

Electrochemical Investigations of Dopamine at Chemically Modified Alcian Blue Carbon Paste Electrode: A Cyclic Voltammetric Study

Rekha¹, B.E. Kumara Swamy^{1,*}, R.Deepa², V.Krishna², Ongera Gilbert¹, Umesh Chandra¹, and B.S. Sherigara¹

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

² Department of P.G. Studies and Research in Biotechnology, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Karnataka, India

*E-mail: kumaraswamy21@yahoo.com

Received: 20 March 2009 / Accepted: 11 May 2009 / Published: 6 June 2009

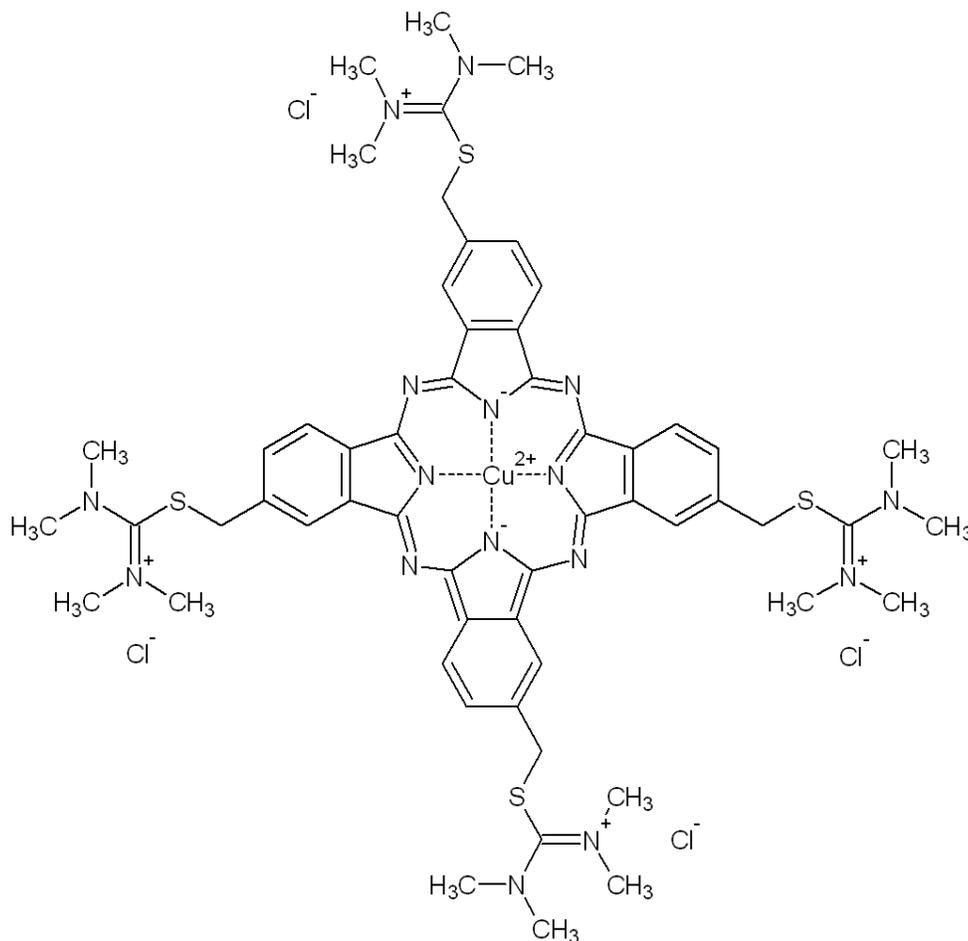
A carbon paste electrode modified by alcian blue was used for detection of dopamine (DA). The modified electrode exhibited strong promoting effect and stability towards the electrochemical oxidation of dopamine at pH 6.6 in phosphate buffer solution (PBS). The effects of scan rate, concentration, pH, surfactants and modifier have been studied. Non-ionic surfactant Triton-X 100(TX-100) showed very good electrocatalytic effect on the modified carbon paste electrode. The detection limit of the modified carbon paste electrode is 1×10^{-7} M for dopamine.

Keywords: Cyclic voltammetry; Dopamine; Alcian Blue; Carbon paste electrode; Surfactant

1. INTRODUCTION

Dopamine was discovered in the year 1950. Dopamine (DA) is one of the most important neurotransmitters and plays a significant role in the functioning of central nervous, renal and hormonal system as well in drug addiction and parkinson's disease [1]. Therefore it is significant to develop sensitive and simple methods for the determination of Dopamine. DA can be determined with electrochemical methods because it is an electrochemically active compound [2-8]. Serious diseases such as Schizophrenia and Parkinsonism may result by loss of DA containing neurons [9]. Patient with this disease shows a low level of DA. Therefore determination of DA concentration has become important and many methods were introduced to determine DA, such as spectroscopy, chromatography and electrochemistry [10]. Since DA is an oxidizable compound it can be easily detectable by electrochemistry methods based on anodic oxidation [11]. One of the most common routes is to use a

modified carbon paste electrode which has the ability to eliminate the interfering substances from DA determination. The study of electrochemical determination of DA with different modified electrode for sensitive and selective [12]. The modification can be done by adding different types of modifiers. One of the modifiers used for this work, the determination of electrochemical response of DA is Alcian Blue.



Scheme 1.

Alcian Blue [Scheme 1] is also a name of noise pop band that broke in 2006. Alcian Blue 8GX, Ingrain blue 1 and C.I 74240 is a phthalocyanine dye that contains copper. Alcian Blue is one of the most widely used cationic dyes (it has many positive charges on the molecule) for the demonstration of Glycosaminoglycans. It is thought to work by forming reversible electrostatic bonds between the cationic dye and the negative (anionic) sites on the Polysaccharide. These electrostatic bonds can be readily broken revealing what appears to be a variation in bonding among different types of Glycosaminoglycans. When the concentration of electrolyte required to break the bond is increased progressively, then neutral sulphated and phosphated mucopolysaccharides may be combined with the tissue section. Alcian Blue is a group of polyvalent basic dyes that are water soluble. The blue color is due to the presence of copper in the molecule. The 3% acetic acid solution (pH 2.5). Alcian blue stains

both sulphated and carboxylated sialomucins (glycoproteins). It is believed to form salt linkage with the acid groups of acid mucopolysaccharides.

Surfactant belongs to a class of molecules with surface active properties. This behaviour is due to their amphiphilic structure, which contains both a polar or hydrophilic head and non-polar or hydrophobic tail [13]. Surfactants are normally classified according to the head group type [14]. Ionic (anionic and cationic), Non-ionic and Amphoterics (Zwitter ionics). Adsorption of ionic surfactants onto the surface generates charge. Cationic surfactants will lead to a positively charged surface and anionic surfactants will give a negative charged surface. A non-ionic surfactant molecule has no charge in aqueous media but normally consists of a highly polar region such as polyoxyethylene groups. Amphoteric surfactants develop a negative or positive charge depending on the pH of the solution. At low concentration, surfactant molecules are unassociated monomers. As the concentration of surfactant is increased, the attractive and repulsive forces between the molecules cause self-aggregation to occur resulting in the formation of monolayer or micelles. The concentration at which these micelles form is called the Critical Micelles Concentration (CMC). The characteristics of micelles can be controlled by small changes in the chemical structure of the surfactant molecules or by varying the conditions of the disperse phase. Changes in the pH, ionic strength and temperature are all known to influence the size and shape of surfactant micelles. Related works have been done by our research group [15-18].

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Alcian Blue was purchased from G.S. Chemical Testing lab and Allied Industries. Dopamine hydrochloride (3 Hydroxytryamine hydrochloride $C_8H_{11}NO_2.HCl$) and Potassium ferrocyanide was purchased from Himedia. Dopamine was dissolved using 0.1M Perchloric acid ($HClO_4$). All other Chemicals were of analytical grade quality and were used without further purification. The water used was a double distilled in all the measurements. Phosphate Buffer [0.2M] was prepared by 0.2M disodium hydrogen phosphate and 0.2M sodium dihydrogen phosphate.

2.2. Apparatus

The electrochemical experiments were carried out using a Model-201 Electroanalyser [EA-201 Chemilink system]. All the experiments were carried out in a convectional three electrochemical cell. The electrode system contained a working carbon paste electrode, home made cavity of 3mm diameter a platinum wire as counter electrode and saturated calomel electrode as reference electrode.

2.3. Preparation of alcian blue modified carbon paste electrode

Alcian Blue Modified Carbon Paste Electrode (ABMCPE) was prepared by grinding the different ratio's of alcian blue dye with 70% graphite powder of 50mm particle size and 30% silicon

oil in an agate mortar by hand mixing for about 30 minute to get homogeneous alcian blue modified carbon paste. The paste was packed into the cavity of home made CPE of 3mm in diameter and smoothened on weighing paper. Similarly the BCPE was prepared without adding modifier.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration of Alcian Blue

Alcian Blue (AB) is a phthalocyanine dye used as a modifier in the preparation of ABMCPE. The characterization of ABMCPE was investigated by using cyclic voltammetric technique.

Alcian Blue Modified Carbon Paste Electrode (ABMCPE) was prepared of different ratio by adding different amount of Alcian Blue. By increasing the concentration of Alcian Blue in the modified carbon paste electrode, the electrochemical redox peak current goes on increasing in 1M KCl and 2mM Potassium ferrocyanide as an analyte. As the concentration of Alcian Blue increases from 1mg to 10mg after the current signal decreases with increasing concentration. Alcian Blue from 1mg to 10mg concentration shows the cathodic peak current increases from 16.2 μ A to 33.1 μ A and anodic peak current increased from -22.2 μ A to -45.7 μ A. The graph of peak current vs. concentration of ABMCPE was plotted showed in Fig 1 Maximum current signal enhancement in 10mg ABMCPE, so 10mg ABMCPE for the study of all other parameters.

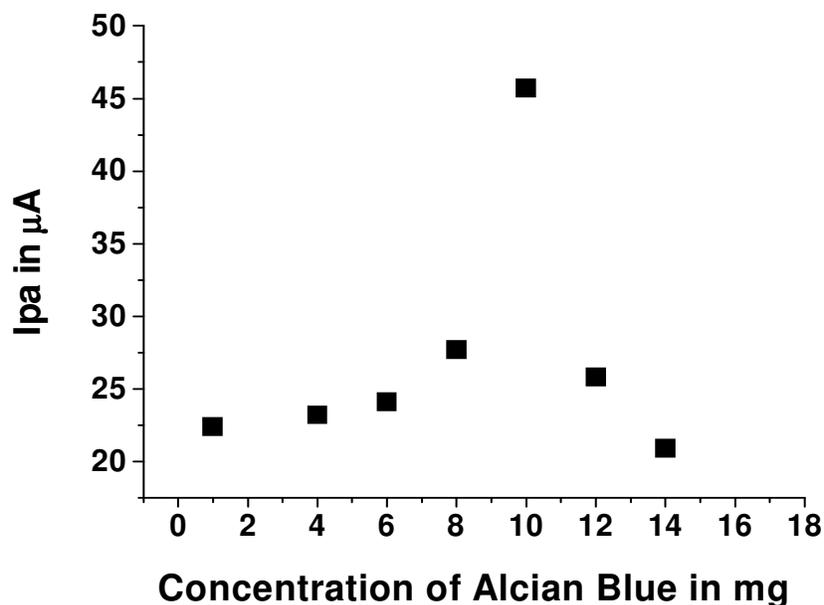


Figure 1. Effect of concentration of alcian blue on anodic peak current in 2mM potassium ferrocyanide and potassium chloride, Scan Rate: 50mVs⁻¹

3.2. Electrochemical characterization of ABMCPE

Fig.2a.shows the electrochemical response of Bare Carbon Paste Electrode (BCPE) and Alcyan Blue Modified Carbon Paste Electrode (ABMCPE) in the presence of 2mM potassium ferrocyanide in 1M KCl solution. The dashed line shows the electrochemical response of BCPE having the cathodic peak current (I_{pc}) 16.3 μ A and anodic peak current (I_{pa}) -22.4 μ A. The electrochemical cathodic peak potential (E_{pc}) 186mV and anodic peak potential (E_{pa}) 257mV. After modification with 10mg ABMCPE shows in solid line the current enhancement of both electrochemical anodic peak current (I_{pa}) -45.7 μ A and cathodic peak current (I_{pc}) 33.1 μ A The anodic peak potential is 283mV and cathodic peak potential is 162mV.

Fig.2b. shows the electrochemical response of Dopamine at BCPE and ABMCPE in the presence of 0.2M phosphate buffer solution in pH 6.6. The dashed line shows the electrochemical response of BCPE having the cathodic peak current (I_{pc}) 7.8 μ A and anodic peak current (I_{pa}) -52 μ A. The electrochemical cathodic peak potential (E_{pc}) 72mV and anodic peak potential (E_{pa}) 211mV. After modification with 10mg ABMCPE shows in solid line the current enhancement of both electrochemical anodic peak current (I_{pa}) -109.3 μ A and cathodic peak current (I_{pc}) 42.8 μ A. The decreasing in the anodic peak potential to 209mV and increasing in the cathodic peak potential 126mV when compared with BCPE. The modified electrode exhibited strong promoting effect and high stability toward the electrochemical oxidation of dopamine in pH 6.6 phosphate buffer solution. The detection limit of the modified carbon paste electrode is 1×10^{-7} M for dopamine.

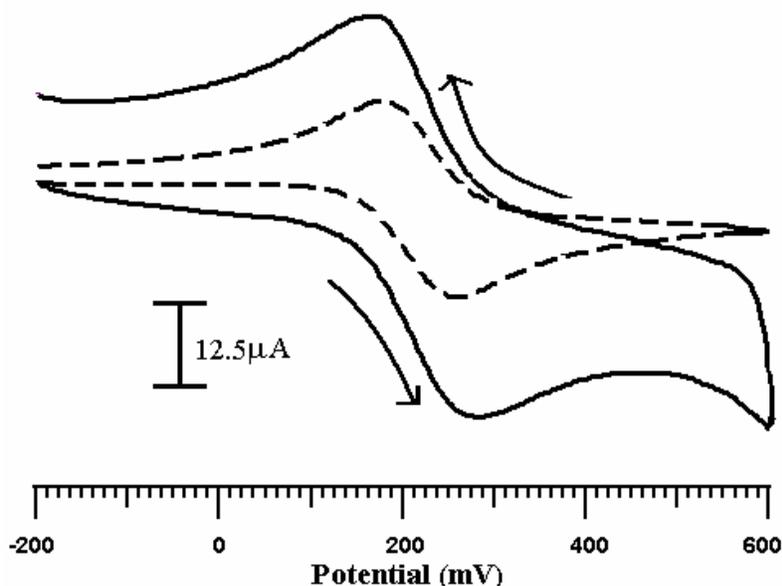


Figure 2a. Cyclic Voltammogram of BMCPE (dotted line) and ABMCPE (Solid line) in the presence of 2mM potassium ferrocyanide and potassium chloride solution, Scan rate= 50mVs^{-1}

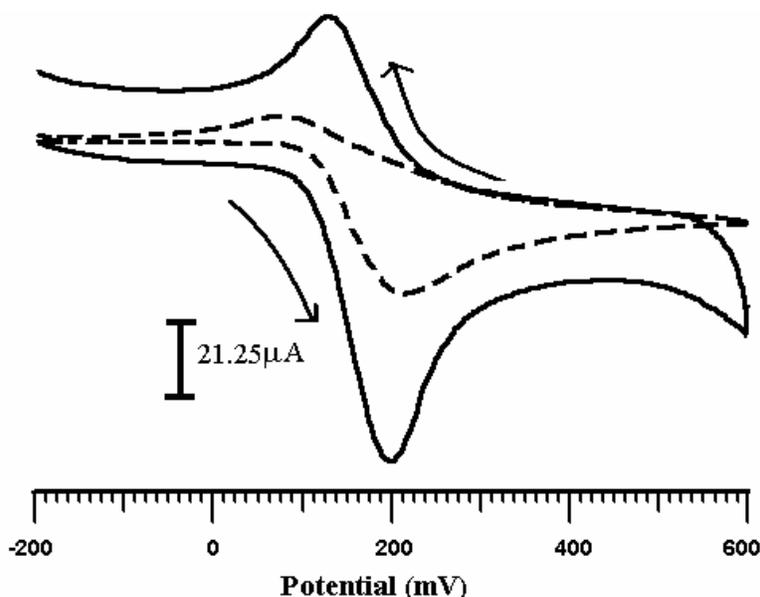


Figure 2b. Cyclic Voltammogram of BMCPE (dotted line) and ABMCPE (Solid line) in the presence of 2mM dopamine and 0.2M phosphate buffer solution in pH 6.6, Scan rate= 50mVs^{-1}

3.3. Electrocatalytic response of dopamine at ABMCPE

Dopamine (2mM) being as easily oxidizable catecholamine showed quasi-reversible voltammogram with supporting electrolyte 0.2M phosphate buffer solution pH 6.6 at 50 mV/s scan rate for BCPE (Fig.2b). Cyclic voltammogram for dopamine at BCPE (dotted line), with cathodic peak potential (E_{pc}) at 72mV and anodic peak potential (E_{pa}) -248mV (vs. SCE) in 0.2M phosphate buffer solution pH 6.6. The anodic peak current (I_{pa}) $-52\mu\text{A}$ and cathodic peak current (I_{pc}) $7.8\mu\text{A}$. The separation of redox peak potential (ΔE_p) 176mV and the ratio of peak current (I_{pa}/I_{pc}) was $6.66\mu\text{A}$, which were characteristics of quasi-reversible electrode process. The formal peak potential (E^0), which is the mid point of E_{pa} and E_{pc} was obtained as 160mV (vs. SCE). However for the ABMCPE a pair of redox peak was obtained with strong increase in anodic peak current and less enhancement in cathodic peak current. The cathodic peak potential (E_{pc}) at 126mV and anodic peak potential (E_{pa}) at 199mV and anodic peak current (I_{pa}) was $-108.5\mu\text{A}$ and cathodic peak current (I_{pc}) was $42.6\mu\text{A}$. The separation of redox peak potential (ΔE_p) was found to be 83mV and the ratio of peak current (I_{pa}/I_{pc}) was $2.54\mu\text{A}$ and (E^0) was 167.5mV. The voltammogram obtained for ABMCPE showed good enhancement of redox peak current and dopamine is an oxidizable compound it can be easily detectable by electrochemical method.

3.4. Effect of scan rate

According to Randles-sevick's equation increase in the scan rate increases the peak current. The ABMCPE showed increase in the peak current with increase in scan rate (50 mV/s to 400mV/s) in 2mM dopamine and 0.2M phosphate buffer solution at pH 6.6. Cyclic voltammogram for dopamine at ABMCPE shown in Fig.3a. The graph of current I_{pa} vs. scan rate (v) and square root of scan rate ($v^{1/2}$)

were plotted. The graph obtained were nearly straight line as shown in Fig.3b.and Fig.3c. In the range from 50 mV/s to 400 mV/s the anodic peak currents were proportional to the scan rate (v) and also to the square root of scan rate ($v^{1/2}$) with correlation coefficient 0.99737 and 0.98137 for I_{pa} vs. v and I_{pa} vs. $v^{1/2}$ respectively. This indicates that, the electrode transfer reaction is adsorption controlled.

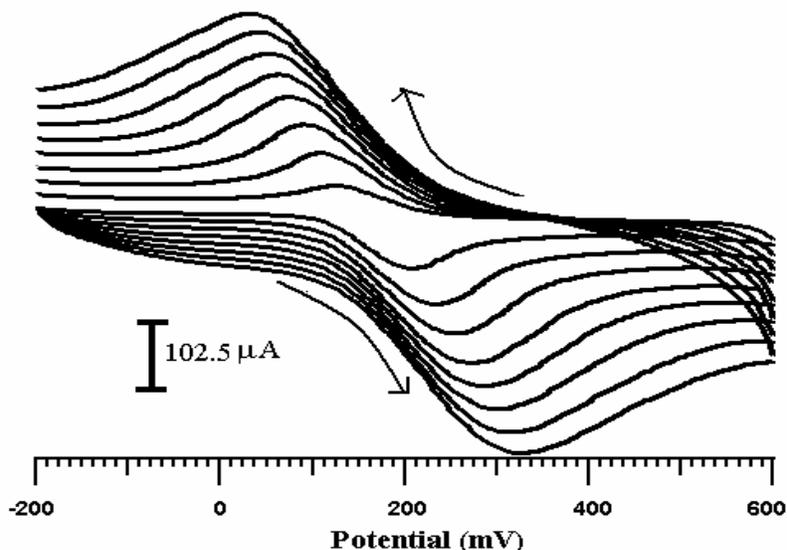


Figure 3a. Cyclic voltammogram of different scan rate in the presence of 2mM dopamine and 0.2M phosphate buffer solution at pH 6.6, scan rate 50mVs⁻¹-400mVs⁻¹

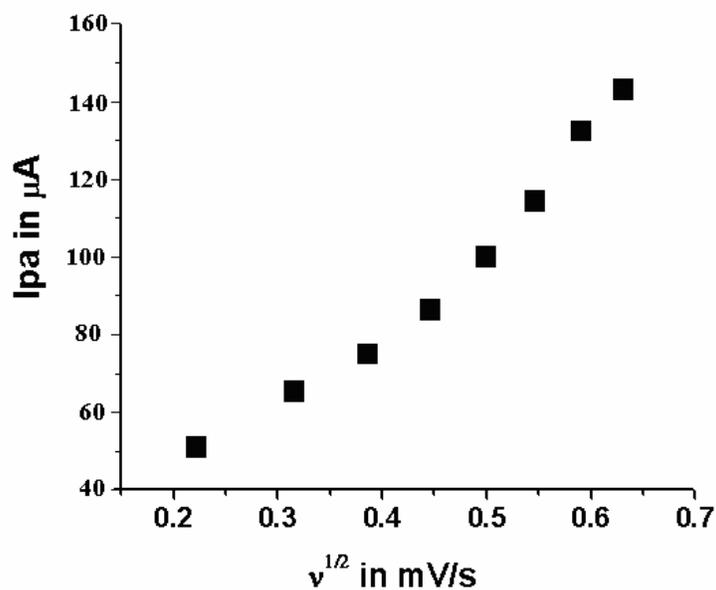


Figure 3b. Effect of variation of square root of scan rate on the anodic peak current of 2mM Dopamine in phosphate buffer solution at pH 6.6

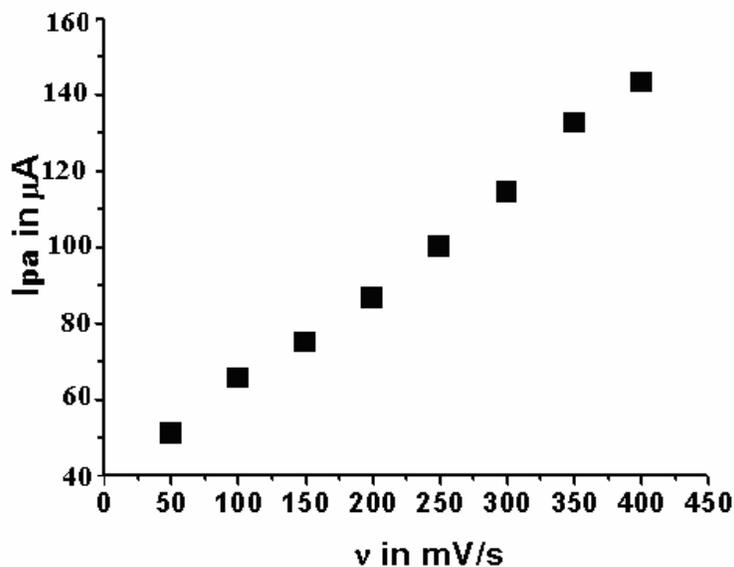


Figure 3c. Effect of variation of scan rate on the anodic peak current of 2mM Dopamine in phosphate buffer solution at pH 6.6

3.5. Effect of Concentration

According to electrochemical response the redox peak current increased with increasing the concentration of analyte. Concentration of dopamine was increased from 1mM to 5mM as shown in Fig.4a Plot of anodic peak current against concentration of dopamine to get a linear relationship between the anodic peak current (I_{pa}) in the range 1mM to 5mM as shown in fig 4b [19-24].

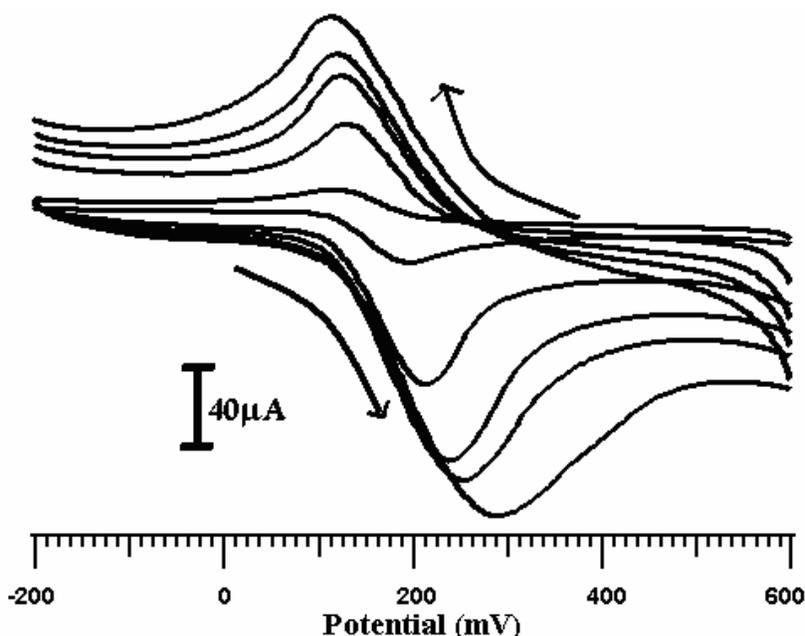


Figure 4a. Cyclic voltammogram of variation of concentration of dopamine from 1 to 5ml in presence of phosphate buffer solution at pH 6.6

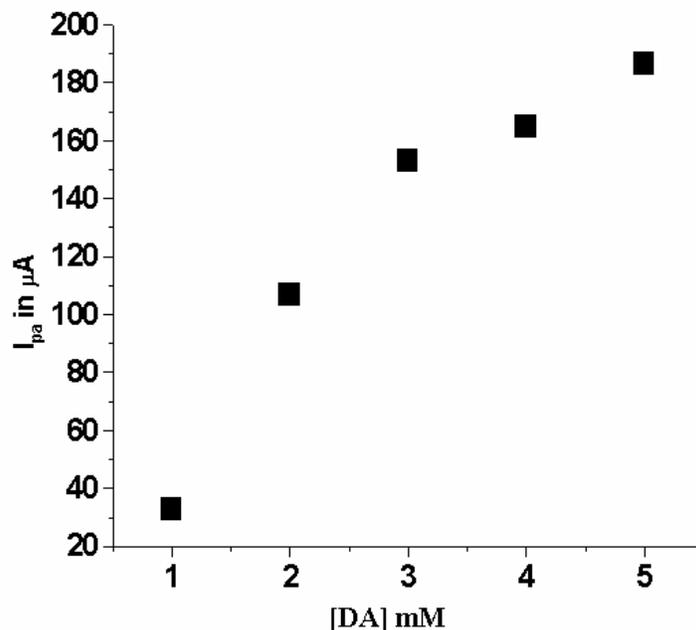


Figure 4b. Effect of variation of concentration of dopamine on the anodic peak current of 2mM Dopamine in phosphate buffer solution at pH 6.6

3.6. Effect of pH

The electrooxidation of dopamine was studied over pH range from 6.0 to 6.6 using 0.2M phosphate buffer as a supporting electrolyte at a scan rate of 50 mVs^{-1} . The oxidation peak potential of 6-DA at ABMCPE decreases with increase in pH from 6 to 7 indicates that the electro-oxidation process becomes easier at higher pH as shown in Fig .5 [25-26].

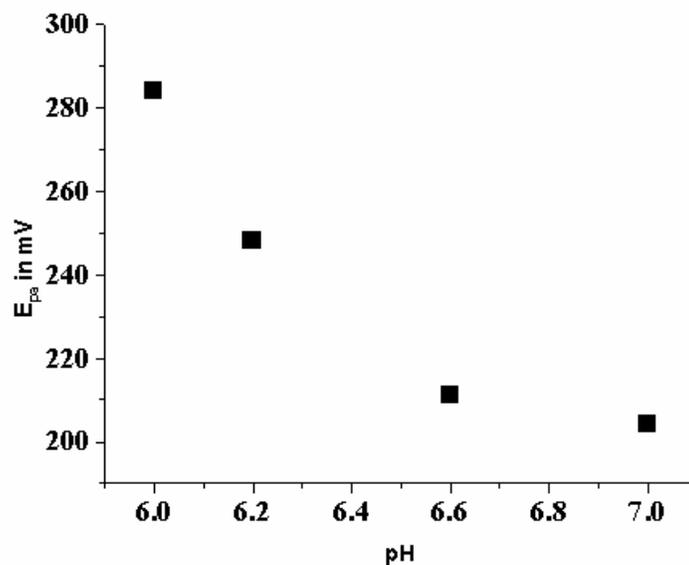


Figure 5. Effect of variation of pH on the anodic peak potential of 2mM Dopamine in phosphate buffer solution at pH 6.6 on the surface of ABMCPE

3.7. Effect of Surfactant

To study the effect of addition of surfactants the experiments were carried out using anionic surfactant Sodium Dodecyl Sulphate (SDS), cationic surfactant Cetyl Trimethyl Ammonium Bromide (CTAB) and non-ionic surfactant Triton-X100 (TX-100). Initially, cyclic voltammogram were recorded for ABMCPE a solution containing Dopamine (2mM) in Phosphate buffer solution pH 6.6. Keeping the concentration of Dopamine constant, the concentration of the surfactant was increased from 1 μ M to 20 μ M by mobilization and immobilization method. Fig.6a. shows the effects of surfactant concentration in mobilization when the surfactant concentration is lower than 10 μ M the critical micelle concentration (CMC) of surfactant at room temperature, both i_{pa} and i_{pc} increases rapidly with the increase of surfactant concentration. However, the signal of dopamine apparently decreased in the range of 10 to 18 μ M.

Fig.6b shows the effect of surfactant concentration by immobilized immobilization method the surfactant concentration below 12 μ M, the CMC of surfactant at room temperature, both i_{pa} and i_{pc} increases rapidly with the increases of surfactant concentration. From these results the immobilization is more favorable than mobilization method. Among these surfactants TX-100 shows good enhancement in the peak current compared to SDS and CTAB.

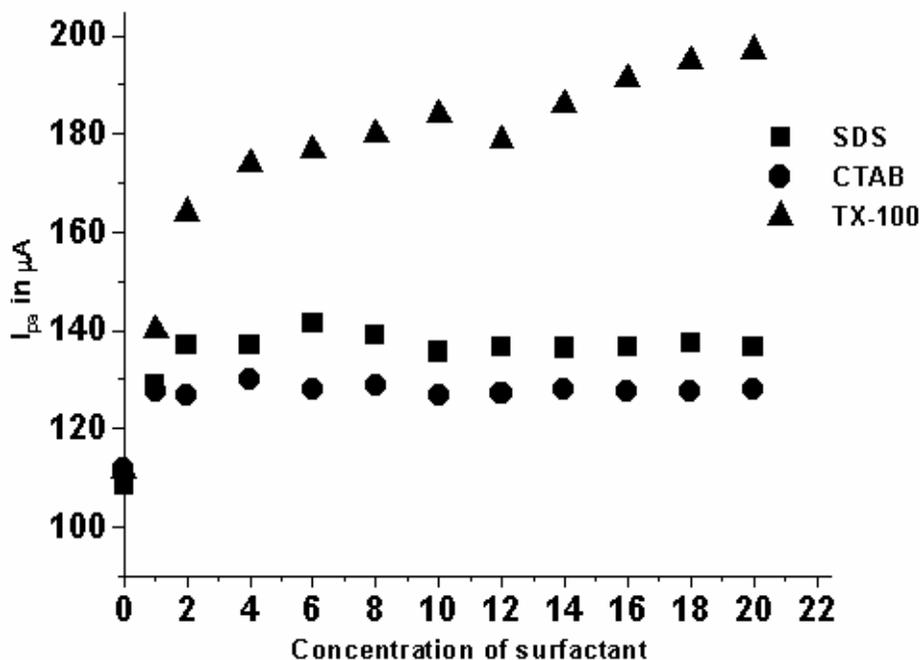


Figure 6a. Effect of variation of concentration of surfactants mobilization for 2mM Dopamine at ABMCPE in 0.2M PBS pH 6.6, scan rate 50 mVs^{-1}

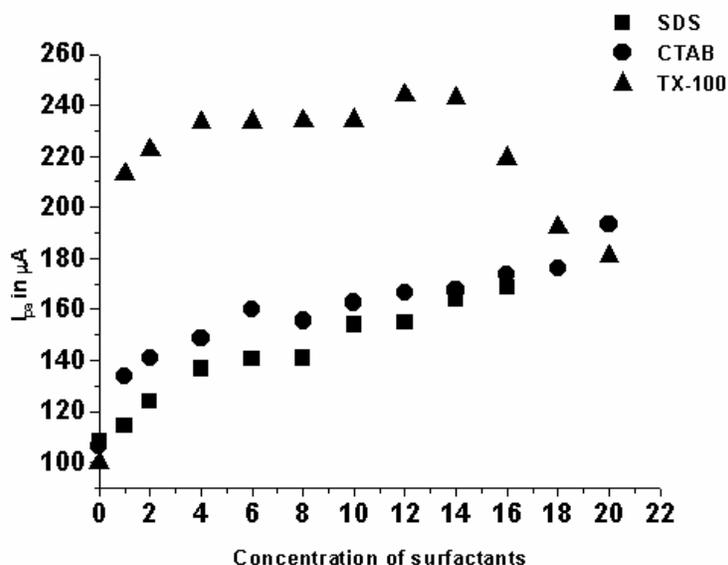


Figure 6b. Effect of variation of concentration of surfactants Immobilization for 2mM Dopamine at ABMCPE in 0.2M PBS pH 6.6, scan rate 50 mVs⁻¹

Fig.7. shows comparison of three surfactants SDS, CTAB and TX-100 on immobilization method ABMCPE in the presence of 2mM Dopamine in Phosphate Buffer Solution pH 6.6. Here more anodic peak current enhancement in TX-100 compared to both SDS and CTAB. In this work, the TX-100 at ABMPCE and Dopamine was explored by cyclic voltammetry, which might be able to explain the enhancement effect of surfactant in electroanalytical chemistry. The result revealed not only the adsorptive behavior TX-100 but also the influence of TX-100 adsorption and diffusion on the surface of the electrode interface. These results might be able to explain the enhancement effect of surfactants in electrochemistry.

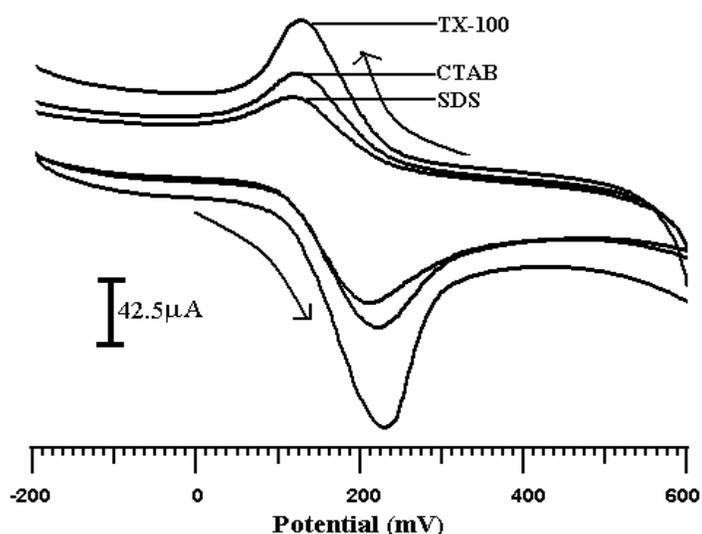


Figure 7. Cyclic voltammogram of comparison of three surfactants in 2ml dopamine in phosphate buffer solution at pH 6.6, scan rate 50 mVs⁻¹

3.8. Effect of scan rate in 12 μ M TX-100 immobilization of ABMCPE

According to Randles Sevcik's equation, increases in the scan rate increase the peak current. 12 μ M TX-100 surfactant on to the surface of ABMCPE showed increase in the peak current with increase in scan rate from 50 to 120mV/s in the presence of 2mM DA and 0.2M Phosphate buffer solution pH 6.6 as shown in Fig.8a.

The plot of anodic peak current (I_{pa}) against square root of scan rate ($v^{1/2}$) shows linear straight line as shown in Fig.8b. that is diffusion controlled and anodic peak current (I_{pa}) against scan rate (v) shows linear straight line as shown in Fig.8c.that is adsorption controlled.

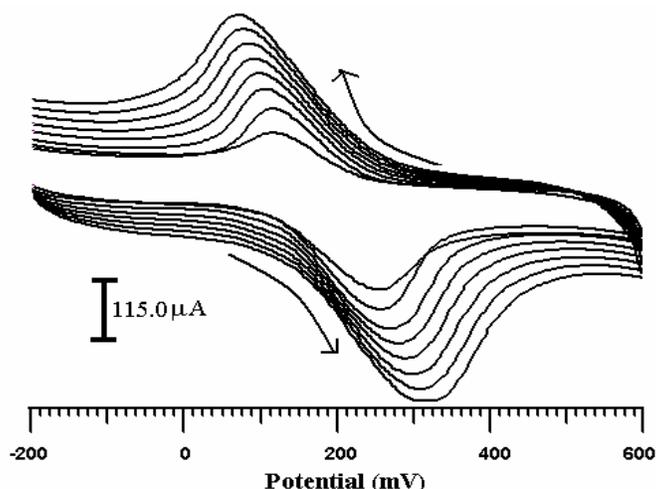


Figure 8a. Effect of variation of scan rate of 2mM Dopamine in phosphate buffer solution at pH 6.6 2 μ M TX-100 in immobilization method, Scan rate=50 -120 mVs⁻¹

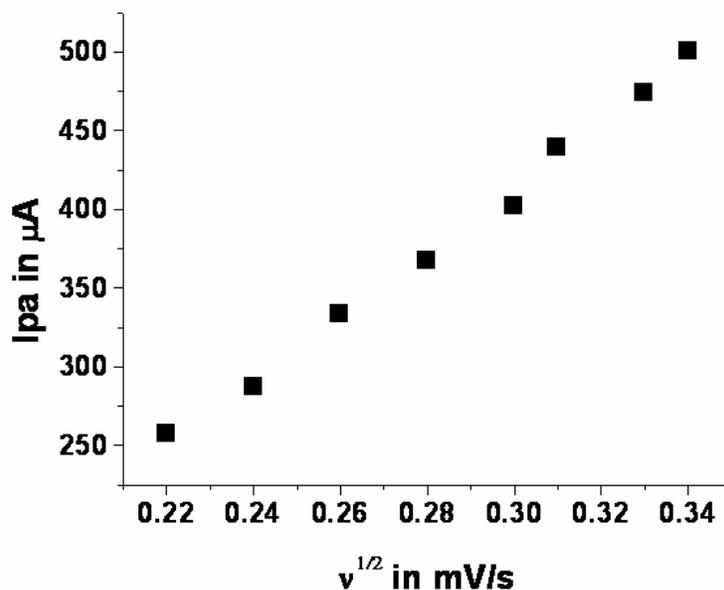


Figure 8b. Effect of variation of square root of scan rate on the anodic peak current of 2mM Dopamine in phosphate buffer solution at pH 6.6 12 μ M TX-100 in immobilization method

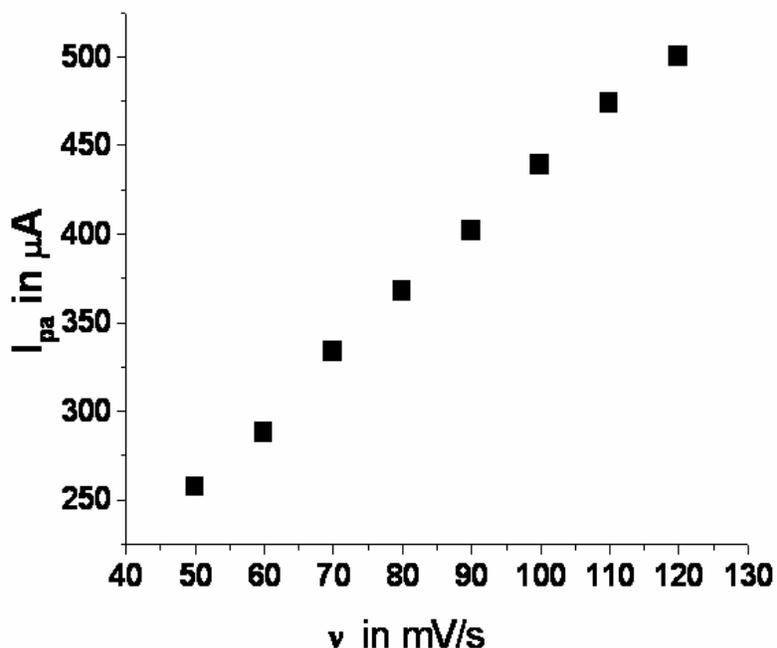


Figure 8c. Effect of variation of scan rate on the anodic peak current of 2mM Dopamine in phosphate buffer solution at pH 6.6, 12 μ M TX-100 in immobilization method

4. CONCLUSIONS

In this work, chemically modified alcian blue carbon paste electrode acts as a good sensor, exhibited strong promoting effect and stability towards the electrochemical oxidation of potassium ferrocyanide in KCl solution and dopamine at pH 6.6 in phosphate buffer solution (PBS). Non-ionic surfactant TX-100 showed very good electrocatalytic effect on the alcian blue modified carbon paste electrode. The detection limit of dopamine at bare carbon paste electrode is 1×10^{-5} M and 1×10^{-7} M for alcian blue modified carbon paste electrode. With its low cost and easy of preparation, the alcian blue modified carbon paste electrode seems to be great utility for further sensor development.

5. ACKNOWLEDGEMENT

The authors are very thankful to the Department of Science and Technology Government of India, New Delhi for the funding given through project No DST/TSG/ME/2007/44.

References

1. T Selvaraju, R Ramaraj, *Electrochem Commun* 5 (2003) 667
2. H Gu, Y Xu, W Peng, Lig, Chen H *Microchim Acta* 146 (2004) 223
3. M Ates, JA Castillo, S Sarac, W Schahmann *Microchim Acta* 160 (2008) 247

4. Y. L. Zeng, C. X. Li, C. R. Tang, X. B. Zhang, G. L. Shen, R. Q. Yu, *Electroanal. Chem.* 18 (2006) 440.
5. Y Zhang, J in G, Yang Z, H Zhao *Microchim Acta* 147 (2004) 225
6. G-S Lai, H-L Zhang, D-Y Han *Microchim Acta* 160 (2008) 223
7. W Chen, X Lin, L Huang, H Luo *Microchim Acta* 151 (2005) 101
8. K Wu, S Hu *Microchim Acta* 144 (2004) 131
9. D.R Shankaran, K.Limura, T.Kato, *Sensors and Actuators B Chemical* 94 (2003) 73
10. J.W. Mo, and B.Ororeve, *Analytical Chemistry* 73 (2001) 1196
11. Zhao Guo-hua, Li ming-fang, Li ming-li, *Central European Journal of Chemistry* 5(4) (2007) 1114-1123
12. S.Surre, Y. Michotte, P.Herregodts, D.Deleu, N.D. Klippel and G. Ebinger, *Journal of Chromatography* 575 (1992) 207
13. D.H. Everett, *Basic principles of colloid science* The Royal Society of chemistry, Cambridge, UK (1988)
14. *Colloid Science; principles methods and applications* (Ed.T. Cosgrove) Blackwell, oxford, UK (2005)
15. Raghavendra Naik, E. Niranjana, B.E. Kumara Swamy, B.S. Sherigara and H. Jayadevappa, *Int. J. Electrochem. Sci.*, 3 (2008) 1574.
16. Panduranga Char, E. Niranjana, B.E. Kumara Swamy, B.S. Sherigara and K.Vasantakumar Pai, *Int. J. Electrochem. Sci.*, 3 (2008) 588.
17. E. Niranjana, R. Raghavendra Naik, B.E. Kumara Swamy, B.S. Sherigara and H.Jayadevappa, *Int. J. Electrochem. Sci.*, 2 (2007) 923
18. Umesh Chandra, Ongera Gilbert, B.E. Kumara Swamy, D. Yadav Bodke and B.S Sherigara *Int. J. Electrochem. Sci.*, 3 (2008) 1044.
19. B.E. Kumara Swamy and B.Jill venton *Anal.chem.* 79 (2007) 744
20. E.Niranjana, R.Raghavendra Naik, B.E. Kumara Swamy, Yadav D.Bodke, B.S.Sherigara, H.Jayadevappa and B.V. Badami, *Int.J.Electrochem.Sci.* 3(2008) 980
21. E.Ramanathan, P.S.M. Kannan, S.Thangavelu, K.S. Udupa, *Bull.Electrochem.* 4 (1988) 365
22. B.Eswarappa, B.S. Sherigara, B.E. Kumara Swamy, *Bull.Electrochem.*20 (2004) 1
23. C.Sliptien, M.Ariel, *J.Electroanal.chem.*75 (1977) 551
24. C.Amatore, J.M. Saveant, D.Tessier, *J.Electroanal.chem.* 146 (1988)37
25. B.E.Kumara Swamy, E.V.S. Subrahmanyam, B.S. Sherigara and G.Venkateswaran, *Bulletin of Electrochemistry* 16 (2000) 533.
26. Nagaraja Chowdappa , B.E. Kumara Swamy, E. Niranjana and B.S. Sherigara, *Int. J. Electrochem. Sci.*, 4 (2009) 425