CHAPTER 3A

CYCLIC VOLTAMMETRIC STUDIES OF POTASSIUM FERRICYANIDE AND DOPAMINE BY USING TRITON X-100 AT CARBON PASTE AND CERESIN WAX CARBON PASTE ELECTRODES
Chapter 3A

CV studies of potassium ferricyanide and dopamine using TX-100

3.1. Introduction

The adsorption of Triton X-100 (TX-100) on a carbon paste and ceresin wax carbon paste electrodes was investigated by cyclic voltammetry. The results showed that TX-100 exhibited two types of adsorptive behavior at a carbon paste and ceresin wax carbon paste electrodes at a different concentration ranges: monomer adsorption at concentration below $3 \times 10^{-6}$M and monolayer adsorption at concentration higher than $3 \times 10^{-6}$M. In the monomer adsorption range, the adsorption of TX-100 could effectively reduce the charge transfer resistance and increase the charge transfer rate. However, the surface properties of the carbon paste and ceresin wax carbon paste electrodes hardly changed. On the formation of a TX-100 monolayer, the structure of the electrode interface changed significantly and the electrode/solution interface was replaced by the TX-100 monolayer/solution interface.

3.2. Chemistry and Biological Relevance of Surfactants and Dopamine

The term surfactant is a blend of "surface acting agent". Surfactants are usually organic compounds that are amphipathic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water. The term surfactant was coined by Antara Products in 1950.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC.

A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more
specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

Triton X-100 \( (\text{C}_1\text{H}_2\text{O}_n\text{C}_2\text{H}_4\text{O})_9 \) is a nonionic surfactant which has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group. The nonionic surfactant Triton-X 100 has many applications in a wide range of different disciplines. As a wetting agent in the microscopy and histology laboratory, in the form of dilute solutions, it is used as a wetting agent for effecting certain staining protocols and is also used as a wetting agent for the cleaning of diamond knives. In the life sciences, it is often times used as an aid for dissolution of protease. It is also commonly used in some formulations for emulsion polymerizations. It can also be used as a detergent and it is considered 100% "active" and biodegradable in liquid form. It has numerous general uses as a wetting agent, emulsifier or even as a mild detergent.

Dopamine is a chemical naturally produced in the body. In the brain, dopamine functions as a neurotransmitter, activating dopamine receptors. Dopamine is also a neurohormone released by the hypothalamus. Its main function as a hormone is to inhibit the release of prolactin from the anterior lobe of the pituitary. Dopamine can be supplied as a medication that acts on the sympathetic nervous system, producing effects such as increased heart rate and blood pressure. However, since dopamine cannot cross the blood-brain barrier, dopamine given as a drug does not directly affect the central nervous system. To increase the amount of dopamine in the brains of patients with diseases such as Parkinson's disease and Dopa-Responsive Dystonia, a synthetic precursor to dopamine such as L-DOPA (levodopa) can be given, since this will cross the blood-brain barrier.

Dopamine has many functions in the brain. Dopamine affects the basal ganglia motor loop which in turn affects the way the brain controls our movements. Shortage of dopamine, particularly the death of dopamine neurons in the nigrostriatal pathway, causes
Parkinson's disease, in which a person loses the ability to execute smooth, controlled movements.

Most importantly, dopamine is central to the reward system. Dopamine is commonly associated with the pleasure system of the brain, providing feelings of enjoyment and reinforcement to motivate a person proactively to perform certain activities. Dopamine is released by naturally rewarding experiences such as food, sex, use of certain drugs and neutral stimuli that become associated with them. This theory is often discussed in terms of drugs (such as cocaine and amphetamines), which seem to be directly or indirectly related to the increase of dopamine in these areas, and in relation to neurobiological theories of chemical addiction, arguing that these dopamine pathways are pathologically altered in addicted persons. However, cocaine and amphetamines influence separate mechanisms of action. Cocaine is a dopamine transporter blocker that competitively inhibits dopamine uptake to increase the lifetime of dopamine and augments an overabundance of dopamine (an increase of up to 150%) within the parameters of the dopamine neurotransmitters. Like cocaine, amphetamines increase the concentration of dopamine in the synaptic gap, but by a different mechanism. Amphetamines are similar in structure to dopamine, and so can enter the terminal button of the presynaptic neuron via its dopamine transporters as well as by diffusing through the neural membrane directly.

3.3. Review of Electrochemistry of Surfactants

The applications of surfactants in electrochemistry and electro analytical chemistry have been widely reported. Hu's group has introduced surfactants to electro analytical chemistry to improve the detection limits of some biomolecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace surfactants. They proposed a synergistic adsorption mechanism to interpret these enhancement effects of surfactants.
combine with the substrate in certain forms and strengthen their adsorption on the electrode surface, which facilitated the electron or the substance transfer between the electrode and the solution. Digua et al.\textsuperscript{6,7} mixed the amphiphile hexadecyl sulphonic acid to carbon paste to produce a surfactant modified carbon paste electrode (CPE). Falars and Petridis\textsuperscript{8} reported organoclay modified glassy carbon electrode (GCE) coated by a cationic surfactant bilayer. Chengguo Hu and Shengshui Hu\textsuperscript{9} reported that CTAB formed a compact monolayer on the electrode surface with high density of positive charges. Jianbin Zheng and Xiaoli Zhu\textsuperscript{10} reported that SDS formed a monolayer on CPE surface with high density of negative charged end directed outside the electrode. Chengguo et al.\textsuperscript{11} studied the adsorption of cetyl trimethyl ammonium bromide at carbon paste electrode and the enhancement effect in thyroxine reduction by voltammetry and electrochemical impedance spectroscopy. Shen-Ming Chen and Wen-Yan Chzo\textsuperscript{12} have studied the simultaneous voltammetric detection of dopamine and ascorbic acid using didodecyl dimethyl ammonium bromide (DDAB) film modified electrodes. Some less soluble surfactants were employed in the immobilization of macro molecules or other fuctional materials, Wu et al.\textsuperscript{13} developed a stable multi-wall carbon nanotube (MWNT) modified electrode based on the immobilization of MWNT in the film of insoluble dihexadecyl phosphate (DHP) on a glassy carbon electrode. This electrode exhibited an electro catalytic activity towards biomolecules and has been used as a sensor for the determination of these species\textsuperscript{14,15}. The applications of surfactants in the immobilization of biomolecules were also reported\textsuperscript{16-18}. Chattopadhyay and Mazumdar\textsuperscript{19} studied the direct electrochemistry of heme proteins and a neutral surfactant modified glassy carbon electrode. The results showed that the surfactant molecules interacted with the electrode surface in a specific manner and anchored the protein molecules to align in a suitable orientation, which promoted the electron transfer between the protein molecules and the glassy carbon electrode. Contrary to the extensive applications of surfactants in the
electro analytical chemistry, little work has been carried out to explore the nature of surfactant adsorption on electrode surfaces. Hu and Bard\(^\text{20}\) have characterized the adsorption of Sodium dodecyl sulfate (SDS) on both charge-regulated and hydrophobic substrates by atomic force microscopy measurement. They found that the interaction between SDS and the positively charged electrode surface was a strong function of SDS concentration, SDS showed different types of adsorptive behaviour on the hydrophobic surface, including the monomer and the monolayer adsorption. These results were consistent with the conclusions drawn by Montgometry and Wirth\(^\text{21}\) using spectroscopic methods. Sigal et al\(^\text{22}\) used surface plasmon resonance spectroscopy to measure the association of surfactants with hexadecanethiolate self assembled monolayers (SAMs) on gold. The adsorption of surfactants on the hydrophobic SAMs was well described by the Langmuir adsorption isotherm and these techniques were powerful tools for characterizing the adsorption of various surfactants on solid surfaces, the apparatus employed was expensive and the operations were complicated. Moreover, these systems were unfit for electrochemical research because the hydrophobic layers on the solid backstos were regulated and compact, which completely blocked the approach of the electrochemical probes to the electrode surfaces. Differently from common solid electrodes, such as the glassy carbon electrode and a variety of metal electrodes, the carbon paste electrode, which is made up of adhesives and carbon particles. Generally, the adhesives in carbon paste electrodes are hydrophobic and can accumulate less soluble substrates from solutions to the electrode surfaces via hydrophobic interactions. This accumulation process may be strengthened through the enhancement effects of surfactants on the substrates. Hu et al studied the chemical responses of several species at carbon paste electrodes in the presence of surfactants, including diethylstilbestrol (4), thyroxin\(^\text{23}\) and dioxygen\(^\text{24}\). The results showed that the addition of trace surfactants to the working solutions could effectively improve the signals of these substances.
In this work, the adsorption of Triton X-100 at carbon paste electrode and ceresin wax carbon paste electrode was explored by voltammetry which might be able to explain the enhancement effects of surfactants in electro analytical chemistry. The results revealed not only the adsorptive behaviour TX-100 but also the influences of TX-100 adsorption on the surface of the electrode interface and the redox reactions in solution. These results might be able to explain the enhancement effects of surfactants in electro analytical chemistry.

3.4. Experimental

Reagents and chemicals

Triton X-100, Potassium Ferricyanide, and dopamine were purchased from Aldrich Company. CTAB was dissolved in double distilled water to form $3 \times 10^{-4}$M stock solution. 10mM Potassium ferricyanide $K_3Fe(CN)_6$ and 1M KCl dopamine was prepared by using double distilled water, 10mM dopamine stock solution was prepared by using 0.1M perchloric acid. All chemicals were of analytical grade quality and were used without further purification. The water used was a double distilled. In all the measurements, the supporting electrolyte used was 1M KCl.

Apparatus

Discussed in Section 2.3

3.5. Results and Discussion

Electrochemical response of $K_3Fe(CN)_6$ at carbon paste electrode onto the surface with TX-100.

The electrochemical responses of $K_3Fe(CN)_6$ at carbon paste electrode was shown in Fig. 3.1a owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of $K_3Fe(CN)_6$ in the absence of TX-100 is low signal (solid line). However, the voltammetric response is apparently improved in the presence of $3 \times 10^{-6}$M TX-100, reflected by the enlargement of cathodic peak current ($i_p$) (dotted line). The probable mechanism is the TX-100 surfactant molecule diffuses into the carbon paste
electrode along with the potassium ferricyanide results increase in the signal. The dependence of the reduction peak current ($i_p$) as well as peak current function ($i_p/ACv^{1/2}$) on the scan rate showed ($v$) were studied in the range 50-300 mV/s as shown in Table 3.1. A linear relationship was observed between log $i_p$ and log $v$ (Fig. 3.2a) was linear with a correlation coefficient of 0.992 and this behaviour was consistent with the EC nature of the reaction $^{25,26}$. The plot of $i_p/v^{1/2}$ vs. log $v$ indicated an increase in peak current with an increase in sweep rate (Fig. 3.2b) confirming that the electrode process at the electrode surface has some adsorption. Also, the plot of peak potential ($E_p$) vs. logarithm of scan rate (Fig. 3.2c) was linear. The electrochemical response of $K_3Fe(CN)_6$ in the presence of TX-100 could be utilized to investigate the adsorptive behaviour of TX-100 at a carbon paste electrode, which might be able to explain the enhancement effects of surfactants in some electro analytical systems.

In case of dopamine the electrochemical response is poor in absence of TX-100 (solid line) and in presence there was an increase in current (dotted line) as shown in Fig. 3.1b and similar mechanism is proposed in this case large signal is obtained and for other higher concentration there is no increase in the signal as shown in Fig 3.3.

*Dependence of TX-100 adsorptive behaviour on TX-100 concentration at carbon paste electrode.*

The dependence of the voltammetric responses for $1.0\times10^{-5}$M $K_3Fe(CN)_6$ on TX-100 concentration was shown in Table 3.2. Obviously, the addition of TX-100 can effectively promote the signals of $K_3Fe(CN)_6$, as shown in Fig. 3.4 even for a trace amount of (TX-100). With the increase of TX-100 concentration, both the peak current varies respectively. As mentioned above, TX-100 might form a monolayer in this concentration range and hence increase in the signal. These results also suggest that completeness of TX-100 concentration above $1.0\times10^{-5}$M. Over the whole concentration range, both the oxidation ($i_{pa}$) and the reduction peak currents ($i_{pc}$) increases with the
increase of TX-100 concentration and that the increase rate is fast at low TX-100 concentrations.

*Electrochemical response of K₃Fe(CN)₆ at ceresin wax carbon paste electrode on to the surface with TX-100.*

The carbon paste electrode impregnated with ceresin wax was first introduced for use in all the common solvents used in electrochemistry due to its low background currents over a wide range of potentials. The electrochemical responses of K₃Fe(CN)₆ at ceresin wax carbon paste electrode was shown in Fig. 3.5a owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of K₃Fe(CN)₆ in the absence of TX-100 is poor curve (solid line). However, the voltammetric response is apparently improved in the presence of 3x10⁻⁵M TX-100, reflected by the enlargement of cathodic peak current ($i_p$) (dotted line) as shown in Table 3.3. The dependence of the reduction peak current ($i_p$) as well as peak current function ($i_p / ACv^{1/2}$) on the scan rate showed ($v$) were studied in the range 50-300 mV/s. A linear relationship was observed between log$i_p$ and log$v$ (Fig. 3.6a) was linear with a correlation coefficient of 0.999 and this behaviour was consistent with the EC nature of the reaction. The plot of $i_p/v^{1/2}$ vs. log$v$ indicated an increase in peak current with an increase in sweep rate (Fig. 3.6b) confirming that the electrode process at the electrode surface has some adsorption. Also, the plot of peak potential ($E_p$) vs. logarithm of scan rate (Fig. 3.6c) was linear. The electrochemical response of K₃Fe(CN)₆ in the presence of TX-100 could be utilized to investigate the adsorptive behaviour of TX-100 at a carbon paste electrode, which might be able to explain the enhancement effects of surfactants in some electro analytical systems.

The electrochemical response of dopamine at ceresin wax carbon paste electrode was shown in Fig. 3.5b. The cyclic Voltammogram of dopamine in the absence of TX-100 is poor curve (solid line). However, the voltammetric response is apparently
improved in the presence of $3 \times 10^{-6}$ M TX-100, reflected by the enlargement of peak current ($i_p$) (dotted line) and the slight increase in the peak potential and similar mechanism is proposed in this case and for other higher concentration there is no increase in the signal as shown in Fig. 3.7.

*Dependence of TX-100 adsorptive behaviour on TX-100 concentration at ceresin wax carbon paste electrode.*

The dependence of the voltammetric responses for $1.0 \times 10^{-3}$ M $K_3Fe(CN)_6$ on TX-100 concentration was shown in Table 3.4. Obviously, the addition of TX-100 can effectively promote the signals of $K_3Fe(CN)_6$, as shown in Fig. 3.8 even for a trace (TX-100). With the increase of TX-100 concentration, both the peak current varies respectively. As mentioned above, TX-100 might form a monolayer in this concentration range and hence increase in the signal. These results also suggest that completeness of TX-100 concentration above $1.0 \times 10^{-5}$ M. Over the whole concentration range, both the oxidation ($i_{pa}$) and the reduction peak currents ($i_{pc}$) increases with the increase of TX-100 concentration and that the increase rate is fast at low TX-100 concentrations.

*Electrochemical response of $K_3Fe(CN)_6$ at carbon paste electrode added directly into the solution with TX-100.*

The electrochemical responses of $K_3Fe(CN)_6$ at carbon paste electrode was shown in Fig. 3.9a. When the TX-100 surfactant was added directly into the solution of $K_3Fe(CN)_6$ there was a decrease in peak current (dotted line) but the peak potential remains constant. Surface active substances have the common tendency of accumulating at interfaces. The lack of affinity between the hydrophobic portion of the surfactant and water leads to a repulsion of these substances from the water phase as a consequence of
reduction of the microscopic amount of K₃Fe(CN)₆ water interface. These particles thus accumulate at the surface of the electrode and thus decrease the current.

Electrochemical response of dopamine at carbon paste electrode when added directly into the solution with TX-100.

The electrochemical response of dopamine at carbon paste electrode with TX-100 was shown in Fig. 3.9b. When the surfactant was added directly into the solution of dopamine there was an increase in peak current but the peak potential remains constant compared to inorganic system there was an increase in the signal in case of dopamine.

Electrochemical response of K₃Fe(CN)₆ at a ceresin wax carbon paste electrode when added directly into the solution with TX-100.

The electrochemical responses of K₃Fe(CN)₆ at ceresin wax carbon paste electrode was shown in Fig. 3.10a. When the surfactant was added directly into the solution of K₃Fe(CN)₆ there was slight decrease in peak current (dotted line) but the peak potential remains constant. Surface active substances have the common tendency of accumulating at interfaces. The lack of affinity between the hydrophobic portion of the surfactant and water leads to a repulsion of these substances from the water phase as a consequence of reduction of the microscopic amount of K₃Fe(CN)₆ water interface. These particles thus accumulate at the surface of the electrode and thus decrease the current.

Electrochemical response of dopamine at a ceresin wax carbon paste electrode when added directly into the solution with TX-100.

The electrochemical responses of dopamine at ceresin wax carbon paste electrode with TX-100 was shown in Fig. 3.10b. When the surfactant was added directly into the solution of dopamine there was an increase in peak current but the peak potential remains same where as in the case of ferricyanide there was a decrease in the signal.
3.6. Conclusion

The adsorption of TX-100 on a hydrophobic carbon paste and ceresin wax carbon paste electrode surface was investigated by cyclic voltammetry. The results showed that TX-100 exhibited different types of adsorptive behavior at carbon paste and ceresin wax electrode at different TX-100 concentrations. Lower the concentration of $3 \times 10^{-6}$M, the adsorption of TX-100 as the monomer and could affect the charge transfer rate instead of the surface properties of the carbon paste electrode. When the concentration of TX-100 was more than $3 \times 10^{-6}$M, TX-100 forms a monolayer on the electrode surface, which was completed at $1.0 \times 10^{-5}$ M and resulted in a change of electrode/solution interface as well as the electrochemical behavior of substrates in solution.
Table 3.1: Effect of scan rate on voltammetric parameters reduction peak current of (1mM) potassium ferricyanide at carbon paste electrode supporting electrolyte 1M KCl.

<table>
<thead>
<tr>
<th>Scan rate (^{v/mVs^{-1}})</th>
<th>(\log{v/mVs^{-1}})</th>
<th>(\log{ip/\mu A})</th>
<th>(i_p{\sqrt 2}/\mu As/mV^{-1})</th>
<th>(E_{pc}, mVs^{-1})</th>
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</thead>
<tbody>
<tr>
<td>50</td>
<td>1.69</td>
<td>1.17</td>
<td>68.59</td>
<td>179</td>
</tr>
<tr>
<td>100</td>
<td>2.0</td>
<td>1.32</td>
<td>68.51</td>
<td>173</td>
</tr>
<tr>
<td>150</td>
<td>2.17</td>
<td>1.41</td>
<td>68.05</td>
<td>170</td>
</tr>
<tr>
<td>200</td>
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<tr>
<td>250</td>
<td>2.36</td>
<td>1.52</td>
<td>67.52</td>
<td>164</td>
</tr>
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</table>

Table 3.2: Effect of concentration variation of TX-100 on voltammetric parameters for (1mM) potassium ferricyanide at carbon paste electrode supporting electrolyte 1M KCl, scan rate 50 mVs\(^{-1}\).

<table>
<thead>
<tr>
<th>[TX-100] X 10(^{-6}) M</th>
<th>(E_{pc}, (mV))</th>
<th>(E_{pa}, (mV))</th>
<th>(\Delta E_p, (mV))</th>
<th>(i_{pc}, (\mu A))</th>
<th>(i_{pa}, (\mu A))</th>
<th>(i_{pc}/i_{pa})</th>
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<td>253</td>
<td>74</td>
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<td>11.43</td>
<td>1.32</td>
</tr>
<tr>
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<td>244</td>
<td>65</td>
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<td>15.7</td>
<td>1.38</td>
</tr>
<tr>
<td>0.2</td>
<td>176</td>
<td>250</td>
<td>74</td>
<td>17.09</td>
<td>13.6</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Table 3.3: Effect of scan rate scan rate on voltammetric parameters for reduction peak current of (1mM) potassium ferricyanide at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.

<table>
<thead>
<tr>
<th>Scan rate v/mVs(^{-1})</th>
<th>log v/mVs(^{-1})</th>
<th>log (i_p/\mu A)</th>
<th>(i_p V^{-1/2}/\mu A s) mV(^{-1})</th>
<th>(E_{pc}, mV s^{-1})</th>
</tr>
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<tbody>
<tr>
<td>50</td>
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<td>250</td>
<td>2.36</td>
<td>1.26</td>
<td>37.18</td>
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</table>

Table 3.4: Effect of concentration variation of TX-100 on voltammetric parameters for (1mM) potassium ferricyanide at ceresin wax carbon paste electrode supporting electrolyte 1M KCl, scan rate 50 mVs\(^{-1}\).

<table>
<thead>
<tr>
<th>[TX-100] (X 10^{-6} M)</th>
<th>(E_{pc}, (mV))</th>
<th>(E_{pa}, (mV))</th>
<th>(\Delta E_p) (mV)</th>
<th>(i_{pc}, (\mu A))</th>
<th>(i_{pa}, (\mu A))</th>
<th>(i_{pc}/i_{pa})</th>
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</thead>
<tbody>
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<td>257</td>
<td>92</td>
<td>15.9</td>
<td>14.7</td>
<td>1.08</td>
</tr>
<tr>
<td>0.2</td>
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<td>271</td>
<td>120</td>
<td>11.63</td>
<td>9.64</td>
<td>1.20</td>
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</table>
Fig. 3.1a. Electrochemical response of 1mM K$_3$Fe(CN)$_6$ at carbon paste electrode in the absence (solid line) and in the presence (dotted line) of TX-100, supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.

Fig. 3.1b. Electrochemical response of 1mM dopamine at carbon paste electrode in the absence (solid line) and in the presence (dotted line) of TX-100, supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.
Fig. 3.2a. Variation of the logarithm of peak current with the logarithm of the sweep rate for 1mM K₃Fe(CN)₆ at carbon paste electrode supporting electrolyte 1M KCl.

Fig. 3.2b. Dependence of $i_p/v^{1/2}$ on log $v$ of 1mM K₃Fe(CN)₆ at carbon paste electrode supporting electrolyte 1M KCl.

Fig. 3.2c. Plot of $E_p$ vs logarithm of sweep rate of 1mM K₃Fe(CN)₆ at carbon paste electrode supporting electrolyte 1M KCl.
Fig. 3.3. Effect of concentration of TX-100 on to the surface of the carbon paste electrode for 1mM dopamine supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.

Fig. 3.4. Effect of concentration of TX-100 on to the surface of the carbon paste electrode for 1mM K$_3$Fe(CN)$_6$ supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.
Fig. 3.5a. Electrochemical response of 1mM K₃Fe (CN)₆ at ceresin wax carbon paste electrode in the absence (solid line) and in the presence (dotted line) of TX-100 supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.

Fig. 3.5b. Electrochemical response of 1mM dopamine at ceresin wax carbon paste electrode in the absence (solid line) and in the presence (dotted line) of TX-100, supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
Fig. 3.6a. Variation of the logarithm of peak current with the logarithm of the sweep rate for 1mM K₃Fe(CN)₆ at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.

Fig. 3.6b. Dependence of $i_p/v^{1/2}$ on log $v$ of 1mM K₃Fe(CN)₆ at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.

Fig. 3.6c. Plot of $E_p$ vs logarithm of sweep rate of 1mM K₃Fe(CN)₆ at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.
Fig. 3.7. Effect of concentration of TX-100 on to the surface of the ceresin wax carbon paste electrode for 1mM dopamine supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.

Fig. 3.8. Effect of concentration of TX-100 on to the surface of the ceresin wax carbon paste electrode for 1mM K₃Fe(CN)₆ supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
Fig. 3.9a. Electrochemical response of 1mM K$_3$Fe(CN)$_6$ at carbon paste electrode directly in to the solution (solid line) in the absence and (dotted line) in the presence of TX-100 supporting electrolyte 1M KCl at scan rate 50mVs$^{-1}$.

Fig. 3.9b. Effect of concentration of TX-100 directly in to the solution at carbon paste electrode for 1x10$^{-3}$ M dopamine, supporting electrolyte 1M KCl scan rate 50mVs$^{-1}$. 
Fig. 3.10a. Electrochemical response of 1mM K₃Fe(CN)₆ at ceresin wax carbon paste electrode directly in to the solution (solid line) in the absence and (dotted line) in the presence of TX-100 supporting electrolyte 1M KCl at scan rate 50mVs⁻¹.

Fig. 3.10b. Effect of concentration of TX-100 directly in to the solution at ceresin wax carbon paste electrode for 1x10⁻³ M dopamine, supporting electrolyte 1M KCl scan rate 50mVs⁻¹.
3.7. References


CYCLIC VOLTAMMETRIC STUDIES OF POTASSIUM FERRICYANIDE AND DOPAMINE BY USING CETYLM TRIMETHYL AMMONIUM BROMIDE AT CARBON PASTE AND CERESIN WAX CARBON PASTE ELECTRODES
3.8. Introduction

The adsorption of Cetyl trimethyl ammonium bromide (CTAB) on a carbon paste and ceresin wax carbon paste electrodes was investigated by cyclic voltammetry. The results showed that CTAB exhibited two types of adsorptive behavior at a carbon paste and ceresin wax carbon paste electrodes at a different concentration ranges: monomer adsorption at concentration below $3 \times 10^{-6} \text{M}$ and monolayer adsorption at concentration higher then $3 \times 10^{-6} \text{M}$. In the monomer adsorption range, the adsorption of CTAB could effectively reduce the charge transfer resistance and increase the charge transfer rate. However, the surface properties of the carbon paste and ceresin wax carbon paste electrodes hardly changed. On the formation of a CTAB monolayer, the structure of the electrode interface changed significantly and the electrode/solution interface was replaced by the CTAB monolayer/solution interface.

3.9. Chemistry and Biological Relevance of Cetyl Trimethyl Ammonium Bromide

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

Cetyl trimethyl ammonium bromide $[(\text{C}_{16}\text{H}_{33})\text{N(\text{CH}_3)_3}\text{Br}]$ is one of the components of the topical antiseptic cetrimide. The Cetyl trimethyl ammonium bromide (or hexadecyl trimethylammonium) cation is an effective antiseptic agent against bacteria and fungi. It is a cationic surfactant. Its uses including providing a buffer solution for the extraction of DNA. It is also widely used in hair conditioning products. As any surfactant it forms micellies with aggregation number 75-120 (depending on method of determination, usually average 9.5) and degree of ionisation $\alpha$ (fractional charge) 0.2 - 0.1 (from low to high concentration). Standard constant of Br- counter ion binding to the micelle at 303K (30°C), calculated from Br- and CTA+ ion selective electrode measurements and conductometry data by using literature data for micellie size ($r =$
Chapter 3B  CV studies of potassium ferricyanide and dopamine using CTAB

~3nm, extrapolated to the micellar concentration is $K^0 \approx 400$ (it varies with total surfactant concentration so it is extrapolated to the point at which the concentration of micelles is zero).

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

3.10. Experimental

Reagents and chemicals

CTAB, Potassium Ferricyanide, and dopamine were purchased from Aldrich Company. CTAB was dissolved in double distilled water to form $3 \times 10^{-6}$M stock solution. 10mM Potassium ferricyanide K$_3$Fe(CN)$_6$ and 1M KCl dopamine was prepared by using double distilled water, 10mM dopamine stock solution was prepared by using 0.1M perchloric acid. All chemicals were of analytical grade quality and were used without further purification. The water used was a double distilled. In all the measurements, the supporting electrolyte used was 1M KCl.

3.11. Results and Discussion

Electrochemical response of $K_3Fe(CN)_6$ onto the surface with CTAB At carbon paste electrode

The electrochemical responses of $K_3Fe(CN)_6$ at a carbon paste electrode was shown in (Fig. 3.11a) owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of $K_3Fe(CN)_6$ in the absence of CTAB is low signal (solid line). However, the voltammetric response is apparently improved in the presence of $3 \times 10^{-6}$M CTAB, reflected by the enlargement of cathodic peak current (i$_p$) (dotted line). The probable mechanism is the CTAB surfactant molecule diffuses in to the carbon paste electrode along with the potassium ferricyanide results increase in the signal. The dependence of the reduction peak current (i$_p$) as well as peak current function (i$_p$/ACv$^{1/2}$) on the scan rate showed (v) were studied in the range 50-300 mV/s as shown in Table 3.5. A linear relationship was observed between logi$_p$ and logv (Fig. 3.12a). The plot of i$_p$/v$^{1/2}$.
vs. log\(v\) indicated an increase in peak current with an increase in sweep rate (Fig. 3.12b) confirming that the electrode process at the electrode surface has some adsorption. Also, the plot of peak potential \(E_p\) vs. logarithm of scan rate (Fig. 3.12c) was linear and this behaviour was consistent with the EC nature of the reaction \(^{1,2}\). The electrochemical response of \(K_3Fe(CN)_6\) in the presence of CTAB could be utilized to investigate the adsorptive behaviour of CTAB at a carbon paste electrode, which might be able to explain the enhancement effects of surfactants in some electro analytical systems.

In case of dopamine the electrochemical response is poor in absence of CTAB (solid line) and in presence there was an increase in current (dotted line) as shown in (Fig. 3.11b) and similar mechanism is proposed. Increase in the current signal was observed in \(0.1\times10^{-6}\) M CTAB and for other higher concentration there is no increase in the signal as shown in (Fig. 3.13).

\textit{At ceresin wax carbon paste electrode}

The carbon paste electrode impregnated with ceresin wax was first introduced \(^{3,4}\) for use in all the common solvents used in electrochemistry due to its low background currents over a wide range of potentials. The electrochemical responses of \(K_3Fe(CN)_6\) at a ceresin wax carbon paste electrode was shown in (Fig. 3.14a) solid line shows cyclic voltammogram of \(K_3Fe(CN)_6\) in the absence of CTAB and dotted line in presence of CTAB. However, the voltammetric response is apparently improved in the presence of \(3\times10^{-6}\)M CTAB, reflected by the enlargement of cathodic peak current \((i_p)\) (dotted line). The dependence of the reduction peak current \((i_p)\) as well as peak current function \((i_p / ACv^{1/2})\) on the scan rate showed \((v)\) were studied in the range 50-300 mV/s Table 3.6. A linear relationship was observed between \(\log i_p\) and \(\log v\) (Fig. 3.15a). The plot of \(i_p/v^{1/2}\) vs. \(\log v\) indicated an increase in peak current with an increase in sweep rate (Fig. 3.15b) confirming that the electrode process at the electrode surface has some adsorption. Also,
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the plot of peak potential ($E_p$) vs. logarithm of scan rate (Fig. 3.15c) was linear and this behaviour was consistent with the EC nature of the reaction \(^1\). The electrochemical response of $K_3Fe(CN)_6$ in the presence of CTAB could be utilized to investigate the adsorptive behaviour of CTAB at a ceresin wax carbon paste electrode, which might be able to explain the enhancement effects of surfactants in some electro analytical systems.

The electrochemical response of dopamine at a ceresin wax carbon paste electrode was shown in (Fig. 3.14b). The cyclic Voltammogram of dopamine in the absence of CTAB is poor curve (solid line). However, the voltammetric response is apparently improved in the presence of $3 \times 10^{-6}$M CTAB, reflected by the enlargement of peak current ($i_p$) (dotted line) and the slight increase in the peak potential and similar mechanism is proposed in this case. Increase in the current signal was observed in $0.1 \times 10^{-6}$M CTAB and for other higher concentration there is no increase in the signal as shown in (Fig. 3.16).

*Dependence of CTAB adsorptive behaviour on CTAB*

*At carbon paste electrode*

The dependence of the voltammetric responses for $1.0 \times 10^{-5}$M $K_3Fe(CN)_6$ on CTAB concentration was shown in Table 3.7. Obviously, the addition of CTAB can effectively promote the signals of $K_3Fe(CN)_6$, as shown in Fig. 3.17 even for a trace amount of (CTAB). With the increase of CTAB concentration, both the peak current varies respectively. As mentioned above, CTAB might form a monolayer in this concentration range and hence increase in the signal. These results also suggest that completeness of CTAB concentration above $1.0 \times 10^{-5}$M. Over the whole concentration range, both the oxidation ($i_{pa}$) and the reduction peak currents ($i_{pc}$) increases with the increase of CTAB concentration and the increase rate is faster at low CTAB concentrations.
At ceresin wax carbon paste electrode

The dependence of the voltammetric responses for $1.0 \times 10^{-3} \text{M} \ K_3 \text{Fe(CN)}_6$ on CTAB concentration was shown in Table 3.8. Obviously, the addition of CTAB can effectively promote the signals of $K_3 \text{Fe(CN)}_6$, as shown in Fig. 3.18 even for a trace (CTAB). With the increase of CTAB concentration, both the peak current varies respectively. As mentioned above, CTAB might form a monolayer in this concentration range and hence increase in the signal. These results also suggest that completeness of CTAB concentration above $1.0 \times 10^{-5} \text{M}$. Over the whole concentration range, both the oxidation ($i_{pa}$) and the reduction peak currents ($i_{pc}$) increases with the increase of CTAB concentration and the increase rate is faster at low CTAB concentrations.

**Electrochemical response of $K_3 \text{Fe(CN)}_6$ and dopamine when added directly in to the solution with CTAB.**

**At carbon paste electrode**

The electrochemical responses of $K_3 \text{Fe(CN)}_6$ at a carbon paste electrode was shown in as shown in Fig. 3.19a. When the surfactant was added directly into the solution of $K_3 \text{Fe(CN)}_6$ there was a decrease in peak current (dotted line) but the peak potential remains constant. Surface active substances have the common tendency of accumulating at interfaces. The lack of affinity between the hydrophobic portion of the surfactant and water leads to a repulsion of these substances from the water phase as a consequence of reduction of the microscopic amount of $K_3 \text{Fe(CN)}_6$ water interface. These particles thus accumulate at the surface of the electrode and thus decrease the current.

The electrochemical response of dopamine at a carbon paste electrode with CTAB was shown in Fig. 3.19b. When the surfactant was added directly into the solution of dopamine there was an increase in peak current but the peak potential remains constant compared to inorganic system where their was an increase in the signal in the case of dopamine.
Electrochemical response of $K_3Fe(CN)_6$ and dopamine when added directly into the solution with CTAB.

At ceresin wax carbon paste electrode

The electrochemical responses of $K_3Fe(CN)_6$ at a ceresin wax carbon paste electrode was shown in Fig. 3.20a. When the surfactant was added directly into the solution of $K_3Fe(CN)_6$ there was slight decrease in peak current (dotted line) but the peak potential remains constant. Surface active substances have the common tendency of accumulating at interfaces. The lack of affinity between the hydrophobic portion of the surfactant and water leads to a repulsion of these substances from the water phase as a consequence of reduction of the microscopic amount of $K_3Fe(CN)_6$ water interface. These particles thus accumulate at the surface of the electrode and thus decrease the current.

The electrochemical responses of dopamine at a ceresin wax carbon paste electrode with CTAB was shown in Fig. 3.20b. When the surfactant was added directly into the solution of dopamine there was an increase in peak current but the peak potential remains same where as in the case of ferricyanide there was a decrease in the signal.

3.12. Conclusion

The adsorption of CTAB on a hydrophobic carbon paste and ceresin wax carbon paste electrode surface was investigated by cyclic voltammetry. The results showed that CTAB exhibited different types of adsorptive behavior at carbon paste and ceresin wax carbon paste electrode at different CTAB concentrations. Lower the concentration of $3 \times 10^{-6}$ M, the adsorption of CTAB as the monomer and could affect the charge transfer rate instead of the surface properties of the carbon paste and ceresin wax carbon paste electrode. When the concentration of CTAB was more than $3 \times 10^{-6}$ M, CTAB forms a monolayer on the electrode surface, which was completed at $1.0 \times 10^{-5}$ M and resulted in a change of electrode/solution interface as well as the electrochemical behavior of substrates in solution.
Table 3.5: Effect of scan rate on voltammetric parameters reduction peak current of (1mM) potassium ferricyanide at carbon paste electrode supporting electrolyte 1M KCl.

<table>
<thead>
<tr>
<th>Scan rate v/mVs⁻¹</th>
<th>logν/mVs⁻¹</th>
<th>log iᵥ/μA</th>
<th>iᵥV⁻¹/μAs mV⁻¹</th>
<th>Epc, mV⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.69</td>
<td>1.26</td>
<td>83.9</td>
<td>177</td>
</tr>
<tr>
<td>100</td>
<td>2.0</td>
<td>1.40</td>
<td>83.4</td>
<td>175</td>
</tr>
<tr>
<td>150</td>
<td>2.17</td>
<td>1.50</td>
<td>82.9</td>
<td>172</td>
</tr>
<tr>
<td>200</td>
<td>2.30</td>
<td>1.56</td>
<td>82.5</td>
<td>170</td>
</tr>
<tr>
<td>250</td>
<td>2.36</td>
<td>1.61</td>
<td>82.0</td>
<td>168</td>
</tr>
</tbody>
</table>

Table 3.6: Effect of concentration variation of TX-100 on voltammetric parameters for (1mM) potassium ferricyanide at carbon paste electrode supporting electrolyte 1M KCl, scan rate 50 mVs⁻¹.

<table>
<thead>
<tr>
<th>[CTAB] X 10⁻⁶ M</th>
<th>Epc, (mV)</th>
<th>Epa, (mV)</th>
<th>ΔEp (mV)</th>
<th>ipc, (µA)</th>
<th>ipa, (µA)</th>
<th>ipc/ ipa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>179</td>
<td>253</td>
<td>74</td>
<td>15.09</td>
<td>11.43</td>
<td>1.32</td>
</tr>
<tr>
<td>0.1</td>
<td>183</td>
<td>247</td>
<td>64</td>
<td>18.46</td>
<td>14.26</td>
<td>1.29</td>
</tr>
<tr>
<td>0.2</td>
<td>177</td>
<td>248</td>
<td>71</td>
<td>16.90</td>
<td>13.52</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Table 3.7: Effect of scan rate on voltammetric parameters for reduction peak current of (1mM) potassium ferricyanide at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.

<table>
<thead>
<tr>
<th>Scan rate (mVs⁻¹)</th>
<th>logv/mVs⁻¹</th>
<th>log iₚ/μA</th>
<th>iₚV⁻¹/μAs mV⁻¹</th>
<th>Eₚc, mVs⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.69</td>
<td>1.11</td>
<td>58.95</td>
<td>173</td>
</tr>
<tr>
<td>100</td>
<td>2.00</td>
<td>1.25</td>
<td>58.25</td>
<td>171</td>
</tr>
<tr>
<td>150</td>
<td>2.17</td>
<td>1.34</td>
<td>57.97</td>
<td>167</td>
</tr>
<tr>
<td>200</td>
<td>2.30</td>
<td>1.40</td>
<td>57.68</td>
<td>165</td>
</tr>
<tr>
<td>250</td>
<td>2.36</td>
<td>1.45</td>
<td>56.60</td>
<td>162</td>
</tr>
</tbody>
</table>

Table 3.8: Effect of concentration variation of TX-100 on voltammetric parameters for (1mM) potassium ferricyanide at ceresin wax carbon paste electrode supporting electrolyte 1M KCl, scan rate 50 mVs⁻¹.

<table>
<thead>
<tr>
<th>[CTAB] X 10⁻⁶ M</th>
<th>Eₚc (mV)</th>
<th>Eₚa (mV)</th>
<th>ΔEₚ (mV)</th>
<th>iₚc (μA)</th>
<th>iₚa (μA)</th>
<th>iₚc/iₚa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>165</td>
<td>269</td>
<td>104</td>
<td>9.27</td>
<td>7.02</td>
<td>1.32</td>
</tr>
<tr>
<td>0.1</td>
<td>172</td>
<td>248</td>
<td>76</td>
<td>12.85</td>
<td>9.32</td>
<td>1.37</td>
</tr>
<tr>
<td>0.2</td>
<td>166</td>
<td>263</td>
<td>97</td>
<td>11.44</td>
<td>8.36</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Fig. 3.11a. Electrochemical response of 1mM K₃Fe (CN)₆ at carbon paste electrode in the absence (solid line) and in the presence (dotted line) of CTAB, supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.

Fig. 3.11b. Electrochemical response of 1mM dopamine at carbon paste electrode in the absence (solid line) and in the presence (dotted line) of CTAB, supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
Fig. 3.12a. Variation of the logarithm of peak current with the logarithm of the sweep rate for 1mM K₃Fe(CN)₆ at carbon paste electrode supporting electrolyte 1MKCl.

Fig. 3.12b. Dependence of $i_p/v^{1/2}$ on log $v$ of 1mM K₃Fe(CN)₆ at carbon paste electrode supporting electrolyte 1M KCl.

Fig. 3.12c. Plot of $E_p$ vs logarithm of sweep rate of 1mM K₃Fe(CN)₆ at carbon paste electrode supporting electrolyte 1M KCl.
Fig. 3.13. Effect of concentration of CTAB onto the surface of the carbon paste electrode for 1mM dopamine supporting electrolyte 1M KCl at scan rate 50 mVs\textsuperscript{-1}.
**Fig. 3.14a.** Electrochemical response of 1mM K$_3$Fe(CN)$_6$ at ceresin wax carbon paste electrode in the absence (solid line) and in the presence (dotted line) of CTAB supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.

**Fig. 3.14b.** Electrochemical response of 1mM dopamine at ceresin wax carbon paste electrode in the absence (solid line) and in the presence (dotted line) of CTAB supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.
Fig. 3.15a. Variation of the logarithm of peak current with the logarithm of the sweep rate for 1mM K3Fe(CN)6 at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.

Fig. 3.15b. Dependence of $i_p/v^{1/2}$ on log $v$ of 1mM K3Fe(CN)6 at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.

Fig. 3.15c. Plot of $E_p$ vs logarithm of sweep rate of 1mM K3Fe(CN)6 at ceresin wax carbon paste electrode supporting electrolyte 1M KCl.
Fig. 3.16. Effect of concentration of CTAB on to the surface of the cerasin wax carbon paste electrode for 1mM dopamine supporting electrolyte 1M KCl at scan rate 50 mVs⁻¹.
Fig. 3.17. Effect of concentration of CTAB on to the surface of the carbon paste electrode for 1mM K$_3$Fe(CN)$_6$ supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.

Fig. 3.18. Effect of concentration of CTAB on to the surface of the ceresin wax carbon paste electrode for 1mM K$_3$Fe(CN)$_6$ supporting electrolyte 1M KCl at scan rate 50 mVs$^{-1}$.
**Fig.3.19a.** Electrochemical response of 1mM K₃Fe(CN)₆ at carbon paste electrode directly in the solution (solid line) in the absence and (dotted line) in the presence of CTAB supporting electrolyte 1M KCl at scan rate 50mVs⁻¹.

**Fig.3.19b.** Effect of concentration of CTAB directly in to the solution at carbon paste electrode for 1x10⁻³ M dopamine, supporting electrolyte 1M KCl scan rate 50mVs⁻¹.
Fig. 3.20a. Electrochemical response of 1mM K$_3$Fe(CN)$_6$ at ceresin wax carbon paste electrode directly in to the solution (solid line) in the absence and (dotted line) in the presence of CTAB supporting electrolyte 1M KCl at scan rate 50mVs$^{-1}$.

Fig. 3.20b. Effect of concentration of CTAB directly in to the solution at ceresin wax carbon paste electrode for $1\times10^{-3}$ M dopamine, supporting electrolyte 1M KCl scan rate 50mVs$^{-1}$. 
3.13. References


