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The Cyclic Voltametric Characteristics of the Interaction Between Phosphoric Acid and Adrenaline

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The interaction of adrenaline with phosphoric acid is investigated by cyclic voltametric (CV) approach. The impact of H_2SO_4 and HCl solution on adrenaline is not obvious. In NaAC-HAC solution, B.R. solution, and phosphate buffer solution, the oxidation peak current (i_{pa1}) and peak potential (E_{pa1}) change with the pH values. In the H_3PO_4 system with pH>4, the oxidation peak 1 of adrenaline at graphite electrode will transform to two peaks. The impacting factors for the change include the concentration of adrenaline, the electrode material, and the pH value and the composition of solution.

Keywords: adrenaline, phosphoric acid, CV

1. INTRODUCTION

Nucleic acid is the polymer of nucleotide, which is constituted by phosphoric acid (H_3PO_4), pentose, and nitrogenous base [1]. Nucleotide can form diester bond of phosphoric acid through the binding of the hydroxyl of pentose with the hydrogen of phosphoric acid. Mononucleotide can form polynucleotide chain further by the polymerization of the diester bond of phosphoric acid. Na_2HPO_4/NaH_2PO_4 buffer pair is also can be found in the blood plasma. Therefore, phosphoric acid and phosphate radical play an important role in the life body. There are lots of studies on phosphate and phosphatase in the fields of the medicine, biochemistry, environmental science, and so on.

Adrenaline belongs to a group of compounds known as catecholamines that plays aparticularly important role in the regulation of physiological process in living systems [2]. It can be oxidized easily and the product of electrooxidation is adrenalinequinone [3]. Adrenaline can not be dissolved in water and organic solvents itself, but the protonated adrenaline will be dissolved in the solvent that can

donor proton. Adrenaline plays a central role in the short-term stress reaction, the physiological response to conditions that threaten the physical integrity of the body. Adrenaline can be studied directly by electrochemical methods because of its structural similarity to o-dihydroxybenzene, and the –CH(OH)– group at the α carbon facilitates the easy donation of an electron [4-10].

In this paper, we investigate the interaction of adrenaline with phosphoric acid and phosphate radical by cyclic voltammetry (CV) approach, and expect to find some useful rules in this field.

2. EXPERIMENTAL

The reagent of adrenaline (>97%) was supplied by Fluka Co. (Sweden). The concentration of adrenaline aqueous solution was 2.5×10^{-3} mol/L. Other employed solutions were prepared with analytic grade reagents and doubly distilled water.

Cyclic voltammetry was performed on an EG&G PAR M398 electrochemical impedance system with an M283 potentiostat/galvanostat. The three-electrode-system was used to carry out electrochemical tests. A graphite electrode served as a working electrode, a platinum wire served as a counter electrode, and a saturation calomel electrode (SCE) served as reference electrode. A Luggin capillary was used to connect the reference and working electrodes. Highly pure nitrogen gas was passed through the solution for 10 min to remove oxygen dissolved in solution before measurements, and all measurements were carried out under nitrogen atmosphere at room temperature (25.0±0.1℃).

3. RESULTS AND DISCUSSION

3.1. The CV behavior of adrenaline in HCl, H_2SO_4, and H_3PO_4 medium

The CV behavior of adrenaline at graphite electrode in the 0.5mol/L HCl, H_2SO_4, and H_3PO_4 solution are shown in Figure 1, respectively. From which, we can find that the peak current of adrenaline in HCl is largest, and the values in H_3PO_4 is smallest. In addition, the peak-to-peak potential separation between anodic and canodic peak potential is largest in 0.5mol/L H_3PO_4. In the H_3PO_4 medium, oxygen atom or hydrogen atom of H_3PO_4 can form hydrogen bonds with the phenolic hydroxyl, alcoholic hydroxyl and imine group of adrenaline and stabilize adrenaline. The hydrogen bonds will inhibite the redox reaction of adrenaline, and induce the peak current decreasing and peak-to-peak potential separation increasing. As shown in Figure 1, the impact of H_2SO_4 on adrenaline is weak. The results suggest that the different acids will play different roles on adrenaline for the forming different microenviromental effects.

To determine the impact of H_3PO_4 on the electrooxidation of adrenaline, and compare the inhibiting of H_3PO_4, and acetic acid (HAc) further, we will select H_3PO_4 buffer solution, HAC/NaAc buffer solution, and Britton-Robinson (B.R.) buffer solution as the studying medium.

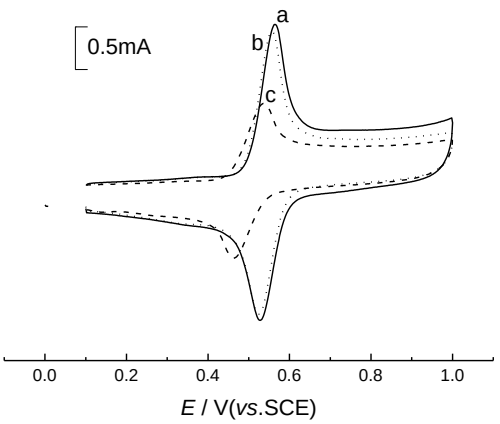

Figure 1. CV curves of 5×10^{-3}mol/L adrenaline at graphite electrode in (a) 0.5mol/L HCl, (b) 0.5mol/L H_2SO_4, (c) 0.5mol/L H_3PO_4 solutions. Scan rate: 100 mV/s.

3.2. The electrochemical property of 2.5×10^{-3} mol/L adrenaline in the different oxyacids solution

The CV curves of adrenaline at graphite electrode in NaAC-HAC solution, B.R. solution, and phosphate buffer solution with pH value of 5.54 are presented in Figure 2. There are five potential peaks. Peak 1 corresponds to the reaction of adrenaline electrooxidated to adrenaline quinine, and peak 2 corresponds the reverse reaction. Peak 3 and 4 correspond the redox reaction between colorless adrenochrome and adrenochrome. Peak 5 corresponds the dehydrated product of adrenochrome. According to the CV characters, we can conclude that the electron transfer in the pH condition accord with the ECCECE mechanism [11].

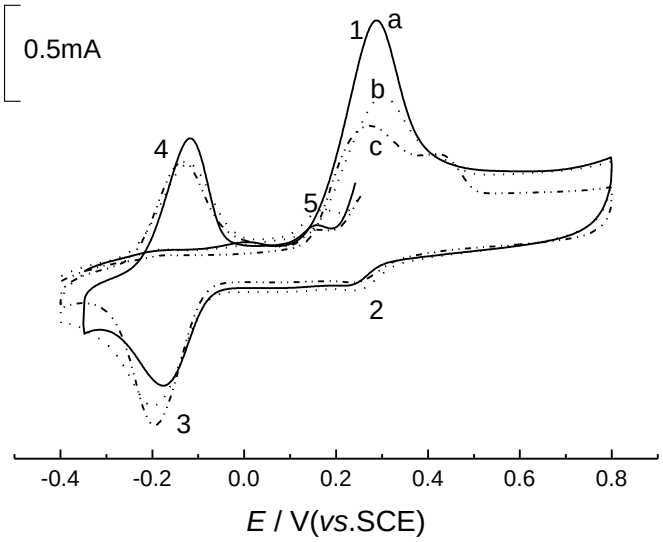

Figure 2. CV curves of 2.5×10^{-3} mol/L adrenaline at graphite electrode in (a) NaAC-HAC solution, (b) B.R. solution, (c) phosphate buffer solution with pH value of 5.54. Scan rate: 100 mV/s.

As shown in Figure 2, the peak current (i_{pa1}) of peak 1 is different in the same pH value and experimental conditions, which suggests that there may be some influencing factors besides the

current. The factors, we think, should be the oxyacid and oxyacid radical ion in the three systems, which will interact with adrenaline and produce different impact on the electron transfer properties of adrenaline. The interaction is the hydrogen bonds between them, which will stabilize adrenaline. The oxidation peak current of adrenaline is highest in NaAC-HAC system and lowest in phosphoric acid system. The reason can attribute to the stronger interaction between phosphoric acid and adrenaline. In contrast, the interaction between HAC and adrenaline is weak. For B.R. solution (the mixture of H_3PO_4 and HAC), the interaction strength lies between them. Therefore, the oxyacid of H_3PO_4 and HAC will influence the electrooxidation reaction of adrenaline with different degrees.

In the three system, the oxidation peak current (i_{pa1}) and peak potential (E_{pa1}) change with the pH values. The corresponding changes are presented in Figure 3 and 4. As shown in Figure 3, with the pH value increasing, the peak current of peak 1 increases at first then decreases in NaAC-HAC system. For B.R. system and H_3PO_4 system, the peak current of peak 1 decreases at first then increases with the pH value increasing. HAC in NaAC-HAC system possesses the stronger ability to supply proton. With the pH value increasing, the ability to supply proton decrease, electrooxidizing reaction ability of adrenaline increase, and the corresponding peak current increase. The current will decrease when it arrives at a maximum for the major factor of pH value. For H_3PO_4 system in the pH value less than 4.3, H_3PO_4 can ionize to $H_2PO_4^-$, which (together with H_3PO_4) will form hydrogen bonds with the phenolic hydroxyl, alcoholic hydroxyl and imine group of adrenaline and stabilize adrenaline, so the current decreases with the pH value increasing. When the pH value is larger than 4.3, the amount of HPO_4^- and PO_4^{3-} will increase. For the larger electronegativity of HPO_4^- and PO_4^{3-}, it is hard for them to form hydrogen bond with adrenaline. Then the current increases with the pH values increasing. In B.R. system, the turning point of the current change appears before the pH value of 4.3, for the HAC, H_3PO_4, H_3BO_3, and the corresponding acid radical. As shown in Figure 4, the peak potential of peak 1 shifts negatively with the pH value increasing, and E_{pa1}~pH presents linear relation basically. The results suggest that there exists electron transfer and proton transfer for adrenaline in the meantime.

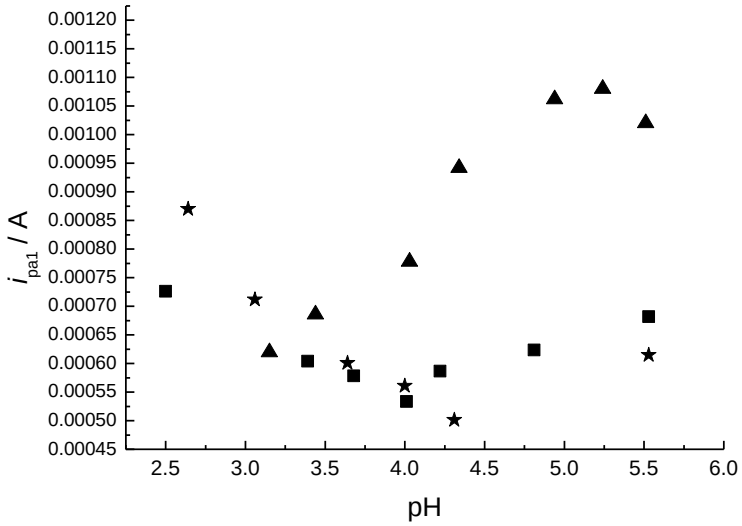

Figure 3. Relationship between i_{pa1} and pH value for the peak 1 of adrenaline electrooxidation at graphite electrode. Scan rate: 100 mV/s. ▲: NaAC-HAC solution; ■:B.R. solution; ★:Phosphate buffer solution.

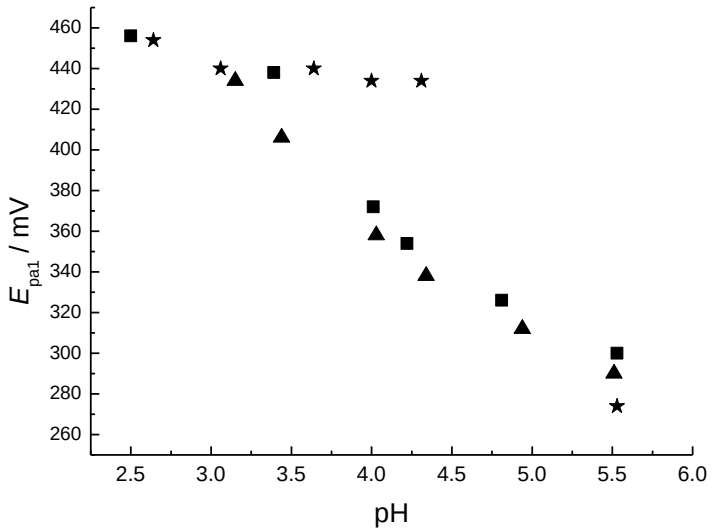

Figure 4. Relationship between E_{pa1} and pH value for the peak 1 of adrenaline electrooxidation at graphite electrode. Scan rate: 100 mV/s. ▲: NaAC-HAC solution; ■:B.R. solution; ★:Phosphate buffer solution.

In the H_3PO_4 system with pH>4, the oxidation peak 1 of adrenaline at graphite electrode will transform to two peaks. Figure 5 lists the CV curves in H_3PO_4 base solution (a) and in the adrenaline solution with the concentration of 2.5×10^{-3} mol/L (b). It can be seen that there is no redox reaction for the base solution in the scanning interval, and will not interfere the electrochemical detection of adrenaline. Therefore, peak 1 transforming to two peaks is not the effect of base solution in this condition.

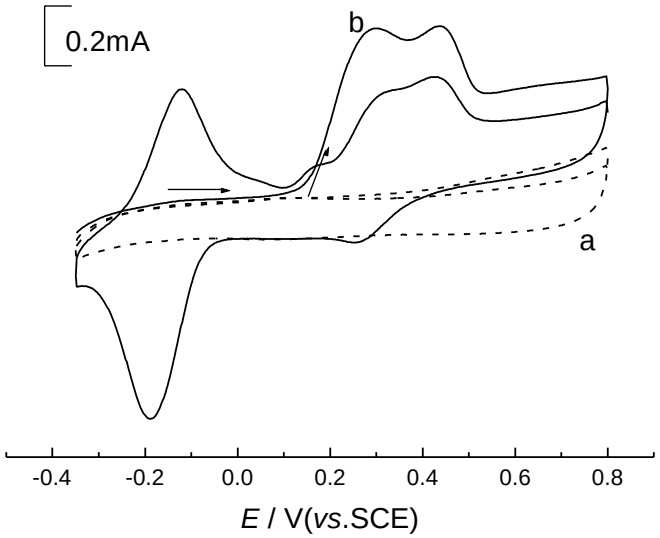

Figure 5. CV curves in Phosphate buffer solution with pH value of 5.36 at graphite electrode. (a) without adrenaline (b) the concentration of adrenaline is 2.5×10^{-3} mol/L. Scan rate: 100 mV/s.

The CV overlying curves of different scan rates for 2.5×10^{-3} mol/L adrenaline in phosphate buffer solution with pH=5.36 are shown in Figure 6. For the prepeak (the arisen peak earlier at scanning), we plot the relation between $\lg i_{pa}$ and $\lg v$. There is good linear relation between them and the slope is about 0.5, indicating the electrode process is diffusion control. The slope of $\log i_{pa}$~$\log v$ line for backpeak is near to 1, which suggests that the electrode process is controlled by adsorption [12]. The corresponding slopes and correlation coefficients are listed in Table 1.

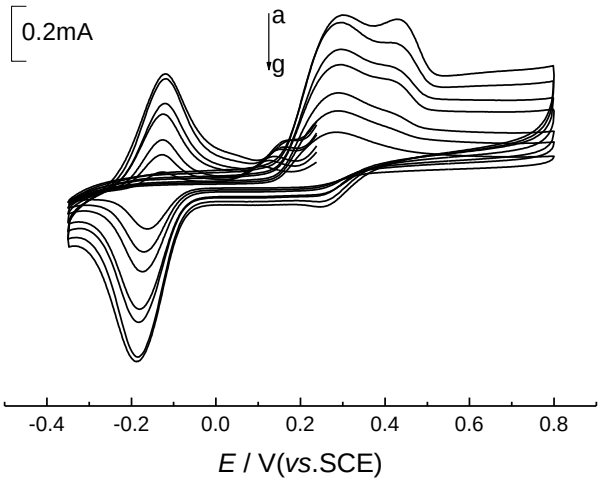

Figure 6. The CV overlying curves of different scan rates for 2.5×10^{-3} mol/L adrenaline in phosphate buffer solution with pH=5.36 at graphite electrode. Scan rate: (a)100; (b) 80; (c) 60; (d) 50 ; (e) 30; (f) 20; (g) 10 mV/s.

Table 1. Slopes and correlation coefficients of $\lg i_{pa}$~$\lg v$

	slopes of $\lg i_{pa}$~$\lg v$	correlation coefficient
prepeak	0.4844	0.9978
backpeak	0.9433	0.9927

We speculate that peak 1 of adrenaline at graphite electrode transforming to two peaks in phosphate buffer solution with pH>4 is related to the factors below:

The first impacting factor is the concentration of adrenaline (shown in Figure 7). With the concentration of adrenaline increasing, backpeak increases gradually and the concentration of adrenaline adsorbed at electrode surface also increases, so the adsorption peak show up gradually.

The second impacting factor is the electrode material. The single oxidation peak transforming to diffusion and adsorption peak only exists at graphite electrode. This phenomenon does not exist at other electrode, such as glass carbon electrode, gold electrode, and platinum electrode (see Figure 8, 9, and 10). The reason is that graphite electrode acts as hydrocarbon and can adsorb another hydrocarbon to its surrounding [13]. Therefore, there is adsorbing peak for adrenaline at graphite electrode.

The third factor is the pH value and the composition of solution. In phosphate buffer solution, prepeak increases and backpeak decreases gradually with the pH value increasing (see Figure 11), which is not found in other system. With the pH value increasing in phosphate buffer solution, the amount of PO_4^{3-} and HPO_4^{2-} will increase. PO_4^{3-} and HPO_4^{2-} have stronger repel effect on adrenaline for their larger electronegativity, which will facilitate adrenaline to be adsorbed at the electrode and turn up the adsorbing peak.

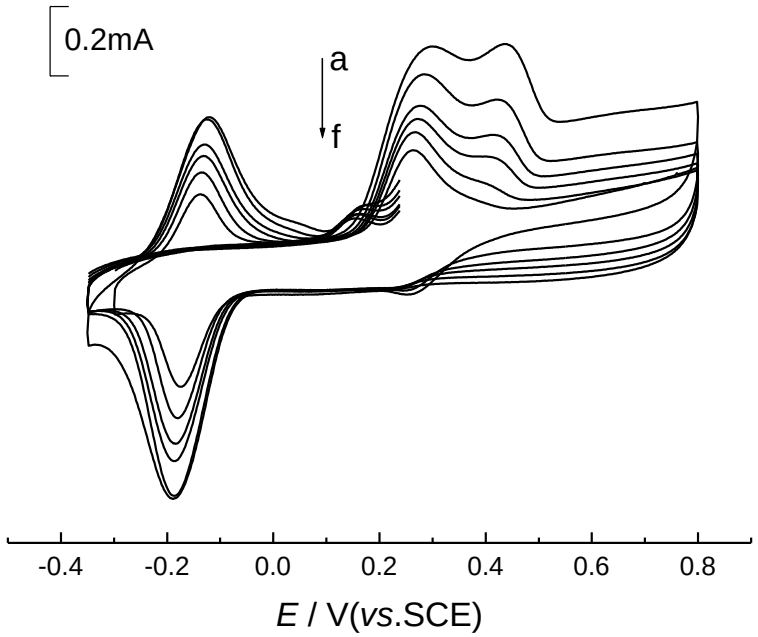

Figure 7. The CV curves of adrenaline with a series of concentration in phosphate buffer solution at graphite electrode. Scan rate: 100 mV/s. $C_{adrenaline}$: (a) 2.5×10^{-3}; (b) 1.48×10^{-3}; (c) 1.03×10^{-3}; (d) 7.64×10^{-4}; (e) 4.8×10^{-4}; (f) 3×10^{-4} mol/L.

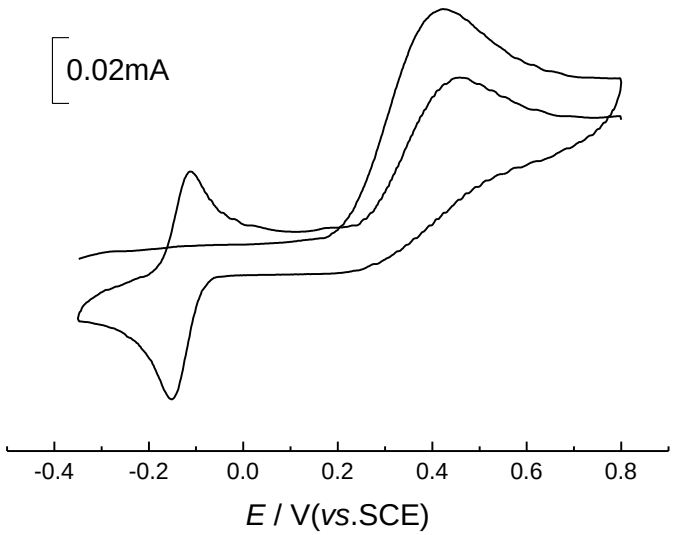

Figure 8. CV curves of 2.5×10^{-3} mol/L adrenaline in phosphate buffer solution with pH value of 5.36 at glassy carbon electrode. Scan rate: 100 mV/s.

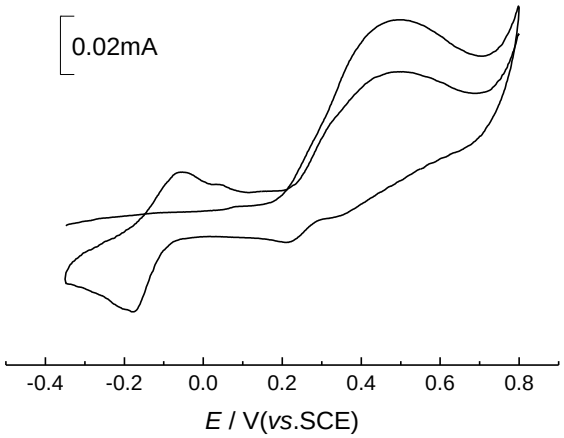

Figure 9. CV curves of 2.5×10^{-3} mol/L adrenaline in phosphate buffer solution with pH value of 5.36 at gold electrode. Scan rate: 100 mV/s.

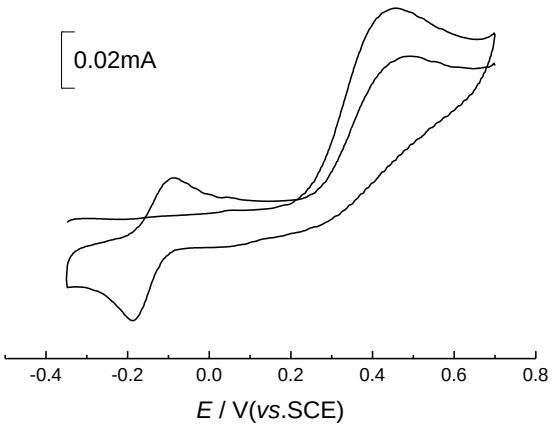

Figure 10. CV curves of 2.5×10^{-3} mol/L adrenaline in phosphate buffer solution with pH value of 5.36 at platinum electrode. Scan rate: 100 mV/s.

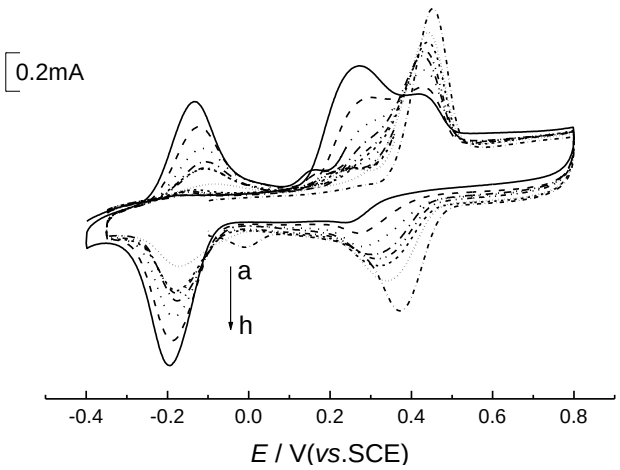

Figure 11. CV curves of 2.5×10^{-3} mol/L adrenaline in phosphate buffer solution with different pH values at graphite electrode. Scan rate: 100 mV/s. pH: (a) 2.64; (b) 3.06; (c) 3.64; (d) 4.00; (e) 4.31; (f) 4.89; (g) 5.28; (h) 5.53.

4. CONCLUSIONS

We study the interaction of adrenaline with phosphoric acid by CV approach. The oxyacid of H_3PO_4 and HAC will influence the electrooxidation reaction of adrenaline with different degrees.

In NaAC-HAC solution, B.R. solution, and phosphate buffer solution, the oxidation peak current (i_{pa1}) and peak potential (E_{pa1}) change with the pH values. In the H_3PO_4 system with pH>4, the oxidation peak 1 of adrenaline at graphite electrode will transform to two peaks. The impacting factors include the concentration of adrenaline, the electrode material, and the pH value and the composition of solution.

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