Int. J. Electrochem. Sci., 4 (**2009**) 1319 - 1328

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Cyclic Voltammetric Investigation of Dopamine at p-aminobenzoic Acid Modified Carbon Paste Electrode

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Received: 4 September 2008 / *Accepted:* 15 September 2008 / *Published:* 1 September 2009

In this investigation the modified carbon paste electrode was fabricated by adding p-amino benzoic acid into the mixture of dry graphite powder with silicon oil in the proportion of 60:40. The Cyclic voltammogram of p- aminobenzoic acid modified carbon paste electrode (PABA/CPE) was investigated with standard potassium ferrocyanide showed a reversible voltammogram. Electrocatalytic oxidation of dopamine is studied in acetate buffer solution at neutral pH-7.0 and the effect of concentration, scan rate, pH and effect of surfactant studies were made. The electrode process was found to be diffusion controlled. The PABA/CPE showed significant enhancement of oxidation peak for dopamine at 6.0 mg into the paste. Hence modifier is selected at 6 mg PABA into the CPE.

Keywords: p-aminobenzoic acid, potassium ferrocyanide, dopamine, SDS, CTAB, cyclic voltammetry.

1. INTRODUCTION

Dopamine (DA) is one of the most significant catecholamine belongs to the family of excitatory chemical neurotransmitter [1,2]. It plays very important role in the function of central nervous, renal, hormonal and cardio vascular system [3, 4]. Because extreme abnormalities of DA level are symptoms of several diseases such as schizophrenia, parkinson’s disease [5], the determination of such compounds in a real biological samples and identify changes in neurotransmission that correlate the behavioral state of animal are an obvious target in neurochemical studies. Generally the determination of DA is performed with high performances liquid chromatography (HPLC) [6], Ion Chromatography [7] and spectrophotometry. DA can be determined by electrochemical methods because it is an electrochemical active compound. The development of voltammetric sensor for the detection of neurotransmitter in the extracellular fluid of the central nervous system as a received much interest in the past few decades [9,10]. The electrochemical methods have more advantages over other methods because the electrodes can be made conveniently to sense the neurotransmitter in the living organism [9]. Whiteman and co-worker have done a lot of merit work on behavior of animal and changes neurotransmitters in a rat by fast scan cyclic voltammetry (FSCV) [11-14] Ewing and Co-worker [15-17] adopt advanced capillary electrophoretic (CE) separation neurotransmmiter in vivo and determination neurotransmitter in single cell cytopalasm using nafion coated carbon fibre microelectrodes as electrochemical detections. Ewing research group have used this methodology to examine the transient chemical events happening in the nanometer environment of the synapse. The major problem in the detection of dopamine in presence of high concentration of ascorbic acid which is oxidized at all most same potential as in DA on the bare electrodes, the bare electrodes very often suffers from a fouling effects due to accumulation of oxidized product on the electrode surface which results in rather poor selectivity and sensitivity. The homogeneous catalytic oxidation of AA by the oxidized DA is another major interference in the measurement of DA. Therefore it is very difficult to determine DA directly [18]. In order to resolves these problems some modified electrode have been used to determine DA [19-22].

Our research group fabricated many such modified electrodes [23-27]. In this work there is an attempt to modify carbon paste electrode sensor to determine dopamine in biological sample in presence of ascorbic acid using modified p-aminobenzoic acid carbon paste electrode.

2. EXPERIMENTAL PART

2.1. Reagents & Chemicals

Potassium ferrocyanide, dopamine, sodium acetate, acetic acid, potassium chloride, perchloric acid, and p-aminobenzoic acid used were of analytical grade in the pure from Fluka and Merck and used without further purification. Dopamine stock solutions (1×10^{-4} M) were prepared by adding dopamine to 0.1 M perchloric acid and it's studies were carried out in acetate buffer solution of pH-7.0 and 10mM potassium ferricyanide was prepared by dissolving in double distilled water.

2.2. Apparatus and procedure

Cyclic voltammetry (CV) was performed on Model 201 Electroanalysis (EA-201, Chemilink System). All the experiments were carried out in a conventional electrochemical cell. The electrode system contained a carbon paste working electrode (3.0 mm in diameter), a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The PABA/CPE modified carbon paste electrode was prepared as follows 70% graphite powder (particle size 50 mm and density is 20mg/100 ml) 30%silicone oil and required quantity of the modifier were mixed by hand to produce a homogeneous PABA/CPE.

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic response of $K_4Fe(CN)_6$ at PABA/CPE modified electrode

Figure 1a shows the calibration of concentration of PABA/CPE for the maximum enhancement of the anodic current for the $K_4Fe(CN)_6$. Fig.1b shows cyclic voltammogram of 1 mM potassium ferrocyanide at bare carbon paste electrode and PABA/CPE in the Potential range of -200 to 600 at the scan rate 100 mVs^{-1} in 1M KCl. The voltammogram of 1m M $K_4Fe(CN)_6$ at bare/CPE and PABA/CPE showed identitical reversible peaks. The PABA/CPE showed excellent electrochemical response when compared to bare CPE. The dashed line shows electrochemical response of bare CPE having E_{pa} 249 mV and E_{pc} 106 mV with the ΔE_{pa}=143 mV with less sensitivity and i_{pa}/i_{pc} ratio is 1.41 μA which reveals the quasireversible electrode process. After modification with 6 mg of PABA, the electrode showed good improved in enhancement of both cathodic and anodic peak current which was shown in solid line. The peak potential differences is 78 mV and the and i_{pa}/i_{pc} ratio is 1.08 μA shows the electrode transfer kinetics.

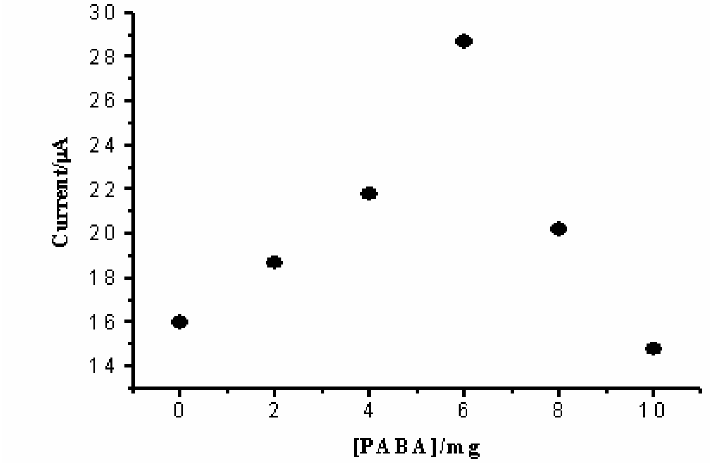

Figure 1a. Graph of concentration of PABA/mg v/s Current/μA for Potassium ferricyanide (1 ×10^{-3}M at 100 mVs^{-1}.in 1M KCl supporting electrolyte

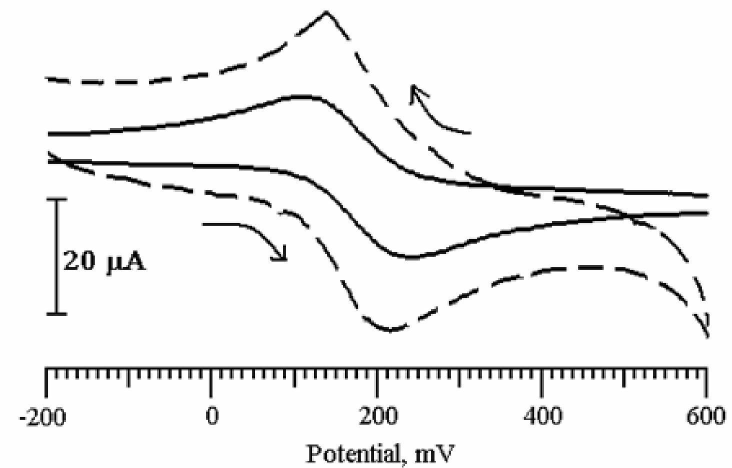

Figure 1b. Cyclic Voltammogram of 1×10^{-3} K_4FeCN_6 at bare CPE(solid line) and PABA/CPE (dashed line) in 1M KCl Supporting Electrolyte at 100 mVs^{-1}

3.2. Electrochemical caliberation of PABA/CPE for the detection of dopamine.

PABA/CPE was prepared of different ratio by adding different amount of PABA. By increasing the quantity of PABA in the modification anodic peak current(i_{pa}) goes on increasing from 2 to 6mg and again it decreases above 8 mg to 10 mg shows changes in the anodic peak current i_{pa}, and hence there is an optimum increase in i_{pa} at 6 mg and the experiment was carried out at 6 mg PABA in carbon paste electrode for dopamine as shown in the figure 2a.

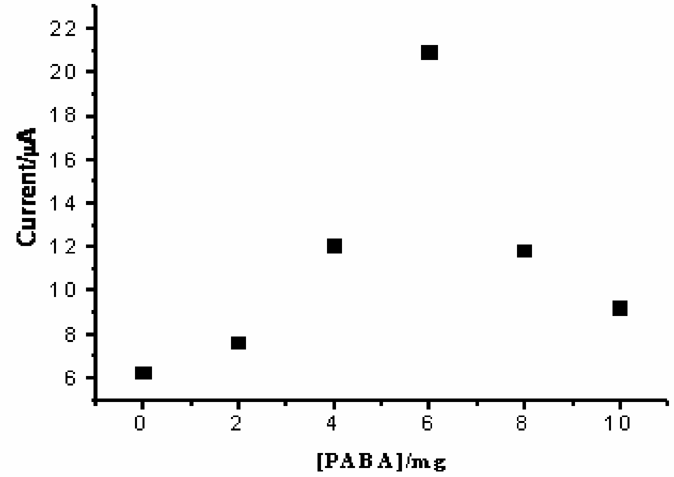

Figure 2a. Graph of concentration of PABA/mg v/s Current/µA for dopamine.

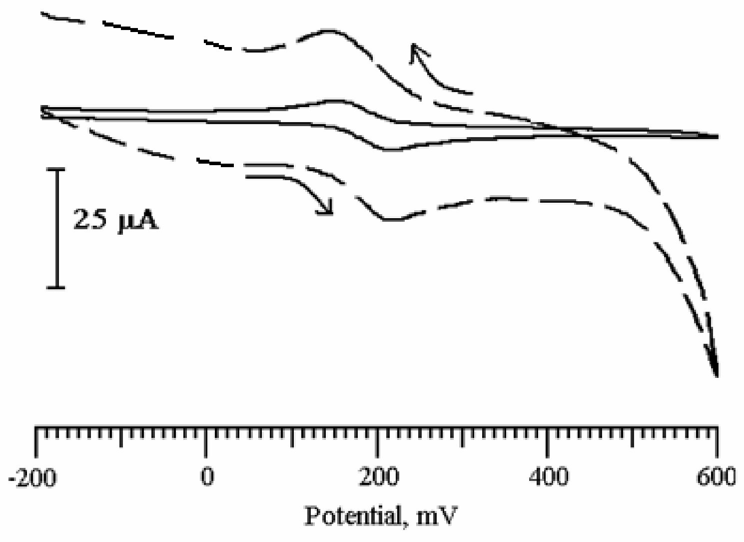

Figure 2b. Cyclic voltammogram of 1×10^{-4} dopamine at bare CPE(solid line) and PABA/CPE (dashed line) in 0.1 M acetate buffer at pH-7.0 at 100 mV/s.

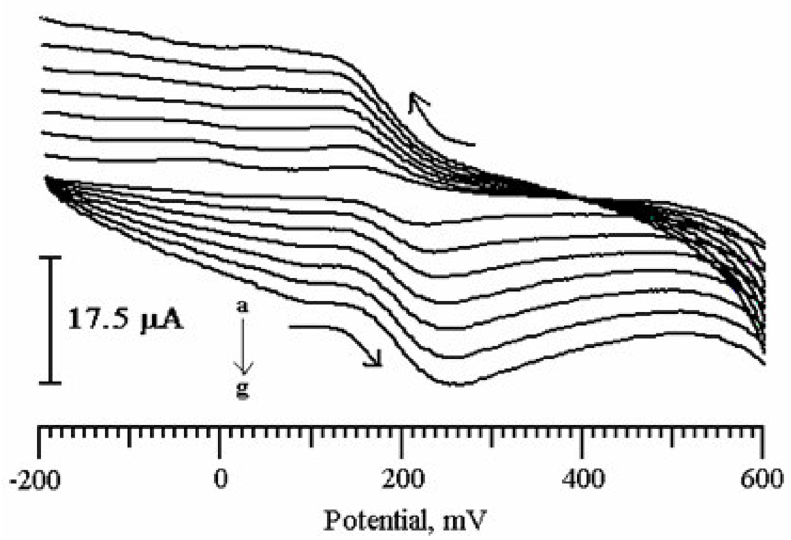

Figure 3a. Cyclic voltammogram of dopamine for scan rate 50mV/s to 350mV/s (a to g)

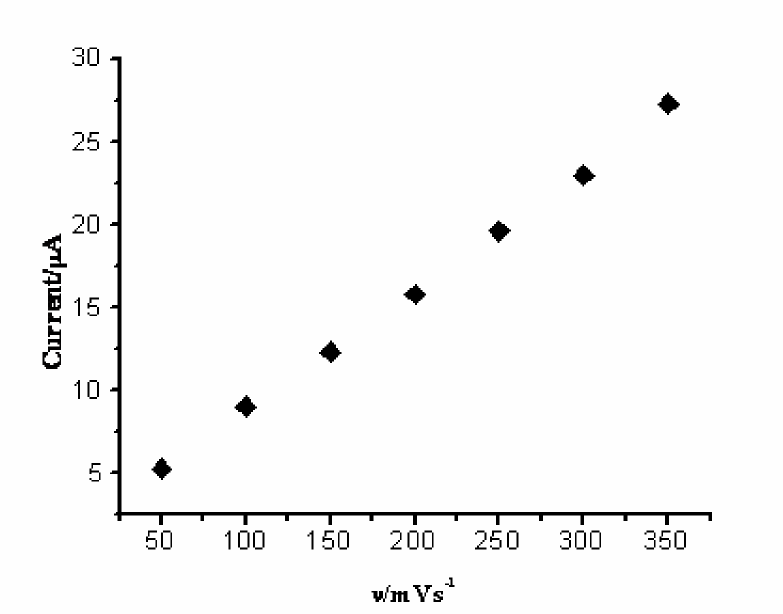

Figure 3b. Graph of scan rate (mV/s) v/s current (µA)

3.3. Electrocatalytic response of dopamine at PABA/CPE modified electrode.

Dopamine is being an easily oxidisable catecholamine, its voltammogram was recorded in the potential range of -200 to 600 mV in the 0.1 M acetate buffer at pH-7.0 at 100mVs^{-1}. Figure. 2b shows the pair of redox peak for 1 ×10^{-4} M DA at bare CPE (dashed line) with E_{pa} 215 mV & E_{pc} 151 mV. The peak to peak separation ΔE_p was found to be 74 mV and ratio of redox peak current i_{pa}/i_{pc} was found to be 1.51 µA which were the characteristics of quasireversible process. However for the

PABA/CPE a pair of redox peak is obtained with strong enhancement in both anodic and cathodic peak current (solid line). The E_{pa} was located at 218 mV and the corresponding cathodic peak potential was located at 149 mV. Peak to peak separation was calculated as 69 mV and the value of i_{pa}/i_{pc} was about 1.11 μA. Hence the voltammogram obtained for PABA/CPE was also reversible with good improvement in enhancement of oxidation and reduction peak current showed electron transfer kinetics.

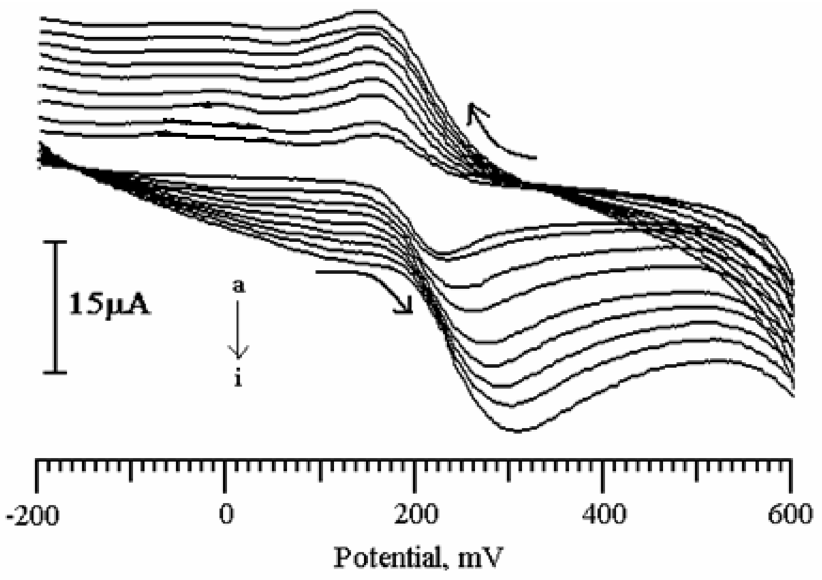

Figure 4a. Cyclic voltammogram of dopamine from 1 ×10^{-4}M to 5 ×10^{-4}M at 100 mV/s in 0.1 M acetate buffer solution

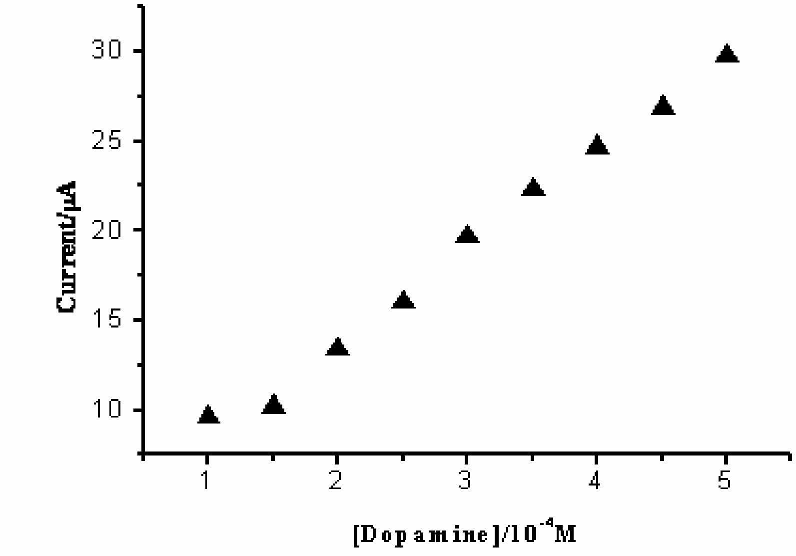

Figure 4b. Graph of concentration of dopamine (10^{-4} M) v/s Current (μA).

3.4 Effect of scan rate.

Cyclic voltammogram of different scan rates 50-350 mVs^{-1} was recorded in PABA/CPE is for 1 $\times 10^{-4}$ M DA figure3a. The graph of current i_{pa} v/s scan rate was plotted figure .3b. The graph obtained is straight line in the range from 50 – 350 mVs^{-1} is redox peak current is proportional to square root of scan rate with co-relation co-efficient 0.9995. This indicates that electron transfer reaction is a adsorption controlled [28, 29, 24].

3.5 Effect of Concentration of Dopamine.

Electrocatalytic oxidation of dopamine was carried out by varying concentration at PABA/CPE from 1×10^{-4} M - 5 $\times 10^{-4}$ M shown in the figure 4a. By increasing the concentration of dopamine i_{pa} and i_{pc} goes on increasing with shifting E_{pa} towards positive potential and E_{pc} towards slightly negative potential. The graph of i_{pa} v/s concentration of DA was plotted in the figure.4b shows increase in the anodic peak current which reveals linear proportional to the concentration of dopamine.

3.6. Effect of pH

Effect of pH for dopamine at PABA/CPE is studied at pH- 5, 7 and 9. The voltammogram of dopamine for pH is shown in the figure 5. As pH varies from 5- 9 it tends to basic media, anodic peak potential shift towards negative potential and as pH varied from 7 to 5 the media tends to acidic, the anodic peak potential shifts towards the positive side and potential is optimum at pH -7.0. Hence the electrocatalytic oxidation of dopamine was carried at neutral pH-7.0

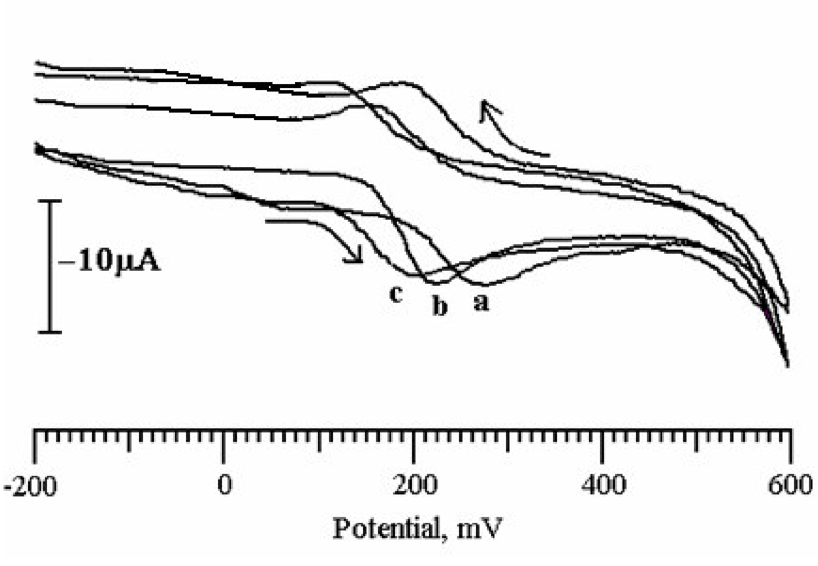

Figure 5. Cyclic voltammogram of dopamine at different pH (5,7 and 9) 0.1 M acetate buffer solution at 100 mV/s.

3.7 Effect of Surfactant.

Dopamine oxidation response was studied at various type of surfactant modified PABA/CPE .the surfactant used were, SDS & CTAB. Cyclic Voltammogram of surfactant Modified PABA/CPE is as shown in the Figure-5a. SDS modified PABA/CPE showed maximum enhancement at 0.5 µL as compared to the CTAB/PABACPE. The electrochemical oxidation enhancement evidence of dopamine at different volume of the surfactant/PABACPE is as shown in the figure-5b.

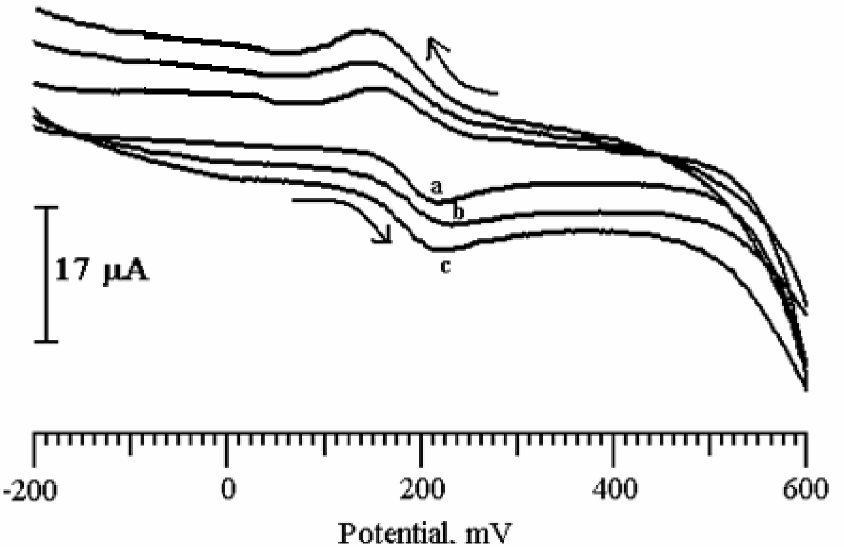

Figure 6a. Cyclic voltammagram of dopamine at (a= PABA/CPE , b=CTAB/PABACPE, c=SDS/PABACPE) at 100 mV/s in 0.1 M acetate buffer solution.

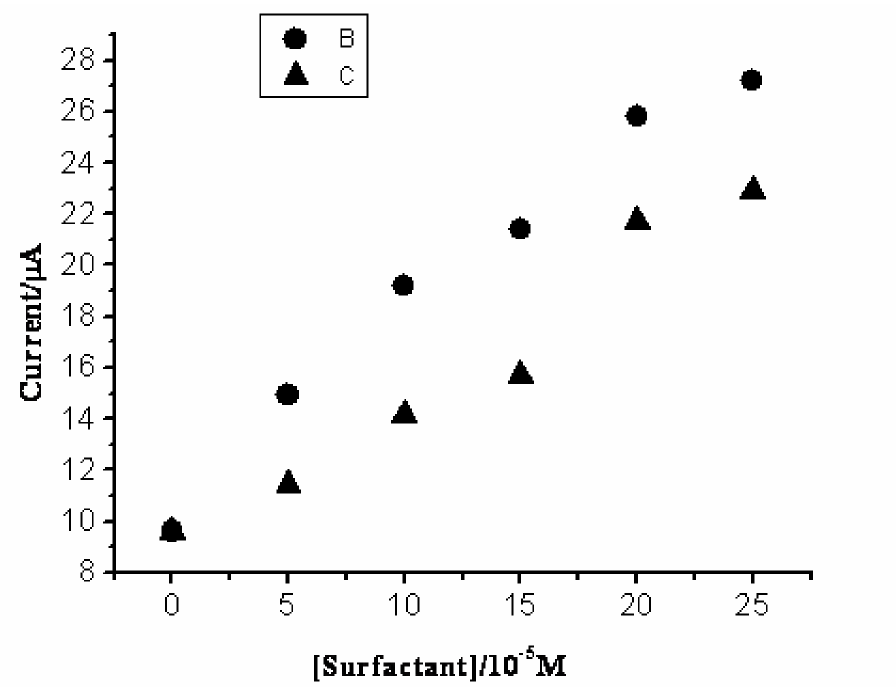

Figure 6b. Graph of dopamine for surfactant (B= SDS/PABACPE, C= CTAB/PABACPE).

4. CONCLUSIONS

A modified PABA/CPE study reveals that 6 mg p-amino benzoic acid in carbon paste electrode enhances the electrocatalytic activity of dopamine and potassium ferrocyanide. The effect of the surfactant showed that the anionic surfactant form monolayer on the PABA/CPE have made better sensor for the detection of dopamine.

References

1. R.M Whiteman, L.J.May and A.C.Michael. *Anal Chem* 60 (1988) 769
2. T.E Smith and T.M.Devlin : Textbook of Biochemistry with Clinical Corelations.Wily Liss,NY(1992)
3. J.R. Cooper, F.E. Bloom and R.H. Roth: The Biochemical Basis of Neuropharmacology. Oxford Univer. Press, Oxford, UK (1982)
4. P. Damier, E.C. Hirsch, Y.agid and A.M.Graybiel: The substantia nigra of the human brain : II. Patterns of loss of dopamine-containing neurons in parkinson's disease. Brain 122, (1999) 1437
5. J.W Mo and B.Ogorevc. *Anal Chem* 73 (2001) 1196
6. S.Sarre, Y.Michotte, P. Herregodts, D. Deleu, N.D.Klippel and G. Ebinger. *J Chromatogr* 575 (2000) 207
7. L.Guan, Ouyang, Q. L.Li, B.H.Liu and W.R.G.Baeyens: *Talanta* 50 (2000) 1197
8. Salem, F. B. *Talanta* 34 (1987). 810
9. R. N Adames, *Anal Shem* 48 (1976) 1128
10. F Gonon , M.Buda and J.F.Pujol, C.A Marsden, Wiley, *Chichester* 153 (1984)
11. E. A Budygin, M. R. Kilpatrick, R. R. Gainetdinov and R. M. Wightman. *Neuroscience Letters* 281 (2000) 9
12. P. A Garris, J. R.C. Christensen, G.V. Rebee and R. M. Wightman. *J Neurochem* 69 (1997) 152
13. Q.D.Walker, M.B.Rooney, R.M.Wightman and C. M. Kuhn. *Neuroscience* 4 (2000) 1061
14. P.A. Garris, M. Kilpatrick, M.A. Bunin, D. Michael, Q.D. Walker and R.M. Wightman. *Nature* 398 (1999) 67
15. T.M. Olefirowicz and A.G. Ewing. *Anal Chem* 62 (1990) 1872
16. S. D Gilman and A.G. Ewing. *Anal Chem* 67 (1995) 58
17. R.D Swanek, G. Y. Chen and A. G. Ewing. *Anal Chem* 68 (1996) 3912
18. T. Zetterstrom , T. Sharp, C. A. Marsden and U. Ungerstedt. *J Neurochem* 41 (1983) 1769
19. C. R Raj, K. Tokuda and T. Ohsaka. *Bioelectrochemistry* 53 (2001) 183
20. H. T Xu, F. Kitaamura, T. Ohsaka and Tokuda. *Elecrochemistry* 60 (1992) 1068
21. A.Dalmia, C.C. Liu and R.F. Savinell.*J Electroanal Chem* 430 (1997) 205
22. A. J Downnard, A.D. Roddisk and A.M.Bond. *Anal Chim Acta* 317 (1995) 303
23. M.Pandurangachar, B. E.Kumara Swamy, Umesh Chandra, Ongera Gilbert, Sherigara.B.S. *Int. J. Electrochem. Sci.*, 4 (2009) 672
24. M. Panduranga Char, E. Niranjana, B.E. Kumara Swamy, B.S. Sherigara, K.Vasantakumar Pai. *Int. J. Electrochem. Sci.*, 3 (2008) 588
25. E. Niranjana, B.E. Kumara Swamy, R. Raghavendra Naik, B.S. Sherigara, H. Jayadevappa. *J.Electroanal.Chem* 631 (2009) 129
26. B.N.Chandrashekar, B.E.Kumara Swamy, K.R.Vishnu Mahesh, Umesh Chandra B.S.Sherigara, *Int. J. Electrochem. Sci.*, 4 (2009) 471
27. Ongera Gilbert, Umesh Chandra, B.E.Kumara Swamy, M.Panduranga Char, C.Nagaraj B.S.Sherigara., *Int. J. Electrochem. Sci.*, 3 (2008) 1186

28. Allan J Bard and L.R.Faulkner, Electrochemical methods and its application, (John wiley, New York) Reprinted Edition 2005
29. M.Noel and K.I.Vasu, Cyclic Voltammetry and the frontiers of electrochemistry (oxford and IBH published in New- Delhi),174 1990