh. J. Yang, and L. X. Zhang, *Chinese Chem. Lett.* 25 (2014) 523.
- [15] M. Mazloun-Ardakani, S. H. Ahmadi, Z. S. Mahmoudabadi, and A. Khoshroo, *Measurement* 91 (2016) 162.
- [16] D. Ragupathy, A. I. Gopalan, and K. Lee, *Sens. Actuators B* 143 (2010) 696.
- [17] S. Shahrokhian, and H. R. Zare-Mehrjardi, *Electrochim. Acta* 52 (2007) 6310.
- [18] P. Kalimuthu, and S. A. John, *Talanta* 80 (2010) 1686.
- [19] C. Y. Yang, S. M. Chen, and S. Palanisamy, *Int. J. Electrochem. Sci.* 11 (2016) 2638.
- [20] B. B. Prasad, D. Jauhari, and M. P. Tiwari, *Biosens. Bioelectron.* 50 (2013) 19.
- [21] S. B. A. Barros, A. Rahim, A. A. Tanaka, L. T. Arenas, R. Landers, and Y. Gushikem, *Electrochim. Acta* 87 (2013) 140.

- [22] M. K. Amini, S. Shahrokhian, S. Tangestaninejad, and V. Mirkhani, *Anal. Biochem.* 290 (2001) 277.
- [23] S. Shahrokhian, and M. Karimi, *Electrochim. Acta* 50 (2004) 77.
- [24] S. Shahrokhian, and M. Ghalkhani, *Electrochim. Acta* 51 (2006) 2599.
- [25] H. R. Zare, N. Nasirizadeh, and M. M. Ardakani, *J. Electroanal. Chem.* 577 (2005) 25.
- [26] S. B. Khoo, and F. Chen, *Anal. Chem.* 74 (2002) 5734.
- [27] S. Shahrokhian, A. Souri, and H. Khajehsharifi, *J. Electroanal. Chem.* 565 (2004) 95.
- [28] S. Shahrokhian, and H. R. Zare-Mehrjardi, *Electroanalysis* 19 (2007) 2234.
- [29] F. Garkani-Nejad, H. Beitollahi, and Sh. Shekari, *Anal. Bioanal. Electrochem.* 8 (2016) 318.
- [30] K. Chattopadhyay, and S. Mazumdar, *Bioelectrochem.* 53 (2000) 17.
- [31] H. Kargar, R. Kia, F. Ganji, and V. Mirkhani, *Acta. Cryst.* 68 (2012) m1135.
- [32] H. Zhao, Y. Zhang, and Z. Yuan, *Anal. Chim. Acta* 441 (2001) 117.
- [33] E. W. Kristensen, W. G. Kuhr, and R. M. Wightman, *Anal. Chem.* 59 (1987) 1752.
- [34] L. Yang, N. Huang, Q. Lu, M. Liu, H. Li, Y. Zhang, and S. Yao, *Anal. Chim. Acta* 903 (2016) 69.
- [35] Kh. Ghanbari, and N. Hajheidari, *Anal. Biochem.* 473 (2015) 53.
- [36] A. C. Anithaa, N. Lavanya, K. Asokan, and C. Sekar, *Electrochim. Acta* 167 (2015) 294.
- [37] P. Gunniff (Ed.), *Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC)*, vol. 2, 16th ed., Association of Official Analytical Chemists, Arlington, VA, (1995).