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Enhancement Effect of Sodium-dodecyl Sulfate on Voltammetric Behaviour and Determination of Phentolamine Mesylate using Carbon Paste Electrode

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A carbon paste electrode (CPE) in the presence of Sodium-dodecyl Sulfate (SDS) was used for determination of phentolamine mesylate (PM), an important cardiovascular dilatation drug. Experiment shows that the drug exhibiting low redox activity at naked CPE can produce a sensitive anodic peak current in the presence of SDS. Investigation indicates that the oxidation of PM at CPE in the presence of SDS is one electron/one proton process which is controlled by adsorption. Under optimal conditions, the anodic peak current is linear to the concentrations of PM within the range of 3.0×10^{-8}—1.0×10^{-6} M with a detection limit of about 1.0×10^{-8} M. The electrode shows good stability and reproducibility. The electrochemical method proposed has been successfully applied to the determination of phentolamine mesylate in pharmaceutical formulations.

Keywords: phentolamine mesylate; SDS; carbon paste electrode; electrochemical method

1. INTRODUCTION

Phentolamine mesylate (PM, as shown in Fig.1) is a competitive alpha(α)-adrenoreceptor blocker [1]. Traditionally PM is used to treat hypertension and heart failure. In fact, PM can also be used for many other diseases, such as Raynaud's disease, acrocyanosis, hyperhidrosis, erectile dysfunction, and the last one is becoming more and more widespread. The long-term safety of oral PM tablets, however, has been questioned by medical scientists [2,3]. To develop rapid, simple and sensitive PM detection methods, therefore, is quite essential for drug quality monitoring and therapeutic concentration optimization. Analytical methods for detection and quantification of PM include various chromatographic procedures, such as high performance liquid chromatography [4-7], thin-layer chromatography [8] and gas chromatography [9]. Of the most commonly used instrumental

techniques, electroanalytical approach in some cases is one of the best choices due to its certain advantages, such as relatively cheap instruments, moderate or no sample preparation, less time consumption. Maybe because of its low sensitivity on common electrodes, only one conference paper to investigate the detection of PM by electroanalysis was found in the literature [10]. However, the detection limit is relatively high and the mechanism of electrode process was not discussed. Clearly, the study of the redox mechanism at electrode is important and beneficial to the pharmokinetic studies. The aim of this article is to develop a new electrochemical method for PM detection with relatively high sensitivity and to give a brief discussion of the electrode reaction mechanism.

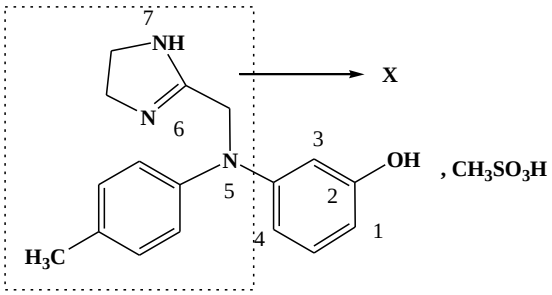


Figure 1. Structure of Phentolamine Mesylate

Surfactants are amphiphilic molecules or ions with hydrophobic and hydrophilic groups. They are readily adsorbed at an electrode/solution interface and form supramolecular structures, which may change the electrical properties of the interface and influence the electrochemical processes of other substances [11, 12]]. Surfactants have been widely used in electrochemistry and electroanalytical chemistry, and sodium dodecyl sulfate(SDS) and cetyltrimethylammonium bromide (CTAB) are the most popular ones. Early in 1980s the reductive electrochemistry of methylviologen in the presence of different kinds of surfactants was surveyed, suggesting that deposition of the cation radical onto the electrode surface was triggered by the adsorption of SDS [13, 14]. It was proved that SDS with a long hydrocarbon chain can readily form a negatively charged hydrophilic film on the hydrophobic acetylene black electrode surface, and the film can adsorb the protonated tetracycline molecules resulting in an increase in its oxidation peak current [15]. SDS was also successfully used to enhance the oxidation signal of buprenorphine at carbon paste electrode (CPE) [16]. CTAB can induce the adsorption of estrogens on the Nafion-modified electrode surface and greatly enhance the oxidation peak current [17]. Investigation shows that addition of SDS to the terazosin-containing elctrolyte was found to enhance the oxidation current signal while CTAB has an opposite effect [18]. There are still some other related works using surfactants as enhancement factor in electrochemical measurements, which are no longer listed here one by one.

A survey of literature reveals that no studies are found concerning the voltammetric behaviour of PM either at CBE or CBE in the presence of surfactants. In this work, anionic surfactant SDS was used to promote the electroxidation of PM at CPE. In the presence of SDS and at low pH value very sensitive oxidation peaks were obtained on voltammograms, and on the basis of this a voltammetric method was proposed for the determination of PM in pharmaceuticals, and the results compared favorably with the drug labeling quantity.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

Standard PM was purchased from Chinese National Institute for the Control of Pharmaceutical and Biological Products. Other chemicals used were from Shanghai Reagent Corporation and of analytical grade. Standard PM were prepared into a stock solution of 1×10^{-3} M with doubly distilled water and kept in a refrigerator at 4 °C. Working aqueous solutions of other different concentrations were prepared by further diluting the aliquots of the stock with B-R buffer prior to every measurement. A series of 0.04 M Britton-Robinson (B-R) buffer, pH 2-12, were prepared and used as the supporting electrolyte. SDS was dissolved into doubly distilled water to prepare 1×10^{-2} M homogeneous solutions. Electrochemical measurements were performed on a CHI 660e electrochemical analyzer (Chenhua Co., Shanghai, China) with a three-electrode system.

The working electrode was a cavity-adjustable Teflon-tube made to order. A Pt wire and a saturated camel electrode (SCE) were employed as the counter and the reference electrode respectively. All potentials were reported versus SCE. All pH-metric measurements were made on a Shanghai Leici pHS-25 digital pH meter which was previously standardized with buffer solutions of known pH.

2.2. Preparation of the Carbon Paste Electrode

Certain graphite powder was manually mixed with proper amount of paraffin oil manually in a small mortar to form a uniform carbon paste, which was pressed into the electrode cavity (2 mm in diameter) and polished shiny on a piece of weighing paper. The content of paraffin oil must be carefully monitored since the conductivity of the electrode decreases with the increase of the proportion of paraffin oil, and insufficient paraffin oil is not beneficial to mixing the graphite powder uniformly and to keeping enough viscosity.

2.3. Preparation of Sample Solutions

The drug samples were prepared as follows. Some commercial tablets containing PM were pulverized and dissolved in doubly distilled water. The obtained solution was filtered through a 0.45-μm nylon filter, and then the filtrate was kept at 4 °C in a refrigerator for use.

2.4. Procedure for the Determination of PM in the Samples

A known volume of sample solution was pipetted into an electrolytic cell containing 10 mL of pH 3 B-R buffer solution and 4×10^{-5} M SDS. After accumulating at open circuit for 120 s and keeping quiescent for 10 s, the voltammograms were recorded by a potential scan from 0.3 to 1.0 V. All the solutions prior to the electrochemical measurements were degassed with N_2 for 120 s so as to remove the dissolved oxygen.

3. RESULTS AND DISCUSSION

3.1. Voltammetric Response of PM at CPE in the Presence of SDS

The structure of PM (Fig. 1) indicates that nitrogen atoms at sites 5, 6, 7 will be protonated and positively charged in acidic solutions, and the electrochemical oxidation is easy to occur at phenolic substituent of site 2. Fig. 2 illustrates the voltammetric response of PM at CPE in B-R buffer solution (pH=3) after accumulation at open circuit for 120 s. PM exhibited a small anodic peak at CPE (curve b) in the absence of SDS. In the presence of 4×10^{-5} M SDS, there appreared a sharp and well-defined oxidation peak at 0.74 V (curve a) and the peak current of PM was remarkably enhanced, suggesting that the oxidation of PM was significantly catalyzed by the anionic surfactant SDS.

It is well known that surfactants are easily adsorbed at an interface to form directional aligned surfactants film. In the absence of SDS, the CPE is hydrophobic and there were little water-soluble PM molecules adsorbed on its surface, so a broad and flat oxidation peak appeared at the voltammogram (shown in Fig. 2). However, in the presence of SDS, a negatively charged film may form on the electrode surface with the hydrophilic head groups orienting to the bulk solution duo to the adsorption of anionic surfactant [15]. In acidic media the protonated PM molecules were positively charged and easily enriched on the negatively charged CPE surface through electrostatic attraction, which may speed the rate of electron transfer [15], and therefore resulted in an increase in peak current and a decrease in overvoltage. Similar sensitive oxidation peaks of PM were also observed at nafion modified CPE and nafion modified glassy carbon electrode (not shown), but the irreversible adsorption of the protonated PM molecules on the nafion modified electrode made it easier to become foul and difficult to renew.

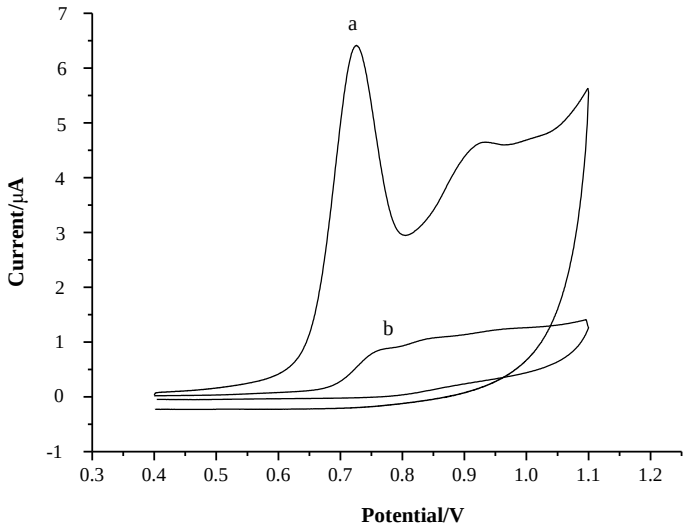


Figure 2. Voltammograms of a carbon paste electrode in B-R buffer solution (pH=3): a) in the presence of 5.0×10^{-6} M PM and 4.0×10^{-5} M SDS; b) in the presence of PM. Accumulation time was 120 s (open circuit); scan rate was $0.1 Vs^{-1}$.

3.2. The pH Dependence of PM Oxidation

In order to find if there were protons participating in the electrode reaction, the relationships between the peak potential and solution pH in the absence and presence of SDS were investigated respectively. As shown in Fig. 3, in the absence of SDS, the peak potential E_p shifted negatively with the increase of pH values, and a good linear relationship was observed in the range of pH 2.6-6.6 (r=0.997), which was in accordance with Nernst equation of an electrode process of dehydrogenation. The slope for the linear regression equation was -0.061 V/pH (inset of Fig. 3), which was close to -0.059 V/pH, suggesting equal number of protons and electrons were lost in the oxidation of PM.

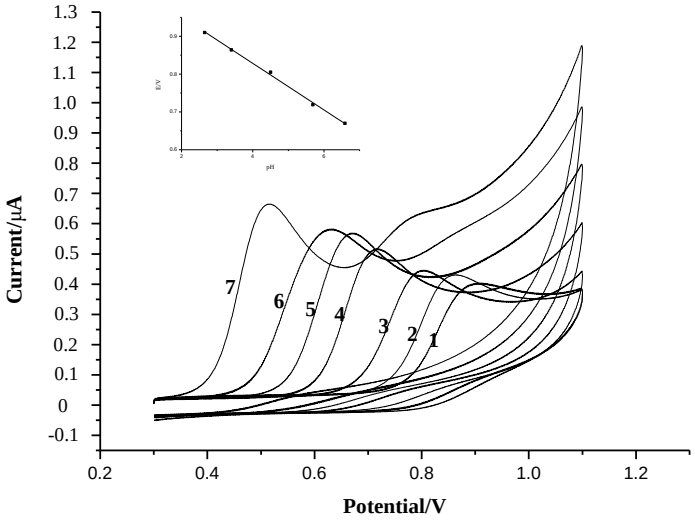


Figure 3. Cyclic voltammograms of 2.0×10^{-6} M PM in 0.04 M B-R buffer solution in the absence of SDS at different pHs, 1–7: pH 2.6, 3.4, 4.5, 5.7, 6.6, 7.6, 8.8, scan rate was 0.1V s^{-1}. The insert is the plot of E_p vs pH (2.6-6.6).

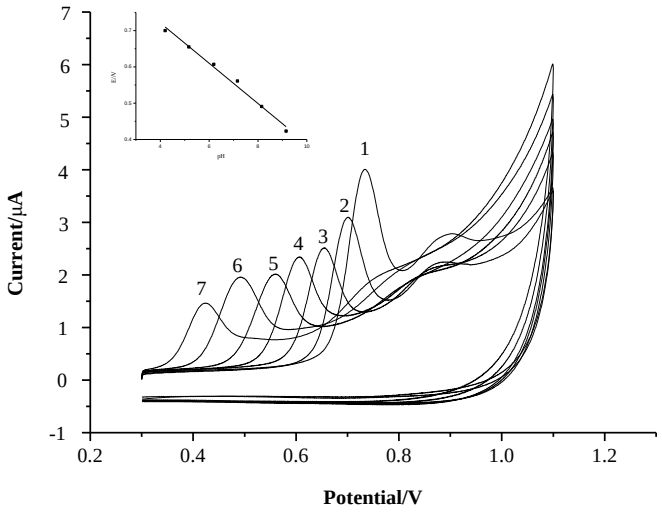


Figure 4. Cyclic voltammograms of 2.0×10^{-6} M PM in 0.04 M B-R buffer solution in the presence of SDS at different pHs, 1–7: pH 3.2, 4.2, 5.2, 6.2, 7.2, 8.2, 9.2, scan rate 0.1V s^{-1}. The insert is the plot of E_p vs pH (4.2-9.2). (r=0.991) . Accumulation time was 120s, scan rate was 0.1Vs^{-1}.

In the absence of SDS the peak current I_p was very small (only an order of magnitude of 10^{-7} A for10^{-6} M PM, shown in Fig. 3), and it increased with the increase of pH from 2.6 to 8.8, which was mainly attributed to the decreased amount of adsorbed phentolamine molecules as the pH decreased. Phentolamine is a water-soluble amphiphilic molecule containing an alkylbenzene and several amino groups. The lower the pH value, the more protonation of amino group, and the less the adsorption of phentolamine molecules was on the lipophilic surface of CPE. From the point of view of equilibrium shift, high pH is favorable for the electrode process of dehydrogenation, which may be another reason for peak current I_p increasing with pH.

Fig. 4 shows the dependence of the peak potential E_p and the peak current I_p of PM oxidation on solution pH from pH 3.2 to 9.2 in the presence of SDS. E_p shifted negatively with the increase of pH, which is the characteristic of the oxidation process of phenolic compounds. The slope for the linear regression equation was -0.055 V/pH (inset of Fig.4), which was close to -0.059 V/pH, thus the number of protons lost was equal to that of electrons lost in the oxidation of PM. Fig.4 shows that I_p increased with the decrease of pH from 9.2 to 3.2, which resulted from the increased amount of protonated PM molecules due to the increase of solution acidity. Experiment shows that neither peak current nor peak potential had significant changes with further decrease of pH, which may be caused by the passivation of phenolic benzene ring due to too much protonated tertiary aromatic amine at site 5. It is very interesting that the pH dependence of I_p in the absence of SDS (Fig. 4) was just contrary to that in the presence of SDS, indicating that the surface wettability was reversed after addition of SDS and the electrostatic attractions between negatively charged electrode surface and the amount of protonated PM molecules became dominant factor affecting the peak current. However, the pH dependence of E_p in the absence of SDS was the same as that in the presence of SDS, in both cases the number of protons and electrons lost in the electrode reaction was equal. In this work pH=3 of the B-R buffer solution was employed.

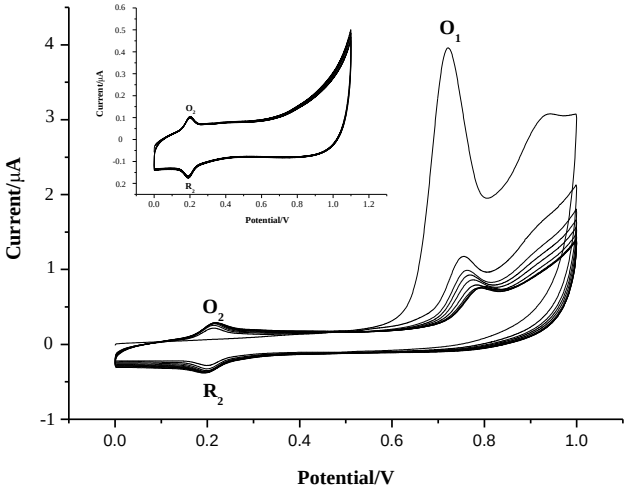


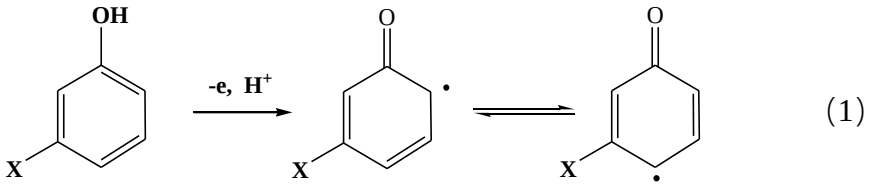
Figure 5. Continuous cyclic voltammogram response of 2.0×10^{-6} M PM at the CPE in the presence of 4.0×10^{-5} M SDS. The insert: repeated cyclic voltammetric sweeps of the used CPE in blank B-R buffer (pH=3) after removing oxidation peaks at about 0.74V. Accumulation time was 120s, and scan rate was $0.1Vs^{-1}$.

3.3. Mechanism of the Electrode Reaction of PM

In order to discuss the mechanism of the electrode reaction of PM, the influence of scan rate (ν) on the oxidation peak current (I_p) and peak potential (E_p) was investigated by CV method. The peak current varied linearly with scan rate from 15 to 165 mVs^{-1}, indicating that the oxidation of PM at the CPE in the presence of SDS was adsorption-controlled. As for a totally irreversible adsorption-controlled process, according to Laviron[19], E_p is expressed by the following relation:

$$E_p = E^{0\prime} - \frac{RT}{\alpha nF}\ln\frac{RTk^0}{\alpha nF} + \frac{RT}{\alpha nF}\ln\nu$$

where α is the transfer coefficient, k^0 the rate constant of the surface reaction for E_p= 0, n is the electron transfer number involved in the electrode reaction, ν is the scan rate, and $E^{0\prime}$ is the formal potential. Other symbols have their usual meaning. Thus, the value of αn can be obtained from the slope of E_p ~lnν fitting line. E_p shifted linearly with lnν in a range of 15–165 $mVs^{-1}$and the linear fitting relationship obtained was E_p= 0.5443 +0.0443lnν (r = 0.996). Combining with the above equation, αn was calculated to be 0.58 (taking T = 298). Assume α to be 0.5, the number of electron (n) transferred in the electro-oxidation of PM was estimated as 1.16~1. Applying the conclusion obtained from the pH dependence of PM oxidation at CPE, the electroxidation of PM was mainly a one-electron/one-proton process. PM can be taken as a m-X substitute of phenol (as shown in Fig.1), referring to the previous work [20], the oxidation site of PM should be at the electroactive phenolic hydroxyl group.

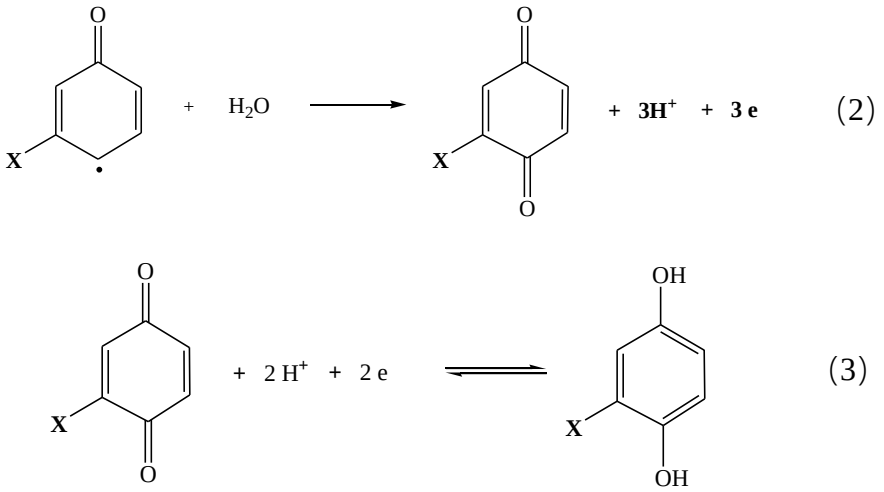


(1)

The electro-generated phenoxyl radicals may polymerize into many kinds of neutral dimers, oligomers or polymers [21,22], and finally formed a thin insoluble and non-conducting passivating layer on the electrode surface and led to electrode fouling [23]. As shown in Fig. 5, the big irreversible oxidation peak O_1 gradually decreased as the number of cyclic potential sweeps increased, indicating that the electrode was becoming fouling. However only several cycles of scanning in the blank solution main adsorbates on the surface would be removed and the activity of CPE restored, suggesting that CPE in presence of SDS had a strong anti-fouling advantage [24]. Another possible reason for the good performance of the electrode may be explained by the large substituent group X which sterically prevents phentolamine from polymerizing into macromolecules. In electrochemical detection of PM, the oxidation peak current in the first scan was recorded for the analysis of PM.

One electron transfer is typical of the electrochemical oxidation of phenol and its derivatives [23], however, if the cyclic voltammograms of the oxidation of PM at CPE in presence of SDS were recorded in a widened potential window between 0-1.1V, an additional pair of weak reversible redox

peaks (O_2/R_2) could be found with a half-wave potential of about 0.20V (as shown in Fig. 5). The first reduction and corresponding oxidation peaks appeared in the second and third segments of the cyclic voltammograms respectively, suggesting that the oxidized substance O_2 had been generated along with the first segment of oxidation of PM. Even more interesting is that the couple of reversible redox peaks (O_2/R_2) remained when the used electrode was dried with filter paper and re-immersed into the blank buffer solution containing no PM. The insert of Fig. 5 is the repeated cyclic voltammograms of the CPE in blank buffer solution after clearing the big irreversible oxidation peaks around 0.74V. Therefore, the oxidation of PM at CPE in the presence of SDS was no longer a pure single electron transfer reaction. At least a small amount of electro-generated phenoxyl radicals continued to undergo multi-electron oxidation to generate derivatives of hydroquinone-benzoquinone and firmly adsorbed on the surface of CPE. Referring to the previous research work [23] and considering the symmetry and stability of electronic structure, the mechanism to explain the weak reversible redox peaks was proposed as follows:



The half-wave potential of the redox pair O_2/R_2 (0.20 V vs. SCE, pH=3) is greater than that of hydroquinone-benzoquinone resulted from phenol adsorbed on carbon nanofiber electrode (0.04 V vs. SCE, pH=7) [23], which is apparently due to the different pH values of the electrolyte based on the previous discussion in part 3.2. However the oxidation potential of PM in solution (0.74 V, pH=3) happens to be the same as that of phenol (0.74 V, pH=7) [23]. The only reasonable explanation for this experimental results is that the oxidation of PM becomes easier at CPE in the presence of SDS. The redox pair O_2/R_2 adsorbed on the electrode may promote rather than hinder the oxidation of PM, which will be explained in the following context according to the previous research results.

Due to the special molecular structure, it has been proved that catechols, quinones and relative derivatives adsorbed on the electrode can promote the electron transfer and catalyze the redox reactions of biomolecules in solution. Physisorbed or chemisorbed monolayers of several quinones, including duroquinone, anthraquinone, and dopamine itself, are catalytic toward dopamine oxidation and reduction [25]. A tetrabromo-p-benzoquinone modified CPE exhibits good electrocatalytic activity to oxidation of ascorbic acid, dopamine and uric acid [26]. Graphite electrode modified with aromatics containing catechol functionalities shows catalytic effect to the oxidation of reduced nicotinamide

adenine dinucleotide [27]. 1,4-benzoquinone adsorbed on a carbon support play a role of a mediator in electron transfer of PQQ-glucose dehydrogenase anodes [28]. Anthraquinone grafted on glassy carbon electrode acts as an electrocatalyst for oxygen reduction in potassium hydroxide solution [29]. Therefore, there is no need to worry that the irreversible adsorption of the redox pair O_2/R_2 generated from multi-electron oxidation of PM may prevent the electron transfer. On the contrary such a surface adsorption layer will accelerate the electron transfer and support further oxidation of PM in a manner similar to oxidation of the biomolecules at tetrabromo-p-benzoquinone modified CPE [26]. Evidently the above viewpoints are in some way different from those reported in the literature [15], which held that the adsorption of derivatives of the redox pair O_2/R_2 will occupy the adsorption sites and result in a decrease of peak O_1.

3.4. Chronocoulometry

The oxidation of PM at the CPE in the presence of SDS was studied by chronocoulometry. According to the integrated Cottrell equation [30], the total charge Q of electrolysis consists of three parts: $Q=2nFAcD^{0.5}t^{0.5}\pi^{-0.5}+Q_{dl}+Q_{ads}$. The first part is the cumulative charge passed in oxidating the diffusing PM, where A is the area of the electrode, c is the concentration of the dissolved PM, D is the diffusion coefficient of PM. Q_{dl} is the capacitive charge from double layer charging, $Q_{ads}=nFA\Gamma$, is the charge from the electroxidation of any PM molecules adsorbed on the surface, and Γ (mol/cm^2) is the amount of adsorbed PM per unit area. Other symbols have their usual significance.The plot of Q vs. $t^{1/2}$ was linear and the slope was determined as 1.33 μCs$^{-0.5}$, and the diffusion coefficient D of PM was calculated to be 1.51×10^{-7} cm^{2}s^{-1} with the parameters A=3.14cm^2, c=10^{-6}M and n=1. On the assumption that Q_{dl} is not changed, Q_{ads} can be calculated by comparing the intercept of the Q-$t^{1/2}$ plot obtained for a solution containing PM with that obtained in the same experiment performed with supporting electrolyte only. In the present case Q_{ads} was 0.125μC, and the surface excess Γ was calculated to be 4.13×10^{-11} molcm^{-2}.

3.5. The Optimum Concentration of SDS and Accumulation Time

The influence of SDS concentration on peak current of PM oxidation is shown in Fig. 6. The peak current rose rapidly with the increase of SDS concentration and reached the maximum at about 4μM, however changes between 30 and 50μM were slow, further increase of SDS concentration led to a decrease in the peak current. The above experimental phenomena can be explained as follows:

According to Langmuir's monolayer adsorption theory, the adsorption of protonated PM molecules and the peak current would reach the maximum when the electrode surface was fully covered with a layer of negatively charged SDS. Further increased SDS may go into solution and combine with the protonated PM molecules to reduce their adsorption on the electrode surface, and therefore resulted in a decline in peak current of PM accordingly.

The effect of accumulation time on the peak current was also examined. The peak current was found to increase with the accumulation time in the range of 0-120 s. With further increase of

accumulation time the peak current increased slowly due to saturation of surface coverage of PM on the electrode surface. The accumulation time of 120 s was employed for determination of PM in this work.

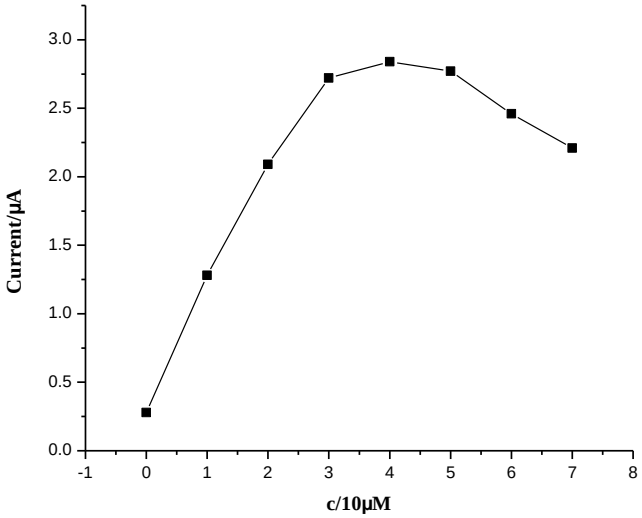


Figure 6. Effects of the amount of SDS on oxidation of 1.0×10^{-6} M PM. Accumulation time 120 s; scan rate was $0.1 Vs^{-1}$.

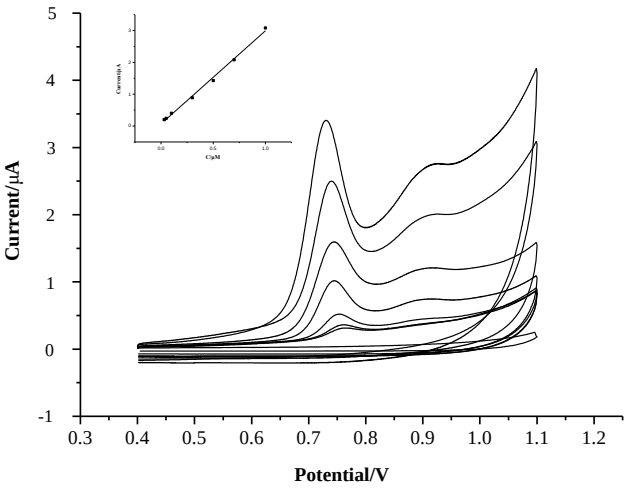


Figure 7. Cyclic voltammograms of PM of different concentrations at CPE in presence of SDS at pH = 3. Curves from the bottom to the top: 0, 3.0×10^{-8}, 5.0×10^{-8}, 1.0×10^{-7}, 3.0×10^{-7}, 5.0×10^{-7}, 7.0×10^{-7}, 1.0×10^{-6} M, respectively. The insert is a linear plot between the peak current and the concentration of PM was in a range of 3.0×10^{-8}–1.0×10^{-6} M. Accumulation time was 120 s, scan rate was $0.1 Vs^{-1}$.

3.6. Electrochemical Detection of PM in Real Samples

The relationship between the oxidation peak current and the concentration of PM was

investigated by determination of a series of standard solutions. It was found that the oxidation peak current of PM had good linear responses with its concentration at the CPE in the presence of SDS. In the range of 3.0×10^{-8} –1.0×10^{-6} M, the linear regression equation was calculated as I_p /μA=2.923*c*/μM+0.0693 (*R*=0.995 for *n*=7), and the detection limit was estimated as 1.0×10^{-8} M (S/N=3) for an accumulation time of 120 s. The reproducibility of the current response was evaluated by repeated measurements of 3.0×10^{-7} M PM standard solution with the same electrode, and the standard deviation of 7 consecutive measurements was about 4.3%. The results in comparison with those reported in related literature are listed in Table 1.

Table 1. Comparison of different modified electrodes for the determination of PM

Electrode	Linear range(μM)	Detection Limit(μM)	Techniques	References
BBDE/SDS	5~42	1.88	SWV	[10]
CPE/SDS	0.03~1	0.01	CV	This work

Interferences of some common inorganic ions and several organic substances were examined in 5.0×10^{-7} M PM solution. Experiment shows that 200 fold of glucose, 20 fold of ascorbic acid, uric acid, 50 fold of Na^+, NH_4^+, Cl^-, NO_3^- and CO_3^{2-}, K^+ have no interferences (signal changes below 5%). Other phenolic derivatives which have a similar structure and a close oxidation potential with PM are certain to influence its detection. This time it is necessary to use the special separation methods (such as chromatography techniques) to complete the determination.

In a further effort to test the validity of our proposed method in the clinical analysis, the recovery test was carried out as follows. First, the current response was measured for each diluted sample solutions. After that, a certain volume of a PM standard solution was added and increasing oxidation current was observed. The results for the determination of PM in tablet samples are summarized in table 2, and the results are in good agreement with the content marked in the label. The recoveries were in the range of 96.9–104.3%, suggesting that the accuracy of this proposed method is very good and has great potential for practical sample analysis.

Table 2. Determination of pM in tablets

original found[a] （$\times10^{-7}$ M）	standard added （$\times10^{-7}$ M）	total found[a] （$\times10^{-7}$M）	R.S.D (%)	Recovery (%)
3.018			4.6	
	2	5.232	3.7	104.3
	4	6.801	4.9	96.9
	6	8.935	4.3	99.1

[a] average value of three parallel measurements

4. CONCLUSION

It has been proved that the CPE in the presence of SDS has a great potential for the direct electrochemical detection of PM in drug formulations, this method has the advantages of simplicity, low cost, high sensitivity and low detection limit. The electrostatic attraction between the analyte and the electrode surface enhanced the enrichment and significantly improved the detection sensitivity. The good reproducibility of electrode was attributed not only to the strong anti-fouling effect of the of SDS but also to the formation of a hydroquinone-benzoquinone layer that accelerated electron transfer. Additional studies are needed for gaining further insights into the mechanism of oxidation of PM at CPE in presence of SDS.

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