

Studies on Adsorption of Triton X-100 at Carbon Paste and Ceresin Wax Carbon Paste Electrodes and the Enhancement Effect in Dopamine Oxidation by Cyclic Voltammetry

E. Niranjana¹, R. Raghavendra Naik¹, B.E. Kumara Swamy^{1,}, B.S. Sherigara¹ and H.Jayadevappa²*

¹ Department of P.G. Studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Karnataka, India

² Department of Chemistry, Sahyadri Science College, Shimoga, Karnataka, India

*E-mail: kumaraswamy21@rediffmail.com

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The adsorption of Triton X-100 (TX-100) on a carbon paste electrode was investigated by voltammetry. The results showed that TX-100 exhibited two types of adsorptive behavior at a carbon paste electrode at different concentration ranges: monomer adsorption at concentrations below 3×10^{-6} M and monolayer adsorption at concentrations higher than 3×10^{-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 electrode 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.

Keywords: Adsorption; Carbon paste electrode; Triton X-100, Dopamine

1. INTRODUCTION

Surfactants are a kind of amphiphilic molecule with a polar head on one side and a long hydrophobic tail on the other. The applications of surfactants in electrochemistry and electro analytical chemistry have been widely reported (1). Hu's group [2-5] 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. i.e., surfactants might 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.

Some less soluble surfactants were employed in the immobilization of macro molecules or other functional materials, Wu et al [6] 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 [7,8]. The applications of surfactants in the immobilization of biomolecules were also reported [9-11]. Chattopadhyay and Mazumdar [12] 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 [13] 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 Montgomery and Wirth [14] using spectroscopic methods. Sigal et al [15] 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 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 backstops 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 [16] and dioxygen [17]. The results showed that the addition of trace surfactants to the working solutions could effectively improve the signals of these substances.

As a part of our research work on the electro organic reactions at the surface of the electrodes we extended our work on the modification of carbon paste electrode [18-20].

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.

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Triton X-100 was dissolved in double distilled water to form 3×10^{-6} M stock solutions. Potassium ferricyanide $K_3Fe(CN)_6$ and 10mM dopamine stock solutions were prepared by adding dopamine to 0.1M perchloric acid and kept in darkness. 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.

2.2. Apparatus and Procedure

Cyclic voltammetry (CV) was performed on Model EA-201 Electroanalyser (EA-201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0mm in diameter), a platinum wire counter electrode and a potassium chloride (KCl) saturated calomel reference electrode (SCE). The Carbon paste electrode was prepared as follows 70% graphite powder and 30% silicone oil were mixed by hand to produce a homogeneous carbon paste. The carbon paste was then packed in to the cavity of a home-made carbon paste electrode and smoothed on a weighing paper.

3. RESULTS AND DISCUSSION

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

The electrochemical responses of $K_3Fe(CN)_6$ at a carbon paste electrode was shown in Fig.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 3×10^{-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 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. A linear relationship was observed between $\log I_p$ and $\log v$ (Fig.2a). The plot of $I_p/v^{1/2}$ vs. $\log v$ indicated an increase in peak current with an increase in sweep rate (Fig.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.2c) was linear with a correlation coefficient of 0.992 and this behaviour was consistent with the EC nature of the reaction. [21,22]. 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.1B and similar mechanism is proposed. Increase in the current signal was observed is 0.1×10^{-6} M TX-100 and for other higher concentration there is no increase in the signal as shown in Fig.3.

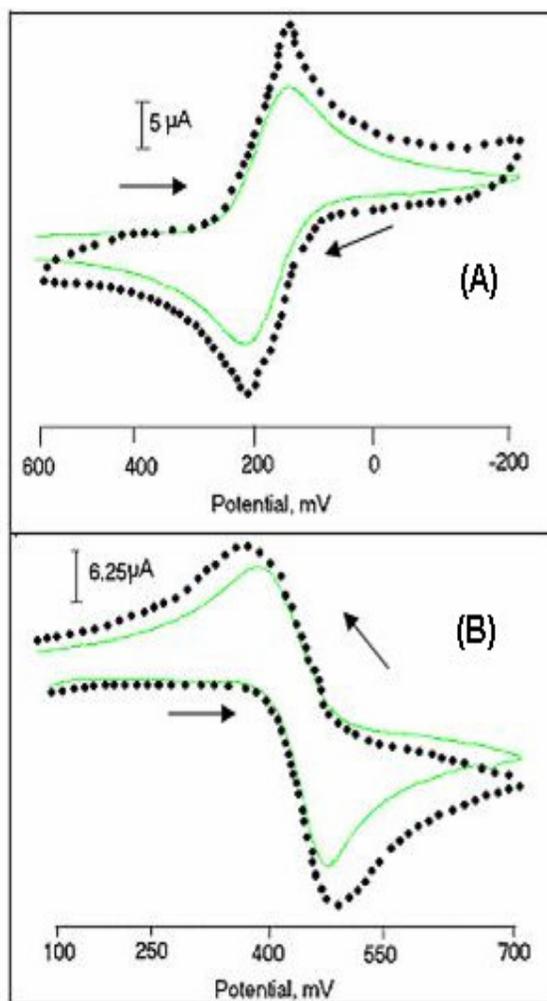


Figure 1. A) Electrochemical response of $K_3Fe(CN)_6$ at a carbon paste electrode in the absence and presence of TX-100. B) Electrochemical response of Dopamine at a carbon paste electrode in the absence and presence of TX-100.

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

The dependence of the voltammetric responses for 1.0×10^{-3} M $K_3Fe(CN)_6$ on TX-100 concentration was shown in Table 1. Obviously, the addition of TX-100 can effectively promote the signals of $K_3Fe(CN)_6$, 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 $1.0 \times 10^{-5} \text{M}$. Over the whole concentration range, both the oxidation (I_{pa}) and the reduction peak currents (I_{pc}) increases with the increase of TX-100 concentration and that the increase rate is fast at low TX-100 concentrations.

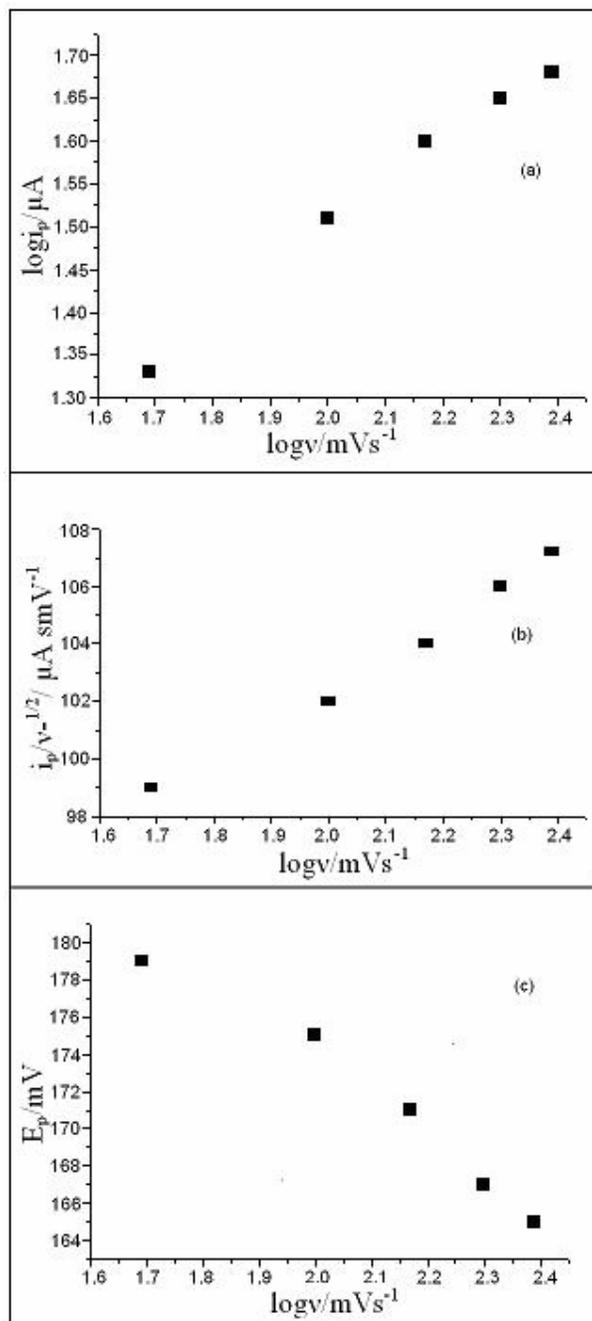


Figure 2. a) Dependence of $i_p/v^{-1/2}$ on $\log v$ for peak Ic of $1\text{mM K}_3\text{Fe}(\text{CN})_6$. b) Variation of the logarithm of peak current with the logarithm of the sweep rate for $1\text{mM K}_3\text{Fe}(\text{CN})_6$. c) Plot of E_p vs logarithm of sweep rate of $1\text{mM K}_3\text{Fe}(\text{CN})_6$.

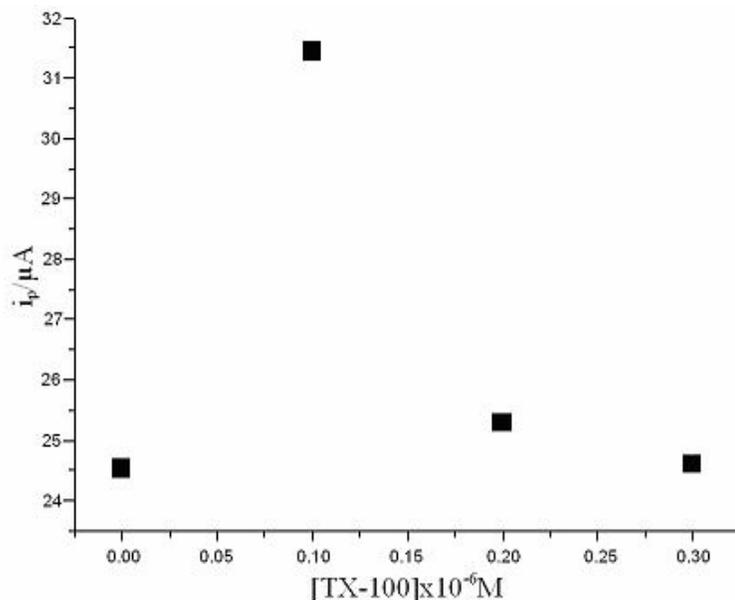


Figure 3. Effect of concentration of TX-100 on to the surface of the carbon paste electrode for dopamine.

Table 1. Carbon paste electrode with Triton X-100

TX-100 Co	Epa mV	Epc mV	Ipa μA	Ipc μA
0	253	179	11.43	15.09
0.1	244	179	15.7	21.79
0.2	250	176	13.6	17.09

3.3. Electrochemical response of $K_3Fe(CN)_6$ at a ceresin wax carbon paste electrode on to the surface with TX-100.

The carbon paste electrode impregnated with ceresin wax was first introduced [23, 24] 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.4.A 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 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 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. A linear relationship was observed between $\log I_p$ and $\log v$ (Fig.5a). The plot of $I_p/v^{1/2}$ vs. $\log v$ indicated an increase in peak current with an increase in sweep rate (Fig.5b) 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.5c) was linear with a correlation coefficient of 0.999 and this behaviour was consistent with the EC nature of the reaction [21, 22]. 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.

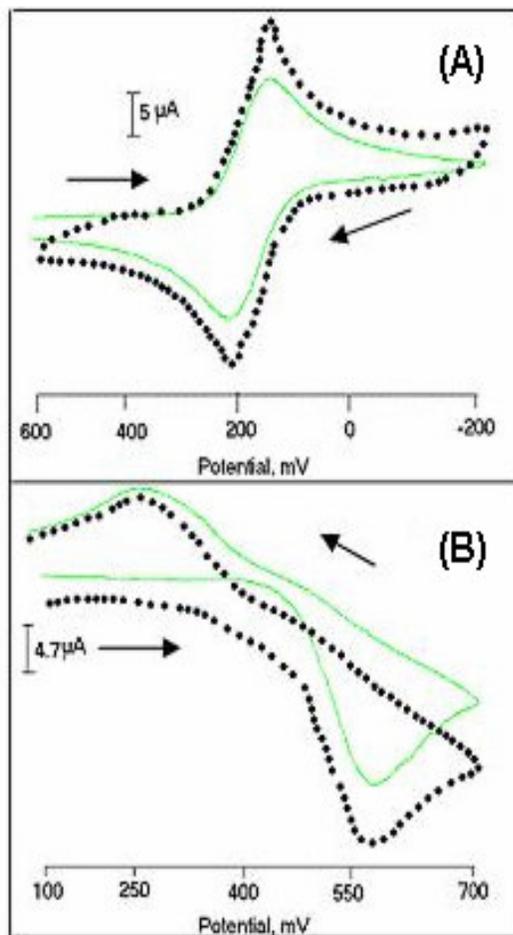


Figure 4. A) Electrochemical response of $K_3Fe(CN)_6$ at a ceresin wax carbon paste electrode directly in to the solution with TX-100. B) Electrochemical response of Dopamine at a Ceresin wax carbon paste electrode in the absence and presence of TX-100.

The electrochemical response of dopamine at a ceresin wax carbon paste electrode was shown in Fig.4.B. 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 3×10^{-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. Increase in the current signal was observed is 0.1×10^{-6} M TX-100 and for other higher concentration there is no increase in the signal as shown in Fig.6.

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

The dependence of the voltammetric responses for 1.0×10^{-3} M $K_3Fe(CN)_6$ on TX-100 concentration was shown in Table 2. Obviously, the addition of TX-100 can effectively promote the

signals of $K_3Fe(CN)_6$, 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.

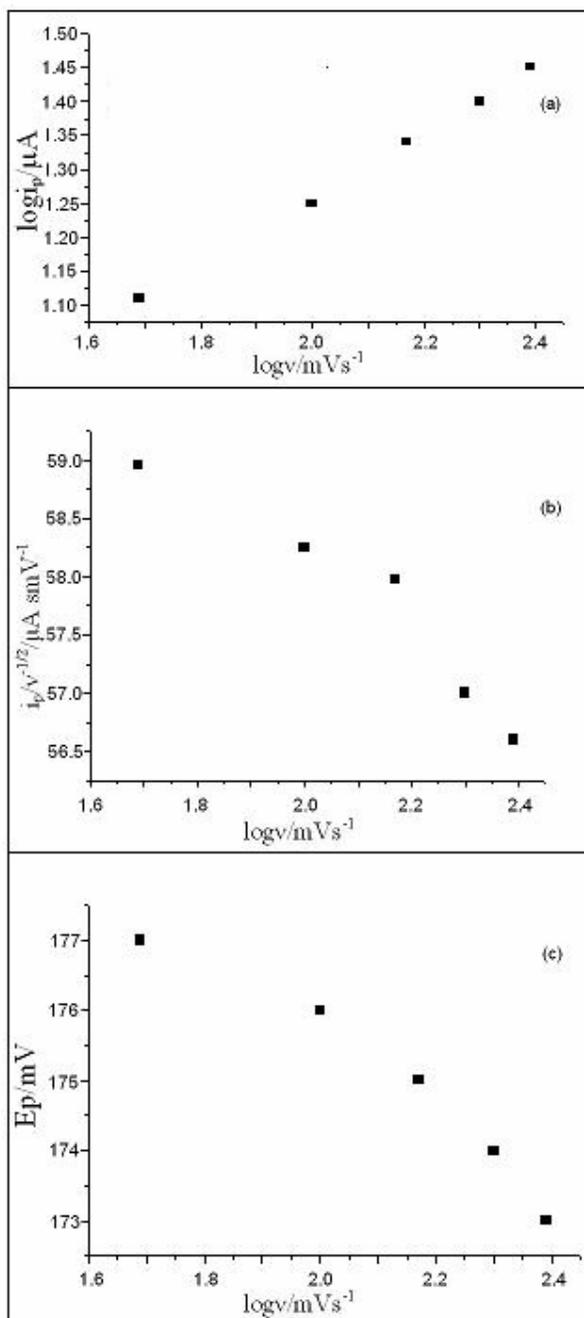


Figure 5. a) Dependence of $I_p/v^{-1/2}$ on $\log v$ for peak I_c of 1 mM $K_3Fe(CN)_6$, b) Variation of the logarithm of peak current with the logarithm of the sweep rate for 1mM $K_3Fe(CN)_6$, c) Plot of E_p vs logarithm of sweep rate of 1mM $K_3Fe(CN)_6$.

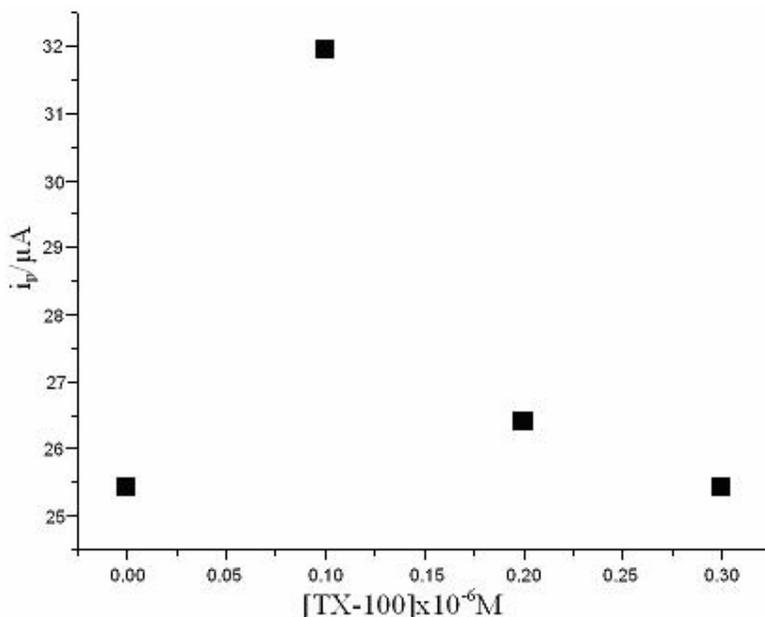


Figure 6. Effect of concentration of TX-100 on to the surface of the ceresin wax carbon paste electrode for dopamine.

Table 2. Ceresin wax Carbon paste electrode with Triton X-100

TX-100 Co	E _{pa} mV	E _{pc} mV	I _{pa} μA	I _{pc} μA
0	269	165	7.02	9.27
0.1	257	165	14.7	15.91
0.2	271	151	9.64	11.63

3.5. Electrochemical response of $K_3Fe(CN)_6$ at a carbon paste electrode directly in to the solution with TX-100.

The electrochemical responses of $K_3Fe(CN)_6$ at a carbon paste electrode was shown in Fig.7.A 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 $K_3Fe(CN)_6$ water interface. These particles thus accumulate at the surface of the electrode and thus decrease the current.

3.6. Electrochemical response of dopamine at a carbon paste electrode directly in to the solution with TX-100.

The electro chemical response of dopamine at a carbon paste electrode with TX-100 was shown in Fig.7.B. 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 the case of dopamine [25].

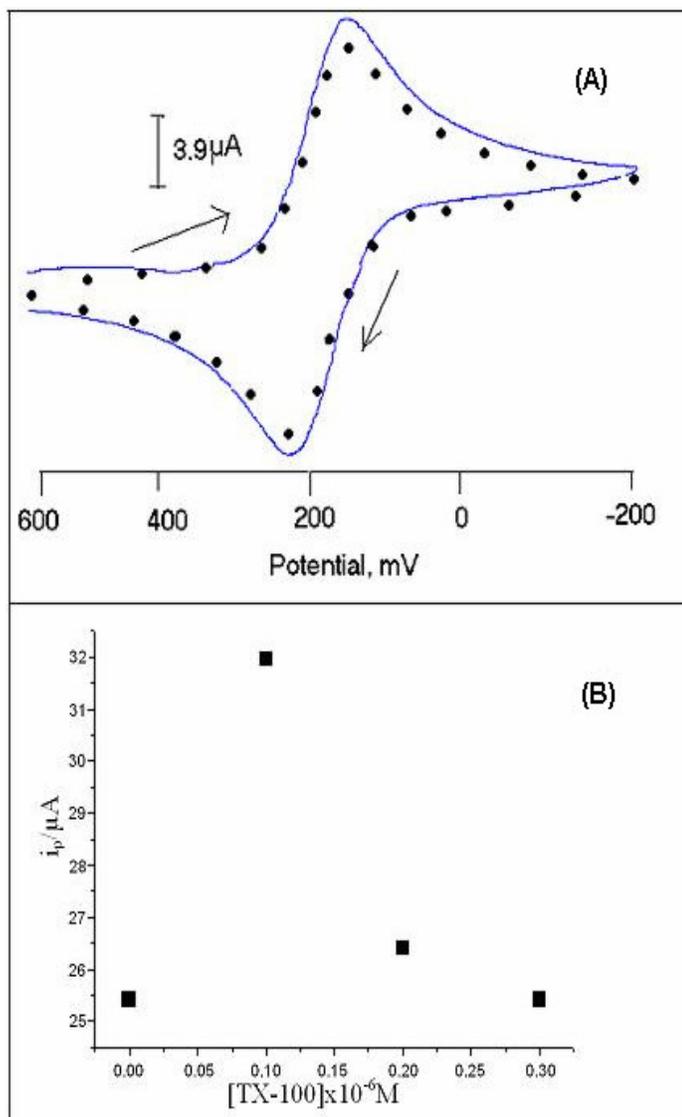


Figure 7. A) Electrochemical response of $K_3Fe(CN)_6$ at a carbon paste electrode directly in to the solution with TX-100. B) Effect of concentration of TX-100 directly in to the solution at carbon paste electrode for dopamine.

3.7. Electrochemical response of $K_3Fe(CN)_6$ at a ceresin wax carbon paste electrode directly in to the solution with TX-100.

The electrochemical responses of $K_3Fe(CN)_6$ at a ceresin wax carbon paste electrode was shown in Fig.8.A. 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 $K_3Fe(CN)_6$ water interface. These particles thus accumulate at the surface of the electrode and thus decrease the current.

3.8. Electrochemical response of dopamine at a ceresin wax carbon paste electrode directly in to the solution with TX-100.

The electro chemical responses of dopamine at a ceresin wax carbon paste electrode with TX-100 was shown in Fig.8.B. 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.

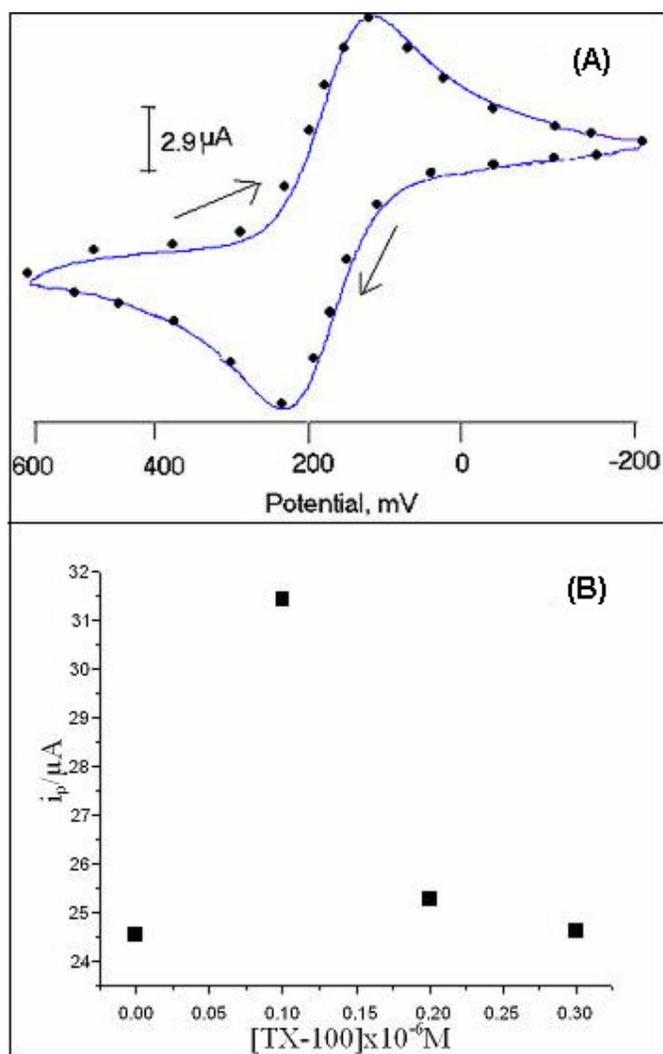


Figure 8. A) Electrochemical response of $K_3Fe(CN)_6$ at a ceresin wax carbon paste electrode directly in to the solution with TX-100. B) Effect of concentration of TX-100 directly in to the solution at ceresin wax carbon paste electrode for dopamine.

4. CONCLUSIONS

The adsorption of TX-100 on a hydrophobic carbon paste electrode surface was investigated by cyclic voltammetry. The results showed that TX-100 exhibited different types of adsorptive behavior at carbon paste electrode at different TX-100 concentrations. Below 3×10^{-6} M, the adsorption of TX-100 as the monomer and could effectively affect the charge transfer rate instead of the surface properties of the carbon paste electrode. When the TX-100 concentration was higher than 3×10^{-6} M, TX-100 formed a monolayer on the electrode surface, which was completed at 1.0×10^{-5} M and resulted in a change of electrode/solution interface as well as the electrochemical behavior of substrates in solution.

References

1. J.F. Rusling, *Acc. Chem. Res.* 24 (1991) 75
2. S. Hu, Y. Yan, Z. Zhao, *Anal. Chim. Acta* 248 (1991) 103
3. H. Yi, K. Wu, S. Hu, *Talanta* 55 (2001) 1205
4. S. Zhang, K. Wu, S. Hu, *Talanta* 58 (2002) 747
5. S. Hu, K. Wu, H. Yi, D. Cui, *Anal. Chim. Acta* 464 (2002) 209
6. K. Wu, J. Fei, S. Hu, *Anal. Biochem.* 318 (2003) 100
7. Y. Sun, J. Fei, K. Wu, S. Hu, *Anal. Bioanal. Chem.* 375 (2003) 544
8. K. Wu, J. Fei, W. Bai, S. Hu, *Anal. Bioanal. Chem.* 376 (2003) 205
9. P. Bianco, J. Haladjian, *Electrochim. Acta* 42 (1997) 587
10. Wang, N. Hu, *J. Colloid interf. Sci.* 236 (2001) 166
11. D. Mimica, J. H. Zagal, F. Bedioui, *Electrochem. Commun.* 3 (2001) 435
12. K. Chattopadhyaya, S. Mazumdar, *Bioelectrochemistry* 53 (2000) 17
13. K. Hu, A. J. Bard, *Langmuir* 13 (1997) 5418
14. M. E. Mongometry, M. J. Wirth, *Langmuir* 10 (1994) 861
15. G. B. Sigal, M. Mrksich, G. M. Whitesides, *Langmuir* 13 (1997) 2749
16. C. Hu, Q. He, Q. Li, S. Hu, *Anal. Sci.* 20 (2004)
17. Q. He, C. Hu, X. Dang, Y. Wei, S. Hu, *Electrochemistry* 72 (1) (2004) 5
18. S. R. Murali, B. E. Kumara Swamy, B. S. Sherigara and B. Kalluraya, *Bull. of Electrochem.* 18(2002)385
19. A. H. M. Siddalingaiah, S. G. Naik, B. S. Sherigara and B. E. Kumara Swamy. *J. of Mole. Str. (Theochem)*, 582 (2002) 69
20. G. P. Mamatha, B. S. Sherigara, K. M. Mahadevan and B. E. Kumaraswamy *Bull. of Electrochem* 21(2005) 9
21. E. R. Brown, R. F. Large, in: A. Weissberger, B. W. Rossiter (Eds.), *Physical Methods of Chemistry*, Wiley Interscience, Rochester, New York, 1964, 423
22. Rajendra N. Goyal, Vinod K. Gupta, Munetaka Oyama, Neeta Bachheti *Electrochem Commun* 8(2006) 65
23. J. Lindquist, *Anal. Chem.*, 45 (1973) 106
24. S. S. Atuma and J. Lindquist, *Analyst*, 98 (1973) 886
25. Ronald. J. Mascarenhas, K. Vijay Kumar Reddy, B. E. Kumara Swamy, B. S. Sherigara and V. Lakshminarayan *Bull. of Electrochem* 21(2005) 341