CHAPTER 5

ELECTROCHEMICAL RESPONSES OF POTASSIUM FERRICYANIDE AND DOPAMINE SEPARATELY BY SODIUM DODECYL SULFATE MODIFIED CARBON PASTE ELECTRODE

Potassium Ferricyanide

Dopamine
5.1. Introduction

A carbon paste electrode (CPE) modified by sodium dodecyl sulphate (SDS) was used for the detection of K$_3$Fe(CN)$_6$ and dopamine. Cyclic voltammetry (CV) demonstrated improved response of K$_3$Fe(CN)$_6$ and dopamine sensor at SDS/CPE compared to bare CPE. The effect of SDS concentration on the electrode quality also reveals that SDS formed a monolayer on a carbon paste electrode surface with a high density of negative charged end directed outside the electrode. On the formation of a SDS monolayer, the structure of the electrode interface changed significantly and the electrode/solution interface was replaced by the SDS monolayer/solution interface. The detection limit for K$_3$Fe(CN)$_6$ is $1 \times 10^{-4}$ M and dopamine $1 \times 10^{-7}$ M.

5.2. Chemistry and Biological Relevance of Dopamine and Sodium Dodecyl Sulphate

The chemistry and biological relevance of dopamine has already been discussed in section 3.2.

Sodium dodecyl sulfate (C$_{12}$H$_{25}$SO$_4$Na), is an anionic surfactant that is used in household products such as toothpastes, shampoos, shavingfoams and bubble baths for its thickening effect and its ability to create a lather. The molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphiphilic properties required of a detergent. In laboratories, SDS is commonly used in preparing proteins for polyacrylamide gel electrophoresis. SDS works by disrupting non-covalent bonds in the proteins, thereby denaturing them, causing the molecules to lose their native shape. Also, anions of SDS bind to the main peptide chain at a ratio of one SDS anion for every two amino acid residues. This effectively imparts a negative charge on the protein that is proportional to the mass of that protein. This new negative charge is significantly greater than the original charge of that protein.

A detailed review of electrochemistry of surfactants has been discussed in section 3.3.
5.3. Experimental

Reagents and chemicals

Potassium ferricyanide $K_3Fe(CN)_6$, dopamine, KCl, sodium do-decyl sulphate and perchloric acid used were of analytical grade quality from sd. Fine chemicals and used without further purification. 10mM dopamine stock solutions were prepared by adding dopamine to 0.1M perchloric acid, 10mM potassium ferricyanide was prepared by dissolving in double distilled water. In all the measurements, the supporting electrolyte used was 1M KCl.

5.4. Results and Discussion

Electrochemical response of $K_3Fe(CN)_6$ at SDS modified carbon paste electrode

Fig. 5.1 shows the electrochemical response of $K_3Fe(CN)_6$ at SDS modified carbon paste electrode. Owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of $K_3Fe(CN)_6$ at bare carbon paste electrode is low current signal (solid line). However, the voltammetric response is apparently improved at SDS modified carbon paste electrode, reflected by the enlargement of the peak currents ($i_{pc}$) and the decline of the potential difference ($\Delta E_p$) between the reduction and the oxidation peaks curve (dashed line).

Improvement of the electrode quality of CPE modified with SDS

Fig. 5.2 shows the voltammograms of $K_3Fe(CN)_6$ at different electrodes. No peaks are observed at both bare CPE (curve a) and SDS/CPE (curve b) in the blank supporting electrolyte. The background current is greatly enlarged at SDS/CPE compared with that at bare carbon paste electrode (more than 100 times). This indicates that the surface property of the modified electrode has been significantly changed. In contrast to the low current response at bare CPE (curve c), the electrochemical signal of $K_3Fe(CN)_6$ is enhanced at SDS/CPE (curve d), which is reflected by the improvement of both the shape of redox peaks and the magnitude of the peak currents ($i_{pc}$).
**Effect of concentration**

The CV's showed successive enhancement of peak current on increasing K₃Fe(CN)₆ concentration Fig. 5.3a. The plot of peak current (obtained by measuring the peak height) versus the respective concentration of K₃Fe(CN)₆ was found to be linear in the range 1.0 to 3.5mM as shown in Fig. 5.3b.

**Effect of scan rate**

The linear dependence of reduction peak current on the scan rate showed that K₃Fe(CN)₆ underwent an adsorption-controlled process as shown in Fig. 5.4a,b. SDS formed a special ion complex with K₃Fe(CN)₆ through electrostatic interaction and might be adsorbed at the interface between the hydrophobic surface and the aqueous solution. The proposed behaviour of K₃Fe(CN)₆ at a carbon paste electrode in the presence of SDS might arise from the adsorption of SDS at the electrode surface and the interaction between SDS and K₃Fe(CN)₆, i.e. the electrochemical response of K₃Fe(CN)₆ in the presence of SDS could be utilized to investigate the adsorptive behaviour of SDS at a carbon paste electrode.

**Effect of SDS on peak current and peak potential**

Fig. 5.5a,b shows the effect of SDS concentration on the peak current and peak potential of 1.0x10⁻³M K₃Fe(CN)₆. When the SDS concentration is lower than the CMC, E_{pc} increases rapidly with increase of SDS concentration. However, the cathodic peak potentials of K₃Fe(CN)₆ apparently decrease in the range of 4-12mg. This plot is very similar to the SDS adsorption isotherm on the graphite surface, which also has the maximum adsorption capacity about CMC. Surfactant molecules will form micelles at high concentration (C_{SDS} > CMC), which causes the decrease of available dissociative SDS molecules and the SDS adsorbed on surface. It indicates the accumulation ability of
SDS/CPE to $K_3Fe(CN)_6$ has a direct proportion with SDS adsorbance on electrode surface. Thus, it is rational infer that the CPE modified by 4mg SDS is covered by a compact SDS monolayer. The hydrophobic alkyl terminal group in the SDS molecule adsorbed at the hydrophobic electrode surface through Vander Walls interaction, and the hydrophilic sulfate terminal group oriented outside. The relevant report has proved that the adsorbed SDS organized in a dense monolayer on a hydrophobic $C_{18}$ surface near the CMC which also supported our inference \(^9\,\text{10}\).

**Effect of SDS concentration on peak potential difference ($\Delta E_p$)**

As the concentration of SDS increases the peak potential difference goes on decreasing up to 4mg SDS and then the potential difference increases as the concentration of SDS increases as shown in Fig. 5.6. For all other voltammetric investigations 2mg SDS was chosen as a constant for further studies.

**Dependence of SDS adsorptive behaviour on SDS modified carbon paste electrode**

Fig. 5.7 shows the dependence of the voltammetric responses for $1.0\times10^{-3}$M $K_3Fe(CN)_6$ on SDS concentration. Obviously, the addition of SDS can effectively promote the signals of $K_3Fe(CN)_6$, even for a trace concentration of SDS (2mg). With the increase of SDS concentration the reduction peak potential ($E_{pc}$) shifts negatively and the oxidation peak potential ($E_{pa}$) shifts in the positive direction. With the continuous increase of SDS concentration, both peak potential tends to be stable up to 6mg SDS (Fig. 7). As mentioned above, SDS might form a monolayer in this concentration range. The further increase of SDS concentration leads to the enlargement of $\Delta E_p$, due to the excessive compactness of the SDS monolayer and subsequently the non-negligible electrostatic interaction between adsorbed substrates. Over the whole concentration range, both the reduction ($i_{pc}$) and the oxidation peak currents ($i_{pa}$) increases with the increase of SDS concentration.
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Accumulation ability of SDS/CPE

The accumulation ability of SDS/CPE but the low determination limit for detecting K$_3$Fe(CN)$_6$ was still unknown. Fig. 5.8 shows the cyclic voltammograms in 1M KCl of SDS/CPE presoaked in a series of dilute K$_3$Fe(CN)$_6$ solutions for 10 min. No apparent peaks were appear in K$_3$Fe(CN)$_6$ 1x10$^{-4}$M K$_3$Fe(CN)$_6$ (solid line) while a pair of well defined redox peaks are found in 1x10$^{-3}$M K$_3$Fe(CN)$_6$ (dashed line). This suggests the strong accumulation ability of SDS/CPE.

Electrochemical response of Dopamine at SDS modified carbon paste electrode

Fig. 5.9 shows the electrochemical response of dopamine at SDS modified carbon paste electrode. The cyclic voltammogram of dopamine at bare carbon paste electrode is low current signal (solid line). However, the voltammetric response is apparently improved at SDS modified carbon paste electrode, reflected by the enlargement of the peak currents ($i_{pa}$) and the decline of the potential difference ($\Delta E_p$) between the reduction and the oxidation peaks curve (dashed line).

Improvement of the electrode quality of CPE with the modification of SDS

Fig. 5.10 shows the voltammograms of dopamine at different electrodes. No peaks are observed at both bare CPE (curve a) and SDS/CPE (curve b) in the blank supporting electrolyte. The background current is greatly enlarged at SDS/CPE compared with that at bare carbon paste electrode (more than 100 times). This indicates that the surface property of the modified electrode has been significantly changed. In contrast to the poor response at bare CPE (curve c), the electrochemical signal of dopamine is enhanced at SDS/CPE (curve d), which is reflected by the improvement of both the shape of redox peaks and the magnitude of the peak currents ($i_p$).
Effect of concentration for dopamine

As the concentration of dopamine was varied from 1.0 to 3.0mM and cyclic voltammograms were recorded Fig. 5.11a. The anodic peak current obtained were found to increase linearly with increase in concentration of dopamine Fig. 5.11b.

Effect of Scan rate

Fig. 5.12 shows the cyclic voltammograms of 1mM dopamine on an SDS/CPE at different scan rate with the increase of scan rate, the peak currents also increases gradually Fig. 5.12a. The relationship of the oxidation peak current with the scan rate was constructed and the results are shown in Fig. 5.12b. In the range from 20-100mV/s the scan rate v, which indicates the electron transfer reaction was adsorption-controlled.

Effect of SDS on peak current and peak potential

Fig. 5.13a and 5.13b shows the effect of SDS concentration on the peak current and peak potential of \(1.0 \times 10^{-3}\)M dopamine. When the SDS concentration is lower than the 6mg the critical micelle concentration (CMC) of SDS at room temperature, both \(i_{pa}\) and \(E_{pa}\) increases rapidly with increase of SDS concentration. However, the signals of dopamine apparently decrease in the range of 6-12mg.

Effect of SDS concentration on peak potential difference (\(\Delta E_p\))

As the concentration of SDS increases the peak potential difference goes on decreasing from 129 to 63mV for 2mg SDS and then there was a slight increase in the \(\Delta E_p\) as shown in Fig. 5.14.

Dependence of SDS adsorptive behaviour on SDS modified carbon paste electrode

Fig. 5.15 shows the dependence of the voltammetric responses for \(1.0 \times 10^{-3}\)M dopamine on SDS concentration (the corresponding data are listed as table 2). Obviously, the addition of SDS can effectively promote the signals of dopamine, even for a trace concentration of SDS (2mg). With the increase of SDS concentration the oxidation peak
potential \( E_{pa} \) shifts positively and the oxidation peak potential \( E_{pc} \) shifts in the negative direction. With the continuous increase of SDS concentration, both peak potential tends to be stable up to 6mg SDS (Fig. 5.15). As mentioned above, SDS might form a monolayer in this concentration range. The further increase of SDS concentration leads to the enlargement of \( \Delta E_p \), due to the excessive compactness of the SDS monolayer and subsequently the non-negligible electrostatic interaction between adsorbed substrates. Over the whole concentration range, both the reduction \( i_{pc} \) and the oxidation peak currents \( i_{pa} \) increases with the increase of SDS concentration. Improvement of the electrode quality of CPE with the modification of CTAB was studied by Hu et al.\(^\text{15} \) and our modification shows maximum increase in the current signal.

**Accumulation ability of SDS/CPE**

Fig. 5.16 shows the cyclic voltammograms in 1M KCl of SDS/CPE presoaked in a series of dilute dopamine solutions for 10 min at SDS/CPE no apparent peaks were appeared in \( 1 \times 10^{-7} \)M dopamine while a pair of well defined redox peaks are found in \( 1 \times 10^{-3} \) to \( 1 \times 10^{-6} \)M dopamine. This suggests the strong accumulation ability of SDS/CPE.

**5.5. Conclusion**

The modified electrode shows enhancement in the current signals for potassium ferricyanide and dopamine. The concentration of SDS shows increase for 4 mg for ferricyanide and 6 mg for dopamine. The electrode has a regulated surface covered by a compact monolayer of SDS with high density of negative charges directed outside. This electrode exhibited strong enrichment ability towards dopamine and ferricyanide systems. The application of this electrode creates a new approach to determine the importance neurotransmitter dopamine sensitivity and it acts as sensor.
Table 1: Cyclic voltammetric parameters for $1 \times 10^{-3} \text{M} \text{K}_3\text{Fe(CN)}_6$ in 1M KCl at carbon paste electrode in the presence of SDS with different concentrations.

<table>
<thead>
<tr>
<th>$C_{\text{SDS}}$ (mg)</th>
<th>$E_{\text{pc}}$, (mV)</th>
<th>$E_{\text{pa}}$, (mV)</th>
<th>$\Delta E_p$, (mV)</th>
<th>$i_{\text{pc}}$, (µA)</th>
<th>$i_{\text{pa}}$, (µA)</th>
<th>$i_{\text{pc}}/i_{\text{pa}}$</th>
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<td>34</td>
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<td>54.7</td>
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<td>279</td>
<td>36</td>
<td>100.8</td>
<td>109.3</td>
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<td>1.00</td>
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<td>237</td>
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Table 2: Cyclic voltammetric parameters for $1 \times 10^{-3} \text{M}$ dopamine in 1M KCl at carbon paste electrode in the presence of SDS with different concentrations.

<table>
<thead>
<tr>
<th>$C_{\text{SDS}}$ (mg)</th>
<th>$E_{\text{pc}}$, (mV)</th>
<th>$E_{\text{pa}}$, (mV)</th>
<th>$\Delta E_p$, (mV)</th>
<th>$i_{\text{pc}}$, (µA)</th>
<th>$i_{\text{pa}}$, (µA)</th>
<th>$i_{\text{pc}}/i_{\text{pa}}$</th>
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<td>21.5</td>
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<td>63</td>
<td>220.3</td>
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<td>336.0</td>
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</tr>
<tr>
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<td>315.1</td>
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<td>274.8</td>
<td>0.81</td>
</tr>
<tr>
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<td>404</td>
<td>101</td>
<td>339.4</td>
<td>289.8</td>
<td>0.85</td>
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Fig. 5.1. Electrochemical response of 1mM K$_3$Fe(CN)$_6$ (solid line) at bare carbon paste electrode and (dashed line) at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mV s$^{-1}$. 

Fig. 5.2. Electrochemical response of 1mM K$_3$Fe(CN)$_6$ (solid line) at bare carbon paste electrode (curves a and c) and SDS modified carbon paste electrode (curves b and d) supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$. 
Fig. 5.3a. Effect of concentration variation of K$_3$Fe(CN)$_6$ at SDS modified carbon paste electrode $a=1.0$, $b=1.5$, $c=2.0$, $d=2.5$, $e=3.0$ mM supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.

Fig. 5.3b. Effect of concentration variation of K$_3$Fe(CN)$_6$ at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$. 
Fig. 5.4a. Effect of scan rate variation of 1 mM K₃Fe(CN)₆ at SDS modified carbon paste electrode \(a=50\), \(b=100\), \(c=150\), \(d=200\), \(e=250\) mV supporting electrolyte 1M KCl

Fig. 5.4b. Effect of scan rate variation of 1 mM K₃Fe(CN)₆ at SDS modified carbon paste electrode supporting electrolyte 1M KCl
Fig. 5.5a. Effect of modifier concentration on peak current for 1mM K$_3$Fe(CN)$_6$ at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.

Fig. 5.5b. Effect of modifier concentration on peak potential for 1mM K$_3$Fe(CN)$_6$ at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$. 
Fig. 5.6. Effect of peak potential difference for 1mM K₃Fe(CN)₆ at SDS modified carbon paste electrode with supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
Fig. 5.7. Dependence of Cyclic voltammograms for 1mM $\text{K}_3\text{Fe(CN)}_6$ at carbon paste electrode on SDS concentration $a=0$, $b=2.0$, $c=4.0$, $d=6.0$, $e=8.0$, $f=10.0$, $g=12.0$ mg supporting electrolyte 1M KCl at scan rate 50 mV/$\text{s}^{-1}$.

Fig. 5.8. Electrochemical response of different concentrations of $\text{K}_3\text{Fe(CN)}_6$ at SDS modified carbon paste electrode (dashed line) $1\times10^{-3}$M; (solid line) $1\times10^{-4}$M supporting electrolyte 1M KCl at scan rate 50 mV/$\text{s}^{-1}$.
Fig. 5.9. Electrochemical response of 1mM dopamine (solid line) at bare carbon paste electrode and (dashed line) at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$. 
Fig. 5.10. Electrochemical response of 1mM dopamine (solid line) at bare carbon paste electrode (curves a and c) and SDS modified carbon paste electrode (curves b and d) supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$. 
Fig. 5.11a. Effect of concentration variation of dopamine at SDS modified carbon paste electrode a=1.0, b=1.5, c=2.0, d=2.5, e=3.0mM supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.

Fig. 5.11b. Effect of concentration variation of dopamine at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
Fig. 5.12a. Effect of scan rate variation of 1mM dopamine dopamine at SDS modified carbon paste electrode a=20, b=30, c=40, d=50, e=60, f=70, g=80, h=90 mV supporting electrolyte 1M KCl

Fig. 5.12b. Effect of scan rate variation of 1mM dopamine dopamine at SDS modified carbon paste electrode supporting electrolyte 1M KCl
Fig. 5.13a. Effect of modifier concentration on peak current for 1mM dopamine at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.

Fig. 5.13b. Effect of modifier concentration on peak potential for 1mM dopamine at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
Fig. 5.14. Effect of peak potential difference for 1mM dopamine at SDS modified carbon paste electrode with supporting electrolyte 1M KCl at scan rate 50 mVs\(^{-1}\).
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Fig. 5.15. Dependence of Cyclic voltammograms for 1mM dopamine at carbon paste electrode on SDS concentration a=0, b=2.0, c=10.0, d=12.0, e=8.0, f=4.0, g=6.0 mg supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.

Fig. 5.16. Electrochemical response of different concentrations of dopamine e=1x10⁻³ d=1x10⁻⁴, c=1x10⁻⁵, b=1x10⁻⁶, a=1x10⁻⁷M at SDS modified carbon paste electrode supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
3.7. References


