

Studies on Enhanced Oxidation of Estrone and Its Voltammetric Determination at Carbon Paste Electrode in the Presence of Cetyltrimethylammonium Bromide

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The electrochemical behaviors of estrone in the presence of various surfactants were examined with great details. It is found that a cationic surfactant, cetyltrimethylammonium bromide (CTAB), obviously facilitates the electro-oxidation of estrone at carbon paste electrode (CPE) from the significant peak current enhancement and the negative shift of peak potential. Additionally, chronocoulometry and electrochemical impedance spectroscopy (EIS) were also used for further investigation of the electrode process of estrone, indicating that low concentration of CTAB exhibits excellent enhancement effects on the electrochemical oxidation of estrone, greatly enhances the diffusion coefficient and the electron transfer rate. Based on this, an electrochemical method was proposed for the determination of estrone. The oxidation peak current is proportional to the concentration of estrone in the ranges over 9.0×10^{-8} - 8.0×10^{-6} mol/L, and a low detection limit of 4.0×10^{-8} mol/L was obtained for 180s accumulation at open circuit (S/N = 3). Finally, this proposed method was demonstrated using estrone tablets with good satisfaction.

Key Words : Surfactant, Estrone, Determination, Carbon paste electrode, Electroanalysis

Introduction

Estrone is one kind of essential substrates of human beings, and plays very important roles in women's fertility. Its concentration and the change of concentration are closely related to human's health since both the lack and overmuch of estrone will lead to diseases.¹ Therefore, developing sensitive, rapid and simple method for the determination of estrone is very important.

So far, various methods such as gas chromatography-mass spectrum (GC-MS),^{2,3} high performance liquid chromatography (HPLC)^{4,5} and immunoassay⁶ have been reported for the determination of estrone. Although these methods possess high sensitivity and excellent selectivity, they have many intrinsic drawbacks: time-consuming, needing complicated and expensive instruments, and high cost.

Electrochemical method is drawing increasing attention due to its many advantages: high sensitivity, good sensitivity, rapid response, low cost and simplicity. To date, a great number of electrochemical methods were developed for the determination of estrogens.⁷⁻¹³ For example, a sensitive electrochemical method for the determination of estrogens based on a Nafion-modified electrode and enhancement effect of surfactant was reported.¹⁰ The detection limit is as low as 10^{-9} mol/L. Otherwise, a voltammetric method utilizing the catalytic effect of carbon nanotubes (CNTs) was also reported for the determination of estradiol with detection limit of 10^{-8} mol/L.¹¹ Nano- Al_2O_3 film-modified glassy carbon electrode was fabricated for the determination of estradiol and the lowest detectable concentration is 8×10^{-8} mol/L.¹² Additionally, an electrochemical method using carbamylcholine (CCh) modified paraffin-impregnated

graphite electrode (CCh/WGE) was reported for the determination of estradiol, estrone and estriol.¹³ However, to the best of our knowledge, electrochemical determination of estrone using a carbon paste electrode and in the presence of CTAB has not been reported.

CTAB, a cationic surfactant with a hydrophilic head on one side and a long hydrophobic head on the other side, had been widely used in electrochemistry and electroanalytical chemistry field for different purposes.¹⁴⁻¹⁷ It is well known that surfactants not only endow the electrode/solution interface with different electrical properties, but also adsorb at electrode surface or aggregate into supermolecular structures to change electrochemical process.¹⁸⁻²¹

The main objective of the current work is to propose an easy, quick and sensitive electrochemical procedure for the determination of estrone utilizing the special electrochemical characterization of CTAB. It is found that the cation surfactant CTAB had a distinct enhancement effect on the oxidation of estrone at carbon paste electrode. Additionally, the reaction mechanism for the oxidation of estrone was explored by chronocoulometry, and then experimental conditions for the determination of estrone were optimized. Finally, this new sensitive method was applied to the determination of estrone in the compound estrone tablets and the results are satisfying.

Experimental

Reagents. 2.0×10^{-3} mol/L estrone stock solution was prepared by dissolving estrone (Sigma chemical reagent Co., USA) in ethanol. Graphite powder was obtained from Shanghai Reagent Corporation, China. CTAB (purchased

from Shanghai Reagent Corporation, China) was dissolved in re-distilled water to form 1.0×10^{-2} mol/L homogeneous solutions. All chemicals were of analytical grade quality and were used without further purification. The experimental results were obtained at room temperature.

Apparatus. Electrochemical measurements were performed on a CHI 660 electrochemical analyzer (Chenhua Co., Shanghai, China). The electrode system contains a carbon paste working electrode (2.7 mm in diameter), a Pt wire counter electrode and a saturated calomel reference electrode (SCE). The electrochemical impedance spectroscopy (EIS) was carried out with the EG&G Model 273 electrochemical workstation and EG&G Model 5210 lock-in amplifier (Princeton Applied Research, PAR, USA) powered by Echem Software.

Preparation of carbon paste electrode. The carbon paste electrode was prepared by mixing 100.0 mg graphite power (320 mesh, Shanghai Reagent Corporation, China) and 25.0 μ L paraffin oil in a small mortar to form a homogeneous carbon paste mixture. Then, the mixture was pressed by hand into the end cavity of a homemade polytetrafluoroethylene (PTFE) cylindrical electrode body. Finally, the electrode surface was polished manually on a piece of weighing paper.

Analytical procedure. Unless otherwise indicated, 0.1 mol/L phosphate buffer solution (PB, pH 8.0) was used as the supporting electrolyte in a conventional electrochemical cell. At the beginning of experiment, The carbon paste electrode was scanned by successive cyclic voltammetric sweeps between 0.00 V and 1.00 V at 100 mV/s to get a steady cyclic voltammograms, and then known volume of estrone stock solution and 1.0×10^{-4} mol/L CTAB were placed into the cell to make up 5 mL mixture solution. After accumulating at open circuit for 180s with stirring the solution and keeping quiescent for 10s, the linear sweep voltammograms were recorded in the potential range 0.0-1.0 V with scan rate of 200 mV/s. The oxidation peak current was measured at 0.52 V.

Results and Discussion

Electrochemical impedance spectroscopy of estrone. The property of electrode interfaces can be investigated by electrochemical impedance spectroscopy (EIS).²²⁻²⁵ In EIS, the semicircle diameter equals the electron transfer resistance. Figure 1 shows the complex plane diagram (Nyquist plot, Z'' versus Z') of estrone at carbon paste electrode in the absence (Fig. 1a) and presence of CTAB (Fig. 1b). From the comparison, it is very clear that the impedance responses of estrone show great difference after addition of CTAB. In the absence of CTAB, the impedance spectra include a semicircle with a large diameter. However, after addition of CTAB, the diameter of semicircle diminishes markedly. It is clear that the charge transfer resistance of electro-oxidation of estrone decreases greatly, and the charge transfer rate speeds up by CTAB, suggesting that CTAB facilitates the electron transfer between estrone and electrode.

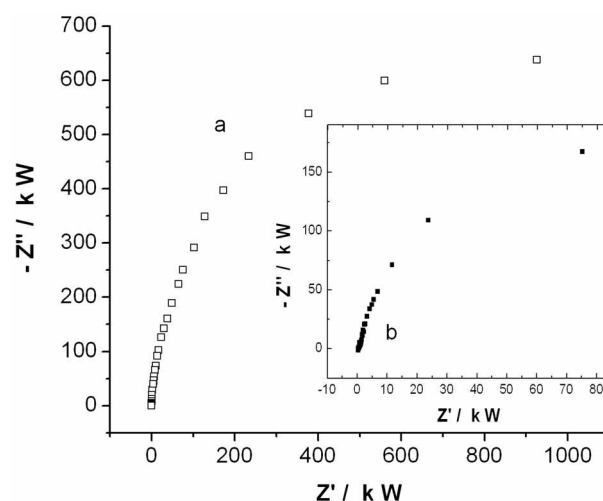


Figure 1. Nyquist diagram (Z'' vs. Z') for estrone at carbon paste electrode in the absence (a) and presence (b) of CTAB. estrone: 2.0×10^{-5} mol/L; CTAB: 1.0×10^{-4} mol/L. Frequency range used, 100 kHz to 0.1 Hz with signal amplitude of 5 mV rms at five steps per decade.

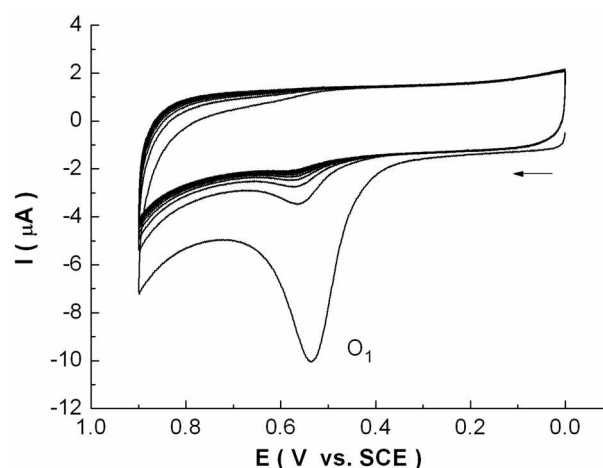


Figure 2. Successive cyclic voltammograms of 8.0×10^{-6} mol/L estrone in 0.1 mol/L phosphate buffer solution (pH 8.0). Scan rate: 100 mV/s; CTAB: 1.0×10^{-4} mol/L; Accumulation time: 180s; rest time: 10s.

The voltammetric behaviors of estrone. Figure 2 shows the successive cyclic voltammograms of 1.0×10^{-5} mol/L estrone in 5 mL phosphate buffer solution (pH 8.0) at CPE in the presence of 1.0×10^{-4} mol/L CTAB. A well-defined oxidation peak (O1) is observed at 0.53 V at the first anodic sweep from 0.00 to 1.10 V. On the reversal scan, no corresponding reduction peak appears. However, during following successive cyclic sweeps, the peak current of O1 decreases greatly and finally disappears. It is resulted from the fact that the electrode surface is blocked by the adsorption of oxidation products, which reducing the effective reaction sites at CPE surface. This is true for the case without CTAB expect that the blocking effect is apparently reduced in the presence of CTAB. Similar results have been reported by us recently.²⁶

The electrochemical behaviors of estrone at CPE in pH 8.0

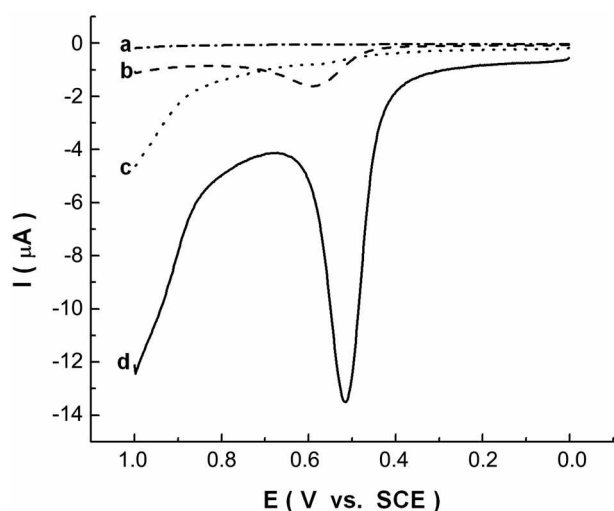


Figure 3. Linear sweep voltammograms in pH 8.0 phosphate buffer at carbon paste electrode: a) in the absence of estrone and CTAB; b) in the presence of estrone; c) in the presence of CTAB; d) in the presence of estrone and CTAB. Scan rate: 200 mv/s; Accumulation time: 180s; rest time: 10s; estrone: 2.0×10^{-5} mol/L; CTAB: 1.0×10^{-4} mol/L.

phosphate buffer were investigated by LSV. Voltammetric responses of estrone are shown in Figure 3. It can be seen that no voltammetric signal appears in the blank buffer solution (curve a) and in the solution only containing CTAB (curve c). However, estrone exhibits a weak oxidation peak at 0.59 V (curve b) in the absence of CTAB. After the addition of 1.0×10^{-4} mol/L CTAB, the oxidation peak current is markedly enhanced and the peak potential shifts negatively to 0.52 V (curve d). Conclusion can be made that cationic surfactant CTAB has obvious enhancement effect to the oxidation of estrone.

Literatures show that CTAB could be adsorbed to the electrode surface to form surfactants film,^{27,28} which might alter the overpotential of the electrode reactions and influence the rate of electron transfer. In this work, estrone may form transient adduct with CTAB through the hydrophobic interaction between the hydrophobic tail of CTAB and the hydrophobic moiety of estrone as well as the electrostatic interaction of positively charged CTAB head and the negatively charged phenol group of estrone, which facilitate the adsorption of estrone at CPE surface and makes the oxidation of estrone easier. Therefore, the addition of CTAB increases the adsorption amount of estrone at CPE surface and consequently leads to the enhancement of the oxidation peak current of estrone, compared with those in the absence of CTAB.

Effects of various surfactants on the electro-oxidation of estrone. The effects of various surfactants on the electro-oxidation of estrone at CPE were explored (depicted in Fig. 4). The electrooxidation response at CPE in the absence of surfactant was shown in curve (a) for comparison. It can be seen that anionic surfactant SDS (curve b), neutral surfactant Triton-X (curve c) and cationic surfactant cetylpyridine bromide (CPB) (curve d), lauryltrimethylammonium bromide

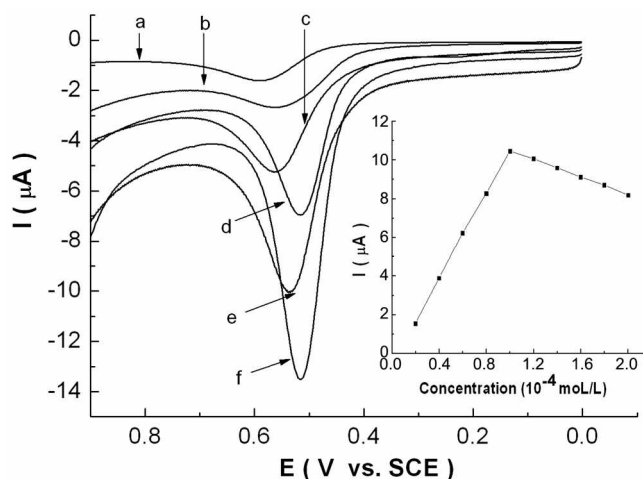


Figure 4. Effects of different surfactants on the oxidation of 2.0×10^{-5} mol/L estrone. a. Blank (without surfactants); b. Triton-X-100; c. SDS; d. CPB; e. LTAB; f. CTAB. Surfactant concentration: 1.0×10^{-4} mol/L. Inset: Effects of the amount of CTAB on the oxidation peak current. Other conditions are the same as Figure 3.

(LTAB) (curve e), CTAB (curve f) all can improve the oxidation peak current of estrone. However, the degree of enhancement is different under different surfactants due to their different structure, hydrophobic interaction as well as the ion-exchange interactions. Among these, the oxidation peak current of estrone is highest in the existence of CTAB (curve f) because of its optimum length of hydrophobic chain and adsorption amount on the electrode surface.^{17,29} With either the increase or the decrease of hydrophobic tail length of cationic surfactants, the response of estrone declines. Furthermore, although LTAB and SDS have the same hydrophobic tail length, LTAB produces the much higher response. This can be well explained by the exclusion of negatively charged estrone at pH 8.0 from the electrode surface by the negatively charged SDS film that is adsorbed on the electrode by hydrophobic interactions. Hence, we chose CTAB in this paper.

In addition, the effect of CTAB concentration on the oxidation peak current is shown in as inset plot in Figure 4. The oxidation peak current increases gradually with increase of the concentration of CTAB and reaches maximum at 100 μ M, at which CTAB might form a compact monolayer on CPE with the hydrophobic tails of CTAB perpendicular to the electrode surface.^{17,29} The increase of estrone oxidation current with increasing CTAB concentration is due to the accumulation of more estrone molecules in the denser CTAB adsorbed monolayer on CPE. However, the peak current decreases slowly as further increasing the CTAB concentration. Because the surface of CPE is hydrophobic, CTAB might adsorb on CPE via the hydrophobic interaction between the hydrophobic tail of CTAB and hydrophobic surface of CPE, resulting in the direction of hydrophilic head of CTAB to solution, *i.e.* CTAB forms a compact monolayer with positive charges on CPE.¹⁴ Thus, the decrease of estrone response by the formation of CTAB micelles should mainly arise from the repress of estrone diffusion in solution

by CTAB micelles.²⁹ So, the oxidation peak current conversely decreases. According to Chidambaram *et al.*, CMC of CTAB in 0.2 M phosphate buffer is about 5.7×10^{-4} M.³⁰ Thus, the optimal concentration of CTAB is close to its CMC in 0.1 M phosphate buffer. In this work, the concentration of CTAB is fixed at 1.0×10^{-4} mol/L for higher sensitivity.

Choice of supporting electrolytes. In this work, several kinds of buffer solutions were optimized for the determination of estrone. They include 0.1 mol/L phosphate buffer solution (PBS, pH 3.0-9.0), 0.1 mol/L sodium acetate-acetic acid buffer solution (NaAc-HAc, pH 3.0-9.0), 0.1 mol/L sodium citrate-hydrochloric acid (HCl) buffer solution (pH 1.0-4.0), 0.1 mol/L sodium citrate-sodium hydroxide (NaOH) buffer solution (pH 5.0-7.0), 0.1 mol/L borax-hydrochloric acid buffer solution (pH 7.6-9.2), 0.1 mol/L borax-sodium hydroxide buffer solution (pH 9.2-12.3). Moreover, different acids and alkalis were investigated too, such as HCl (0.1 mol/L), HAc (0.1 mol/L), and NaOH (0.1 mol/L). It is found that higher peak current and better peak shape was obtained in 0.1 mol/L phosphate buffer solution. Consequently, 0.1 mol/L phosphate buffer solution was chosen as support electrolyte for quantitative analysis of estrone.

The effects of solution pH played an important role in quantitative detection of trace estrone. Figure 5 depicts the influences of pH of phosphate buffer on the oxidation peak current and peak potential were researched by LSV. When the pH increases from 4.0 to 10.0, the oxidation peak current of estrone changes remarkably, and reaches maximum at pH 8.0. However, the oxidation peak potential (E_p) shifts negatively, obeying the equation $E_p = 1.1246 - 0.0621 \text{ pH}$ ($R = 0.9977$). The slope of -0.062 mV/pH suggested that the number of the electrons transferred in the oxidation of estrone is equal with that of protons. Therefore, 0.1 mol/L phosphate buffer solution (pH 8.0) was used as supporting electrolyte for estrone analysis.

Influences of accumulation potential and time. Effect

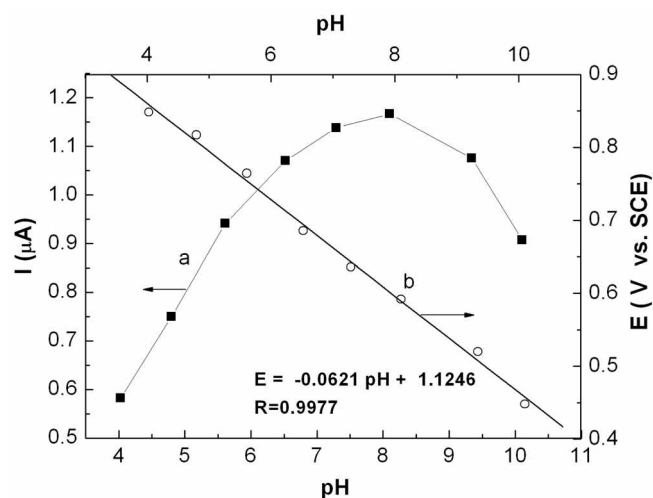


Figure 5. The pH dependence on 2.0×10^{-5} mol/L estrone oxidation peak current (a) and peak potential (b) in the presence of CTAB. Other conditions are the same as in Figure 3.

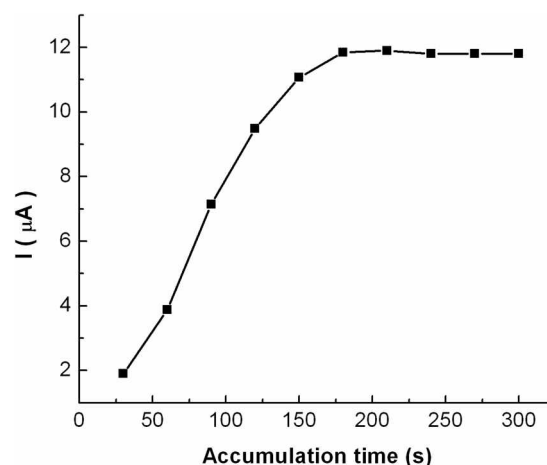


Figure 6. Effects of accumulation time on the oxidation peak current of 2.0×10^{-5} mol/L estrone. Other conditions are the same as in Figure 3.

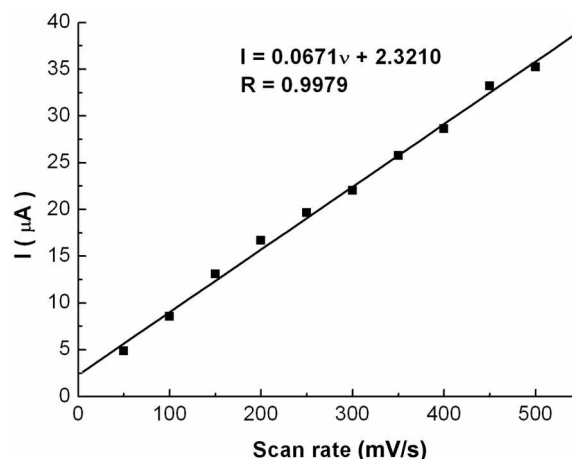


Figure 7. Voltammograms of 2.0×10^{-5} mol/L estrone with different scan rates. Other conditions are the same as in Figure 3.

of accumulation potential on the oxidation peak current of estrone at CPE was examined. When the accumulation potential shifts from -0.3 to 0.3 V, the oxidation peak current varies slightly, demonstrating that the adsorption of CTAB is independent of the charge on electrode surface. That is to say, the accumulation potential has no obvious influence on the oxidation of estrone.

Influence of accumulation time on the oxidation peak current of estrone at CPE was shown in Figure 6. The oxidation peak current increases linearly with accumulation time in the range of 30-180 s. Afterwards, the peak current tends to be stable with further increasing accumulation time due to the saturated adsorption of estrone on the electrode surface. Therefore, the optimal accumulation time of 180s was employed in the experiment.

Scan rate. The effects of scan rate (v) on the oxidation of 2.0×10^{-5} mol/L estrone were examined by LSV and the data were list in Figure 7. The peak current increased linearly with scan rate from 50 to 500 mV/s, and can be expressed as follows:

$$I_p (\mu\text{A}) = 0.067 v (\text{mV/s}) + 2.3210 (R = 0.9979)$$

Which indicates that the oxidation process of estrone is mainly controlled by adsorption.

Additionally, the relationship between E_p and v was also investigated, described by following equation:

$$E_p = 0.0536 \ln v + 0.2325 (R = 0.9974)$$

As far as totally irreversible electrode process controlled by adsorption step was concerned, the relationship between E_p and v is defined by the following equation³¹:

$$E_p = E^{\theta} + (RT/\alpha n_a F) \ln (RTk^0/\alpha n_a F) + (RT/\alpha n_a F) \ln v$$

where E^{θ} is formal potential, T is temperature, α is the transfer coefficient and n_a is the number of the electron transfer in the rate-determining step, k^0 is the electrochemical rate constant, F is the Faraday constant. The slope $RT/\alpha n_a F$ of 0.0536 indicates that the value of αn_a is 0.505. Based on the assumption of α of 0.5 for the multi-electron transfer process, the value of n_a is calculated to be 1. Combining with the data from the plots of E_p vs. pH, it is very clear that the electrochemical oxidation of estrone at CPE in the presence of CTAB involves one electron and one proton.

Chronocoulometry. The electrooxidation of estrone at CPE in the absence and presence of CTAB was characterized by chronocoulometry. After the deduction of the background charge, the plot of the charges (Q) against the square root of time ($t^{1/2}$) shows a linear relationship (Fig. 8). According to the integrated Cottrell equation³², the diffusion coefficient of estrone can be estimated from the slope of the plot of Q vs. $t^{1/2}$.

$$Q = 2 n F A c D^{1/2} t^{1/2} \pi^{-1/2} + Q_{dl} + Q_{ads}$$

Where A is the area of carbon paste electrode, c is the concentration of estrone, Q_{dl} is the double layer charge, Q_{ads} is the adsorption charge. Other symbols have their usual

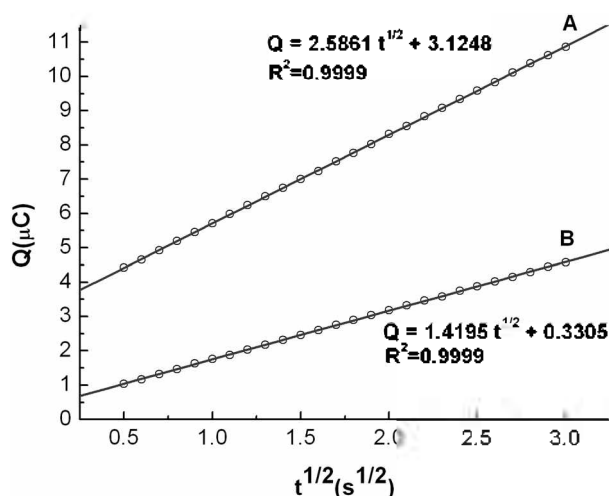


Figure 8. The plot of Q vs. $t^{1/2}$ for 2.0×10^{-5} mol/L estrone at carbon paste electrode in the presence (a) and absence (b) of 1.0×10^{-4} mol/L CTAB. Initial potential 0.33 V, final potential 0.53 V and pulse width 9s. Other conditions are the same as in Figure 3.

significance. In this system the number of transfer electrons involved in the oxidation of estrone is one as calculated above and $A = 0.057 \text{ cm}^2$, $c = 2.0 \times 10^{-5} \text{ mol/L}$. In the absence and presence of CTAB the value of slope is $1.42 \mu\text{C}\cdot\text{s}^{-1/2}$ and $2.59 \mu\text{C}\cdot\text{s}^{-1/2}$, respectively. It is calculated that $D = 1.33 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ without CTAB, which is increased to $4.40 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ after the addition of CTAB.

Meanwhile the surface coverage Γ of estrone can be evaluated from the following equation:

$$Q_{ads} = nFA\Gamma$$

Q_{ads} can be obtained by the intercept difference from plot of Q vs. $t^{1/2}$ in the absence and presence of estrone when Q_{dl} is assumed unchanged. In the absence of CTAB, Q_{dl} is 0.3305 μC , and the value of Γ is $6.01 \times 10^{-11} \text{ mol}\cdot\text{cm}^{-2}$. After the addition of CTAB, Q_{ads} increased to 3.1248 μC , and Γ increases to $5.68 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$. Due to the complicated surface properties of CPE, it is impossible to compare the adsorbed amount of estrone to the calculated coverage with the geometrical dimension of estrone. Whereas, the surface coverage of estrone reported here is reasonable because it is close to our previous reports.³³ It reveals that the adsorption amount of estrone on the electrode surface increased in the presence of CTAB.

Calibration and interferences. Under optimal working conditions described above, the calibration curve of estrone at CPE in the presence of CTAB was characterized. In the range of 9.0×10^{-8} – 8.0×10^{-6} mol/L, the oxidation peak current was linear with the concentration of estrone. The linear regression equation can be described as following:

$$I_p (\mu\text{A}) = 0.87764 c (\mu\text{mol/L}) + 0.85262 (r = 0.9945)$$

A detection limit of 4.0×10^{-8} M estrone was obtained with 180s accumulation time under open circuit. In this work, the used CPE was refreshed after each measurement, and the relative standard deviation (RSD) was 3.2% for 8 times parallel detection of 2.0×10^{-6} mol/L estrone, suggesting excellent reproducibility.

If this electrochemical method would be proposed to detect estrone in real samples, the interferences of some concomitant substances should be estimated. So the effects of some organic compounds on the oxidation of 2.0×10^{-5} mol/L estrone were evaluated. It is found that 100-fold concentration of glucose, amyllum and dextrin, 50-fold concentration of ascorbic acid (AA), dopamine (DA), uric acid (UA) almost had no interferences on the electrochemical detection of estrone (signal change < 5%). In addition, effects of many inorganic ions had also been tested. 100-fold concentration of Fe^{3+} , Cu^{2+} , Zn^{2+} , Ca^{2+} , Al^{3+} , Mg^{2+} , SO_4^{2-} , NO_3^- , HCO_3^- did not affect the determination of estrone. However, the influences of hexestrol, estriol and diethylstilbestrol are serious. Because these hormones are hydrophobic and contain hydroxy group, which in benzene ring and may be oxidized, they will cause increase to the oxidation peak current of estrone. What is more, the influences increase as improving their concentration.

Determination of estrone in estrone tablets. The pro-

Table 1. Determination of estrone in the sample

Sample	Added (mol/L)	Expected (mol/L)	Founded (mol/L)	Recovery (%)
1	0.00		9.85×10^{-8}	
	1.0×10^{-7}	1.985×10^{-7}	1.956×10^{-7}	97.1
2	0.00			3.15×10^{-7}
	4.0×10^{-7}	7.15×10^{-7}	7.246×10^{-7}	102.4
3	0.00			9.37×10^{-7}
	1.0×10^{-6}	1.937×10^{-6}	1.969×10^{-6}	103.2

posed method was applied to determine estrone in estrone tablets. The results are illustrated in Table 1. In our experiments, the concentration of estrone was calculated using standard addition method. The relative standard deviation of each sample for three times parallel detections is less than 4.0%. In addition, the recovered ratio on the basis of this method was investigated and the value is between 97.1 and 103.2%, indicating that determination of estrone using carbon paste electrode in the presence of CTAB is effective and sensitive.

Conclusion

In this paper, the electrooxidation of estrone at CPE in pH 8.0 phosphate buffer was studied. Cationic surfactant CTAB was successfully introduced to enhance the oxidation of estrone. Due to the amphiphilic character of CTAB, the C-H chain can easily adsorb on the carbon paste electrode surface, estrone may form transient adduct with CTAB, which can increase the adsorption amount of estrone on the electrode surface, reducing the overvoltage of the electrode reaction and accelerating electron transfer. Finally, a simple, sensitive, rapid and accurate method was successfully applied for the determination of estrone in the compound estrone tables sample.

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