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Cyclic Voltametric Studies on the Interaction of Adrenaline With Formic Acid and Acetic Acid

Tao Liu[1,2,*]

[1] Department of Chemistry and Chemical Engineering, Jining University, Qufu 273155, Shandong, China
[2] School of Chemistry and Chemical Engineering, Shandong University, Jinan 250010, Shandong, China
[*]E-mail: zhy_yu@126.com

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The interaction of adrenaline with formic acid and acetic acid is investigated by cyclic voltametric (CV) approach. With the concentration of formic acid and acetic acid increasing, the electron transfer ability of adrenaline decreases, the peak-to-peak potential separation between anodic and canodic peak potential increases, and the anodic and canodic peak current decrease significantly. The CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in a series of KCl-HCl solution with different high concentrations of formic acid (or acetic acid) and different PH values indicate that the effect of hydrogen bond interaction on the adrenaline is much stronger than the effect of PH value on it. The change degree of peak current and peak potential of adrenaline in acetic acid system is more obvious than those in formic acid system.

Keywords: Cyclic voltametric, Adrenaline, Formic acid, Acetic acid

1. INTRODUCTION

Adrenaline belongs to a group of compounds known as catecholamines that plays aparticularly important role in the regulation of physiological process in living systems [1]. It can be oxidized easily and the product of electrooxidation is adrenalinequinone [2]. 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 [3-8].

Formic acid is the simplest fatty acid, which have many physiological functions, such as regulating insulin secretion. Formic is a major organic constituent in cloud and fog-water, as well as in precipitation [9]. A significant amount of formic acid in the atmosphere is present in the aqueous phase. Formic acid is one of the simplest molecules usually chosen as a model for studying the biological systems exhibiting the organic acidic type of bonding [10,11]. The nature of interaction of adrenaline with formic acid can explain the mechanism expected in the physiological functions of organic acids. In this sense, studying the interaction of adrenaline with formic acid is of essential importance for understanding the physiological functions of organic acids. By performing density functional theory calculations at the B3LYP/6-31G+(d) level [12], we have found that protonated adrenaline can form stable supermolecular complexes with formate anion and its derivatives. In this paper, we investigate the interaction of adrenaline with formic acid by cyclic voltammetry (CV) approach. For comparison, we also study the cyclic voltametry of the supermolecular complexes of adrenaline with acetic acid. In the present article, we will compare the experimental results with the theoretical results previous, 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 6×10^{-3} mol/L. KCl-HCl solution was used as the studying medium with constant ionic strength (I=1) of KCl. 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 platinum circular electrode and a graphite electrode served as a working electrode, respectively, 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. CV of adrenaline in the solution with different concentration of formic acid

The CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in the KCl-HCl solution (constant ionic strength (I=1) and constant PH value is 1) with different concentration of formic acid are presented in Fig. 1. Peak 1 of curve a corresponds to the oxidation of adrenaline into adrenalinequinone (anodic peak), and Peak 2 of curve a corresponds to the reduction of adrenalinequinone into adrenaline (canodic peak). It can be seen that with the addition of formic acid, the electron transfer ability of adrenaline decreases as follows: the anodic peak potential (E_{pa}) shifts positively, the canodic peak potential (E_{pc}) shifts negatively, the peak-to-peak potential separation between anodic and canodic peak potential (ΔE_p) increases, and the anodic and canodic peak current (i_{pa} and i_{pc}) decrease significantly. The results demonstrate the inhibition effect of formic acid on the electron transfer reaction of adrenaline, which has been verified by the fact that formic acid can form stable supramolecular complexes with adrenaline by hydrogen bond interaction and the formed supramolecular complexes will protect the phenolic hydroxyl groups of adrenaline and make it hard to donate H^+ and be oxidized [12].

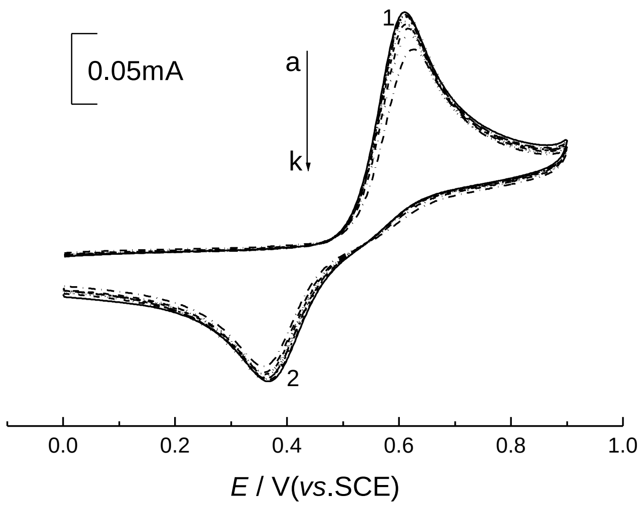

Figure 1. CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in KCl-HCl（pH =1）solution with different concentration of formic acid. Scan rate: 100 mV/s. $C_{adrenaline}$:$C_{formic\ acid}$ (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:10; (f) 1:20; (g) 1:50; (h) 1:100; (i) 1:200; (j) 1:500; (k) 1:750

3.2. CV of adrenaline in solution with different high-concentration of formic acid and different PH value

The CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in a series of KCl-HCl solution (constant ionic strength (I=1) of KCl) with different high concentrations of formic acid and different PH values are shown in Fig. 2. It can be seen from Fig. 2 that with the concentration of formic acid increasing and the PH value of solution decreasing, the peak-to-peak potential separation between anodic and canodic peak potential becomes larger, while the anodic and canodic peak current becomes smaller. In this experimental condition, there is a linear relationship between E_{pa} (and i_{pa}) with PH value. The linear regression analyses with different PH values are shown in Table 1.

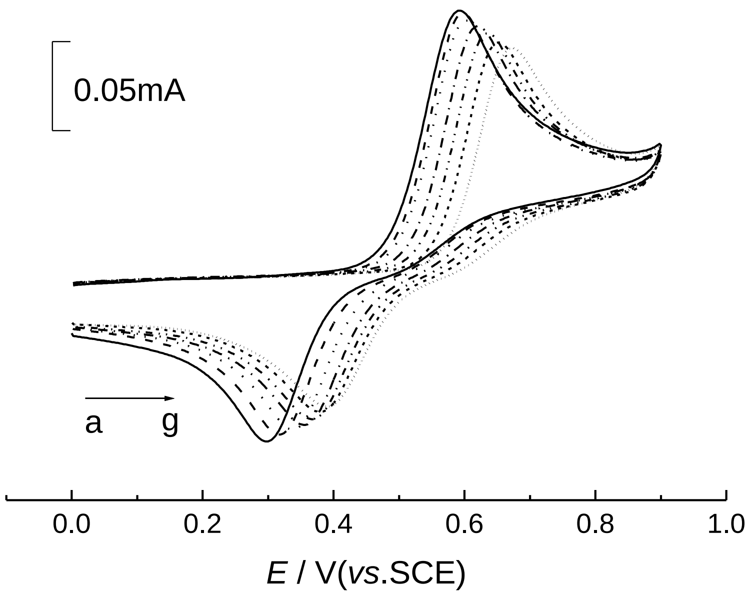

Figure 2. CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in a series of KCl-HCl solution with different high concentrations of formic acid and different PH values. Scan rate: 100 mV/s. pH: (a) 1.84; (b) 1.59; (c) 1.34; (d) 1.00; (e) 0.71; (f) 0.43; (g) 0.16. $C_{formic\ acid}$: (a) 0.47; (b) 1.17; (c) 2.33; (d) 4.66; (e) 6.99; (f) 9.34; (g) 11.66 mol/L.

Table 1. Relationship between E_{pa}、 i_{pa} and pH at a scan rate of 100 mV/s in a series of KCl-HCl solution with different high concentrations of formic acid and different PH values

Linear equation	Coefficient of correlation
E_{pa}=0.6797-0.0585pH	0.9944
$10^4 i_{pa}$=1.2039+0.1307 pH	0.9956

In order to eliminate the influence of PH values on the experimental results, we drew the CV curves of 6×10^{-3} mol/L adrenaline at graphite electrode in the HCl solution (constant ionic strength) with different PH values (see Fig. 3). We can find that in the HCl solution without formic acid, ΔE_p decreases and i_p increases with the PH value becoming smaller, which is contrary to the changing trend of ΔE_p and i_p for adrenaline in the solution with different high concentrations of formic acid and different PH values. The phenomenon can be interpreted by the hydrogen bond interaction between adrenaline and formic acid, which will protect the phenolic hydroxyl groups of adrenaline and make it hard to donate H^+ and be oxidized. The effect of hydrogen bond interaction on the adrenaline is much larger than the effect of PH value on it. Therefore, ΔE_p will decrease and i_p will increase with the PH values increasing in the solution with different high concentrations of formic acid and different PH values.

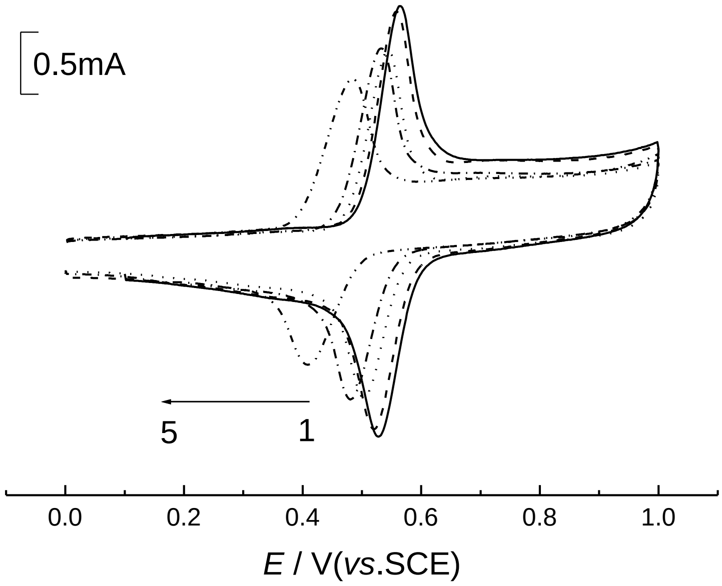

Figure 3. CV curves of 6×10^{-3} mol/L adrenaline at graphite electrode in the HCl solution with different PH values. Scan rate: 100 mV/s. C_{HCl}: (1) 0.5; (2) 0.4; (3) 0.2; (4) 0.1; (5) 0.01 mol/L

3.3. CV of adrenaline in the solution with different concentration of acetic acid

In this section, the KCl-HCl solution (constant ionic strength (I=1) and constant PH value is 1) was also used as the studying medium as the experiment about acetic acid. The CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in the KCl-HCl solution with different concentration of acetic acid are presented in Fig. 4.

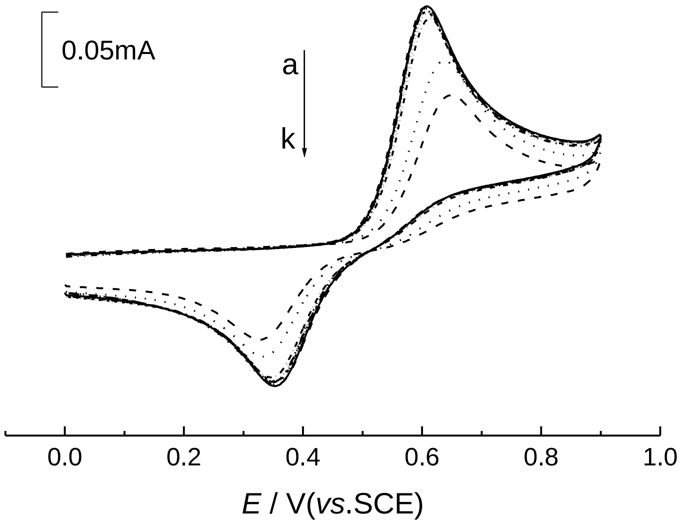

Figure 4. CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in KCl-HCl（pH =1）solution with different concentration of acetic acid. Scan rate: 100 mV/s. $C_{adrenaline}$:$C_{acetic\ acid}$ (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:10; (f) 1:20; (g) 1:50; (h) 1:100; (i) 1:200; (j) 1:500; (k) 1:1000

The changing trend is similar to the experimental phenomena of formic acid system. With the concentration proportion of acetic acid increasing, E_{pa} shifts positively, E_{pc} shifts negatively, ΔE_p increases, and i_p decreases. The results show that there is also inhibition effect of acetic acid on the electron transfer reaction of adrenaline. The hydrogen bond interaction will protect the phenolic hydroxyl groups of adrenaline and make it hard to donate H^+ and be oxidized.

3.4. CV of adrenaline in solution with different high-concentration of acetic acid and different PH value

The CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in a series of KCl-HCl solution (constant ionic strength (I=1) of KCl) with different high concentrations of acetic acid and different PH values are shown in Fig. 5. It can be seen from Fig. 5 that with the concentration of acetic acid increasing and the PH value of solution decreasing, the peak-to-peak potential separation between anodic and canodic peak potential becomes larger, while the anodic and canodic peak current becomes smaller. The cause can be attributed to the stronger proton self-transferring role and the stronger ability of donating proton for acetic acid. The ability of donating proton for acetic acid is stronger in the low PH value system than that in the high PH value system, which will stabilize adrenaline and decrease the electro-oxidation reaction ability of adrenaline. In addition, E_{pa} shifts negatively with the PH value increasing and E_{pa} linear relates with PH value, which shows that there exist electron transfer and proton transfer simultaneously. In this experimental condition, there is a linear relationship between E_{pa} (and i_{pa}) with PH value. The linear regression analyses with different PH values are shown in Table 2.

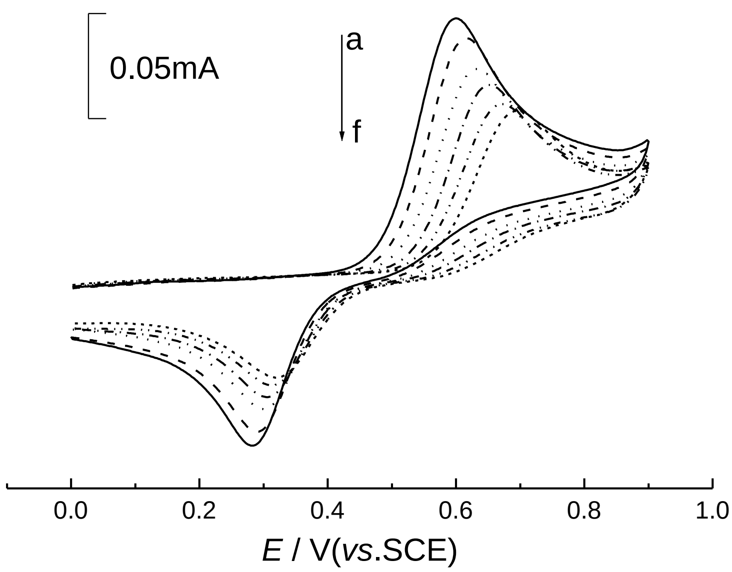

Figure 5. CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in a series of KCl-HCl solution with different high concentrations of acetic acid and different PH values. Scan rate: 100 mV/s. pH: (a) 1.94; (b) 1.74; (c) 1.51; (d) 1.28; (e) 1.07; (f) 0.81. $C_{\text{acetic acid}}$: (a) 1.74; (b) 3.13; (c) 5.04; (d) 6.85; (e) 8.59; (f) 10.34 mol/L.

Table 2. Relationship between E_{pa}、i_{pa} and pH at a scan rate of 100 mV/s in a series of KCl-HCl solution with different high concentrations of acetic acid and different PH values

Linear equation	Coefficient of correlation
E_{pa}＝0.7626-0.0847pH	0.9984
$10^4 i_{pa}$＝0.2926＋0.4487 pH	0.9953

Compared the CV experiments of acetic acid with those of formic acid, the change degree of peak current of adrenaline in acetic acid system is larger than that in formic acid system. The possible reason, we suppose, is that acetic acid can provide more effective protection on the phenolic hydroxyl groups of adrenaline. As we reported previous, the hydrogen bond interaction between acetic acid and adrenaline is stronger than that between formic acid and adrenaline, so the inhibition effect of acetic acid on adrenaline is larger than that of formic acid on adrenaline. Therefore, as shown in Figs. 1 and 4, the change degree of peak current and peak potential in acetic acid system is more obvious than those in formic acid system.

Therefore, comparing the five Figures as shown in the text, we can conclude that the hydrogen bond interaction on the electrochemical behavior of adrenaline is much larger than the effect of PH value on it and the inhibition effect of acetic acid on adrenaline is larger than that of formic acid on adrenaline. We would expect that the results will be useful for experimental researchers working in this field.

4. CONCLUSIONS

We study the interaction of adrenaline with formic acid and acetic acid by CV approach. With the addition of formic acid and acetic acid, the electron transfer ability of adrenaline decreases, the peak-to-peak potential separation between anodic and canodic peak potential increases, and the anodic and canodic peak current decrease significantly. The CV curves of 6×10^{-3} mol/L adrenaline at platinum electrode in a series of KCl-HCl solution with different high concentrations of formic acid (or acetic acid) and different PH values indicate that the effect of hydrogen bond interaction on the adrenaline is much larger than the effect of PH value on it.

The change degree of peak current of adrenaline in acetic acid system is larger than that in formic acid system, which is consistence with the calculational results.

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