Int. J. Electrochem. Sci., 5 **(2010)** 1187 - 1202

International Journal of
ELECTROCHEMICAL
SCIENCE
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Electrochemical Investigations of Potassium Ferricyanide and Dopamine by 1-butyl-4-methylpyridinium tetrafluoro borate Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

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Received: 1 July 2010 / *Accepted:* 15 July 2010 / *Published:* 10 August 2010

A carbon paste electrode (CPE) modified by 1- butyl 4- methylpyridinium tetrafluoro borate (BMPTB) was used for the detection of $K_3Fe(CN)_6$ and dopamine. Cyclic voltammetric technique demonstrated highly improved response of $K_3Fe(CN)_6$ and dopamine at BMPTB /CPE compared to bare CPE with different shape of cyclic voltammorams. The effect of BMPTB concentration on the electrode quality also reveals that BMPTB formed on a CPE surface with a high density of negative charged end directed outside the electrode. The detection limit for modified electrode for $K_3Fe(CN)_6$ is 1×10^{-4} M and dopamine 1×10^{-5} M.

Keywords: Carbon paste electrode, 1- butyl 4- methylpyridinium tetrafluoro borate ionic liquid, Dopamine, Cyclic voltammetry.

1. INTRODUCTION

Potassium ferricyanide is used as an oxidizing agent to remove silver from negatives and positives, a process called dot etching. In color photograph, potassium ferricyanide is used to reduce the size of color dots without reducing their number, as a kind of manual color correction. Potassium ferricyanide is the chemical compound with the formula $K_3Fe(CN)_6$. This bright red salt consists of the coordination compound $[Fe(CN)_6]$. It is soluble in water and its solution show some green yellow fluorescence. Potassium ferricyanide is often used in physiological experiments as a means of increasing a solutions redox potential (E^o 436 mV at pH 7) [1,2]. Hu et al. [3,4] studied potassium ferricyanide as a standard for modified cetyl trimethyl ammonium bromide carbon paste electrode.

Dopamine is a neurotransmitter associated with proper functioning of several organs such as the heart, brain, and suprarenal glands. The determination of dopamine is a subject of great significance for investigating its physiological functions and diagnosing nervous diseases resulting from dopamine abnormal metabolism, such as epilepsy, Parkinsonism and senile dementia [5]. The fact compound makes their detection possible by electrochemical methods based on anodic oxidation [6]. Dopamine has been determined using various electrochemical methods [7-9].

Recently room temperature ionic liquid [RTIL] has been used as a new kind of modifier for a chemically modified electrode. RTIL are composed entirely of ions and exist as a liquid at room temperature with the characteristics of negligible vapour pressure and good solubility and chemically stability.

As a new green media, RTIL have many unique electrochemical properties, such as higher ionic conductivity and wider electrochemical windows [10-12]. Rozniecka et al [13, 14] and Shul et al. [15] studied the ion transfer process occurring across the interface of RTIL and an aqueous solution with different working electrodes as the supports for the RTIL phase.

Zhao et al [16] investigated the direct electrochemistry of an enzyme in a RTIL/ carbon nanomaterials composite film modified electrode. Lu et al. [17] applied the RTIL/Chitosan composite film for the direct electrochemistry and electrocatalysis of Horseradish peroxides and haemoglobin. The RTIL film modified electrode was also use for determination of uric acid, chloropromazine, nitric oxides etc [18-20]. Zhao et al. [21] prepared a RTIL/carbon nanotube film modified electrode for the voltammetric determination of dopamine in the presence of uric acid and ascorbic acid. RTIL have also been used as a new kind of binder for the preparation of carbon paste electrode since RTIL have high viscosity and ionic conductivity, the ionic liquid modified carbon paste electrode shows an excellent chemical behavior.

Maliki et al [22] fabricated octylpytridiniumhexafluorophosphate modified carbon paste electrode which provides a remarkable increase in the rate of electron transfer and decrease in the over potential of some organic substances. Sun et al. [23] fabricated 1-butyl-3-methylimidazoliumhexafluro phosphate modified CPE and studied the direct electrochemistry of hemoglobin immobilized in sodium alginate hydra gel on the surface of an ionic liquid CPE.

Wei Sun et al [24] fabricated ionic liquid modified CPE using ionic liquid 1- butyl 4-methylpyridinium tetrafluoro borate and study the electrocatalytic activity of dopamine at an ionic liquid modified carbon paste electrode and its analytical application. In this paper Ionic liquid 1-butyl -4-methylpyridinium tetrafluoroborate modified carbon paste electrode was fabricated and characterized potassium ferricyanide and dopamine by cyclic voltammetric technique and established good approach to determine the importance of neurotransmitter dopamine sensitivity and it acts as sensor.

Our group has been working in the field of modified carbon paste electrode in the detection of neurotransmitters by cyclic voltammetric technique [25-29].

2. EXPERIMENTAL PART.

2.1. Reagents and chemicals

Potassium ferricyanide $K_3Fe(CN)_6$, dopamine, KCl, 1-butyl-4-methylpyridinium tetrafluoroborate and perchloric acid, sodium dihydrogen phosphate and disodium hydrogen phosphate used were of analytical grade quality from sd. Fine chemicals. Dopamine stock solutions (10 mM) were prepared by adding dopamine in 0.1 M perchloric acid, 10mM potassium ferricyanide was prepared by dissolving in double distilled water.

2.2. Apparatus and procedure

Cyclic voltammetry (CV) was performed on Model 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 (3.0 mm in diameter), a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The BMPTB 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 BMPTB modified carbon paste electrode. Similarly bare carbon paste is prepared without modifier. The carbon paste was then packed into the cavity of a homemade carbon paste electrode and smoothened on a weighing paper

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical response of $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode.

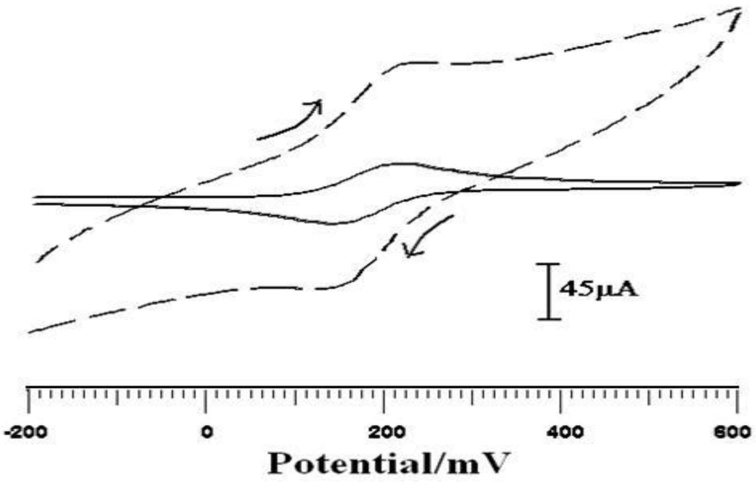

Figure 1. Cyclic voltammograms of 1 mM $K_3Fe(CN)_6$ (solid line) at bare carbon paste electrode and (dashed line) at BMPTB modified carbon paste electrode. Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

Fig. 1 shows the electrochemical response of $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode. Owing to the complex properties and the roughness of the electrode surface, the cyclic voltammogram of $K_3Fe(CN)_6$ at bare carbon paste electrode (solid line) is low current signal [ΔEp for bare carbon paste electrode is 69 mV]. However, the voltammetric response is apparently improved at BMPTB modified carbon paste electrode, reflected by the enlargement of the peak currents (i_p) and the decline of the potential difference [ΔEp for BMPTB modified carbon paste electrode is 65 mV] between the reduction and the oxidation peaks curve (dashed line). The enhancement shows the strange cyclic voltammograms by the addition of BMPTB at carbon paste electrode.

3.2. Improvement of the electrode quality of CPE with the modification of BMPTB Ionic liquid

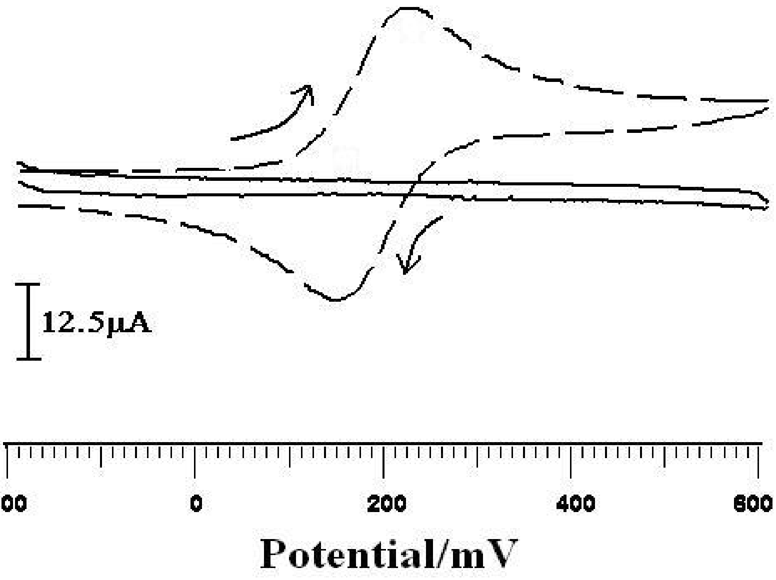

Figure 2a. Cyclic voltammograms at bare carbon paste electrode with 1 mM $K_3Fe(CN)_6$ (dashed line) and without ferricyanide (solid line). Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

Fig.2a and 2b shows the voltammogram of $K_3Fe(CN)_6$, no peaks are observed at both bare cpe and BMPTB/CPE [solid line] in the 1 M KCl supporting electrolyte without analyte. The background current is greatly increased at BMPTB/CPE compared with that at bare cpe (more than 20 times). This indicates that the surface property of the modified electrode has been significantly changed. In contrast to the low current signal response at bare cpe [Fig.2a, dashed line]. The electrochemical response signal of $K_3Fe(CN)_6$ is significantly enhanced at BMPTB/CPE [Fig.2b, dashed line] which reflects the improvement of both the shape of redox peak and the magnitude of the peak current i_p.

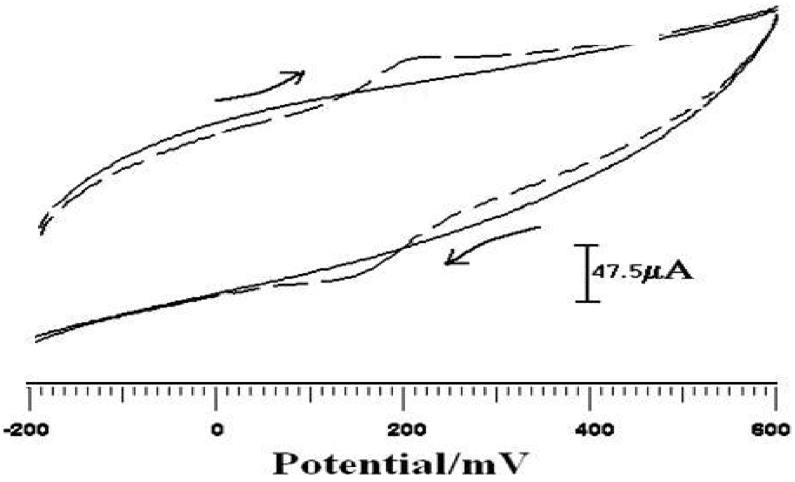

Figure 2b. Cyclic voltammograms at BMPTB modified carbon paste electrode with 1 mM $K_3Fe(CN)_6$ (dashed line) and without ferricyanide (solid line). Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

3.3. Effect of concentration

The CV shows successive enhancement of peak current on increasing $K_3Fe(CN)_6$ concentration [Fig.3a]. The plot of anodic peak current versus the respective concentration of $K_3Fe(CN)_6$ was found to be linear in the range 0.5–3.0 mM, increasing concentration of $K_3Fe(CN)_6$ there is a linear enhancement in i_{pa}. Figure 3b shows graphical interdependent between the concentration and the oxidation of $K_3Fe(CN)_6$ on BMPTB/CPE [30-32, 25].

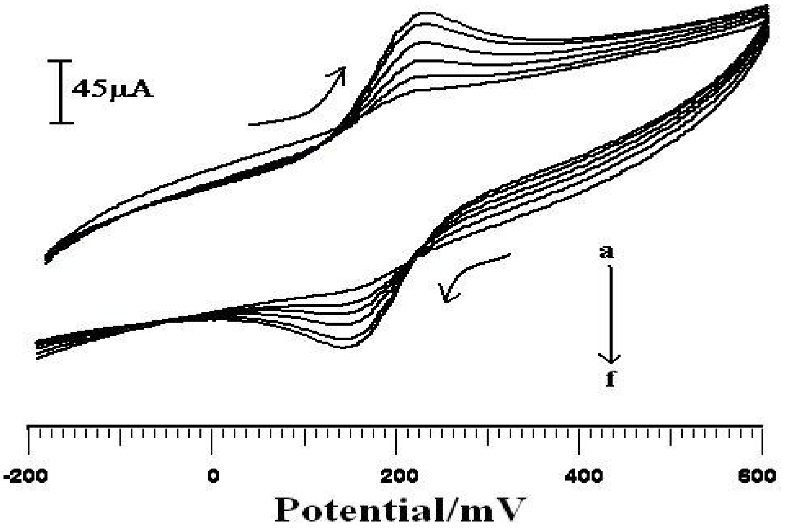

Figure 3a. Effect of concentration variation (CV) of $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode [a = 0.5, b = 1.0, c = 1.5, d = 2.0, e =2.5, f=3.0 mM]. Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

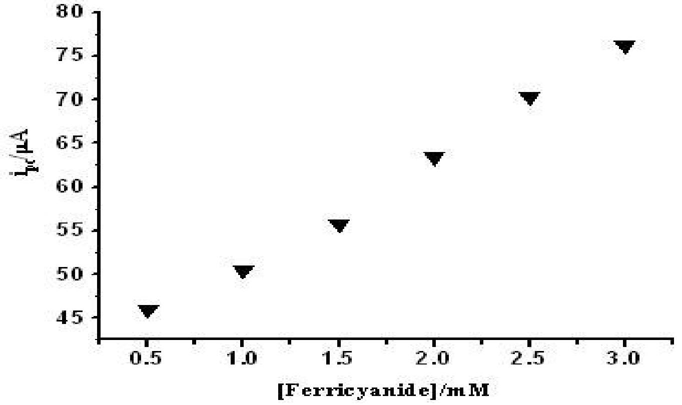

Figure 3b. Effect of concentration variation of $K_3Fe(CN)_6$ at BMPT modified carbon paste electrode. Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

3.4. Effect of scan rate

The linear dependence of reduction peak current on the scan rate showed that the process was diffusion-controlled [Fig. 4a]. The proposed behaviour of $K_3Fe(CN)_6$ at a carbon paste electrode in the presence of BMPTB might arise from the diffusion of BMPTB at the electrode surface and the interaction between BMPTB and $K_3Fe(CN)_6$. The scan rate dependence cyclic voltammetric response of BMPTB for $K_3Fe(CN)_6$ was shown in the Figure.4b. The relationship between square root of scan rate and anodic peak current is a good linearity and it is in the range of 50-350 mV/s. The electrochemical property was diffusion controlled since co-relation constant was found 0.99962 [30-32,25].

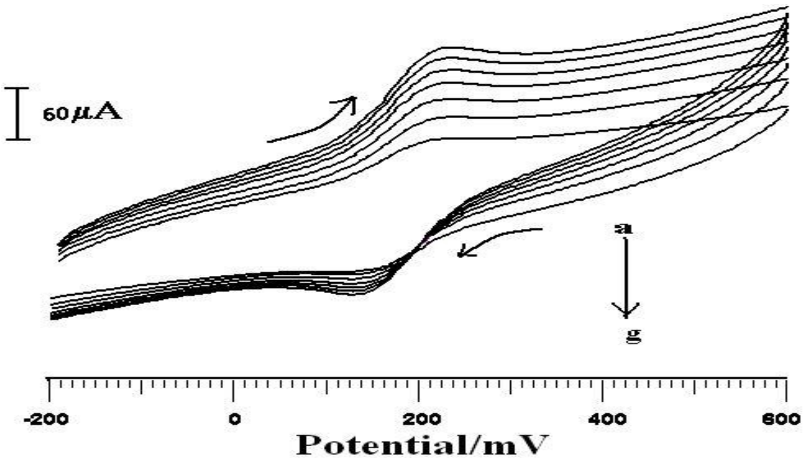

Figure 4a. Effect of scan rate variation (CV) of 1 mM $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode [a = 50, b = 100, c = 150, d = 200, e = 250,f=300,g=350 mV]. Supporting electrolyte 1 M KCl

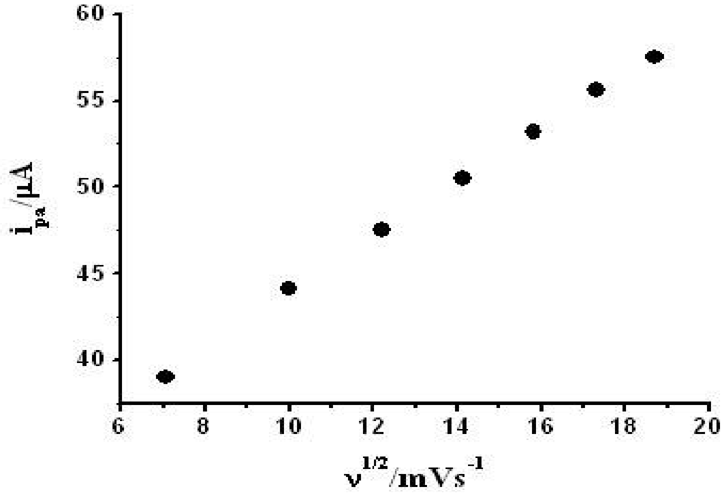

Figure 4b. Effect of scan rate variation of 1 mM $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode. Supporting electrolyte 1 M KCl

3.5. Effect of BMPTB on peak current and peak potential

Fig. 5a and 5b shows the effect of BMPTB concentration on the peak current and peak potential of 1.0×10^{-3} M $K_3Fe(CN)_6$. When the concentration of BMPTB was increased from 1.25- 10 µL the cathodic peak current increases upto 5 µL and then decreases after increasing the concentration. In case of cathodic peak potential, when the concentration of BMPTB was higher than the 1.25µL Epc decreases rapidly with increase of BMPTB concentration. However, the cathodic peak potentials of $K_3Fe(CN)_6$ apparently decreases in the range of 1.25 – 10 µL. It indicates the accumulation ability of BMPTB/CPE to $K_3Fe(CN)_6$ has a direct proportion with BMPTB absorbance on electrode surface. Thus, the CPE was modified by 1.25µL BMPTB.

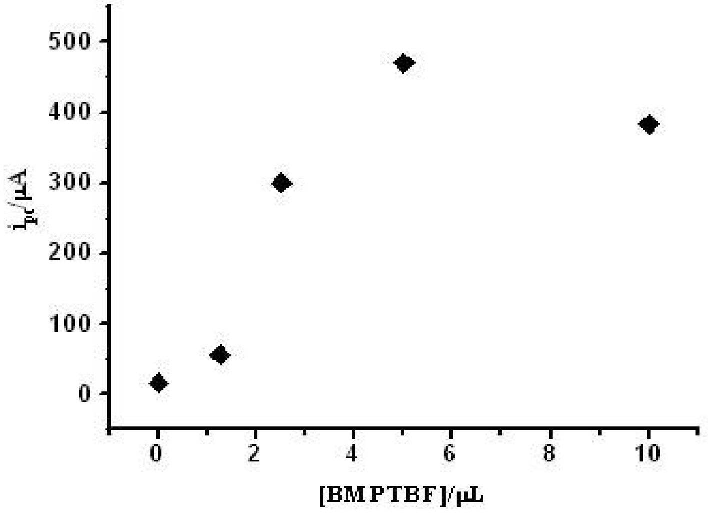

Figure 5a. Effect of modifier concentration on peak current for 1 mM $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode. Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

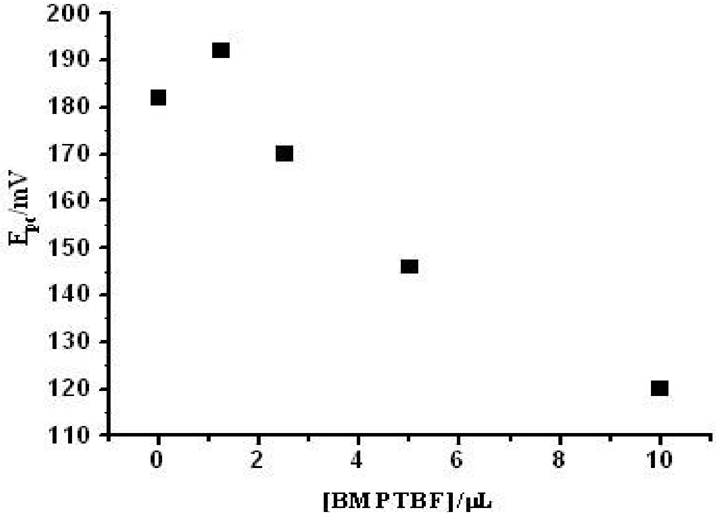

Figure 5b. Effect of modifier concentration on peak potential for 1 mM $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode. Supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

3.6. Effect of BMPTB concentration on peak potential difference (ΔEp)

As the concentration of BMPTB increases the peak potential difference goes on increasing from 1.25 μL to 10 μL BMPTB and then the potential difference increases as the concentration of BMPTB increases as shown in Fig. 6. For all other voltammetric investigations 1.25 μL BMPTB was chosen as modifier concentration for the further studies.

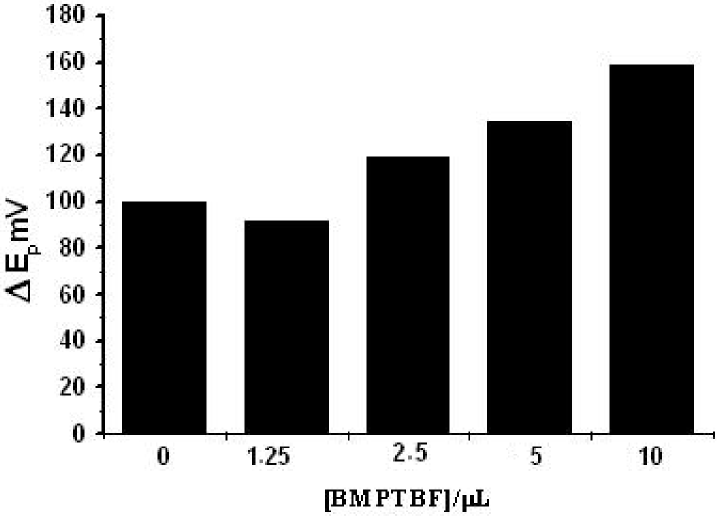

Figure 6. Effect of peak potential difference for 1 mM $K_3Fe(CN)_6$ at BMPTB modified carbon paste electrode supporting electrolyte 1 M KCl at scan rate 100 mV s^{-1}

3.7. Detection ability of BMPTB Modified CPE

Detection limit is determined by using different concentration of potassium ferricyanide solution in 1 M KCl supporting electrolyte is shown. It is observed that detection limit of potassium ferricyanide is 1×10^{-4} at BPPTB/CPE.

3.8. Electrochemical response of dopamine at BMPTB modified carbon paste electrode

Fig. 7 shows the electrochemical response of dopamine at BMPTB modified carbon paste electrode. The cyclic voltammogram of dopamine at bare carbon paste electrode is low current signal (solid line). However, the voltammetric response is apparently improved at BMPTB modified carbon paste electrode, reflected by the enlargement of the peak currents (ip) and the peak potential difference (ΔEp) between the reduction and the oxidation peaks curve (dashed line). The anodic peak current enhancement shows the different cyclic voltammogram which is the characteristic of BMPTB ionic liquid at carbon paste electrode.

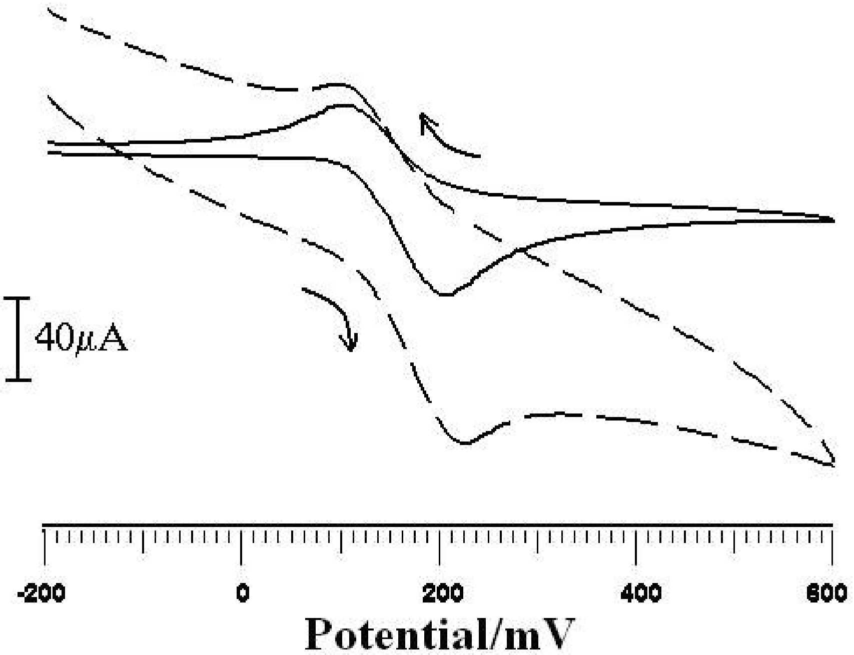

Figure 7. Cyclic voltammograms of 1 mM dopamine (solid line) at bare carbon paste electrode and (dashed line) at BMPTB modified carbon paste electrode. Supporting electrolyte 0.1 M phosphate buffer at scan rate 100 mVs^{-1}

3.9. Improvement of the electrode quality of CPE with the modification of BMPTB

Fig8a and 8b shows the voltammogram of dopamine. No peaks are observed at both bare cpe and BMPTB/CPE [solid line] in the 0.1 M phosphate buffer solution with absence of analyte. The background current is greatly enhanced at BMPTB/CPE compared with that at bare cpe [more than 20 times]. This indicates that the surface property of the modifier of the electrode has been significantly changed. In contrast to the poor signal current response at bare cpe [Fig.8a dashed line], the electrochemical response signal current of dopamine is enhanced at BMPTB/CPE [Fig.8b dashed line] which reflects the improvement of both the shape of the redox peak and magnitude of peak current signal i_p.

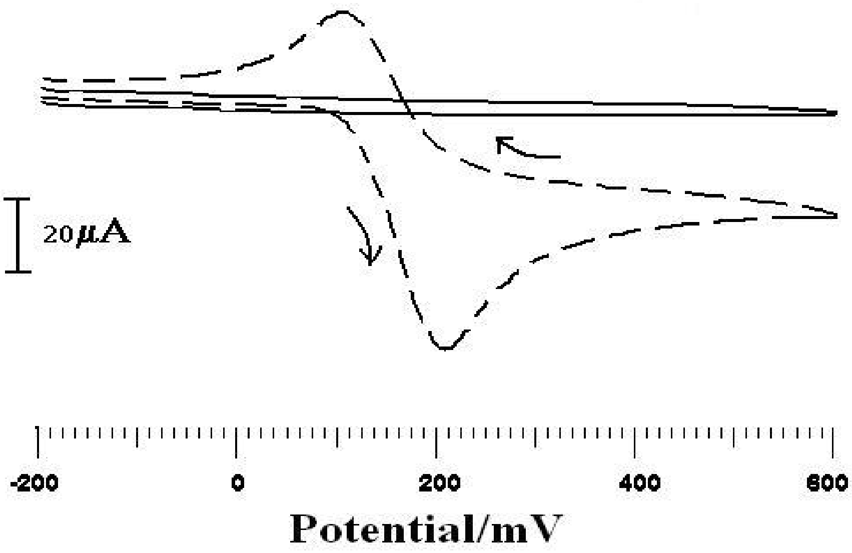

Figure 8a.Cyclic voltammograms at bare carbon paste electrode with dopamine (dashed line) and without dopamine (solid line). Supporting electrolyte 0.1 M phosphate buffer at scan rate 100mVs^{-1}

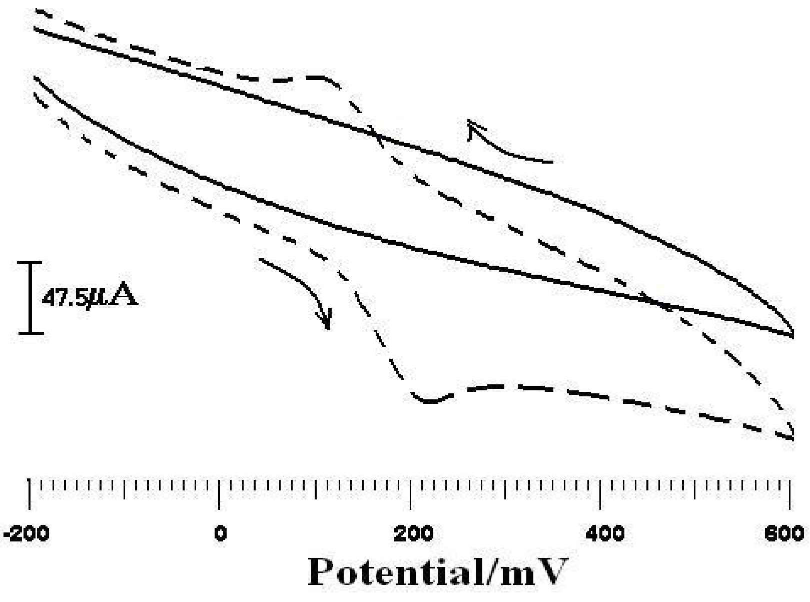

Figure 8b. Cyclic voltammograms at BMPTB/CPE with dopamine (dashed line) and without dopamine (solid line). Supporting electrolyte 0.1 M phosphate buffer at scan rate 10 mVs^{-1}

3.10. Effect of concentration for dopamine

As the concentration of dopamine was varied from 1.0 to 4.0 mM and cyclic voltammograms were found to increase in the anodic peak current as shown in Fig. 9a. The anodic peak current obtained were found to increase linearly with increase in concentration of dopamine is shown in Fig. 9b [30-32, 25].

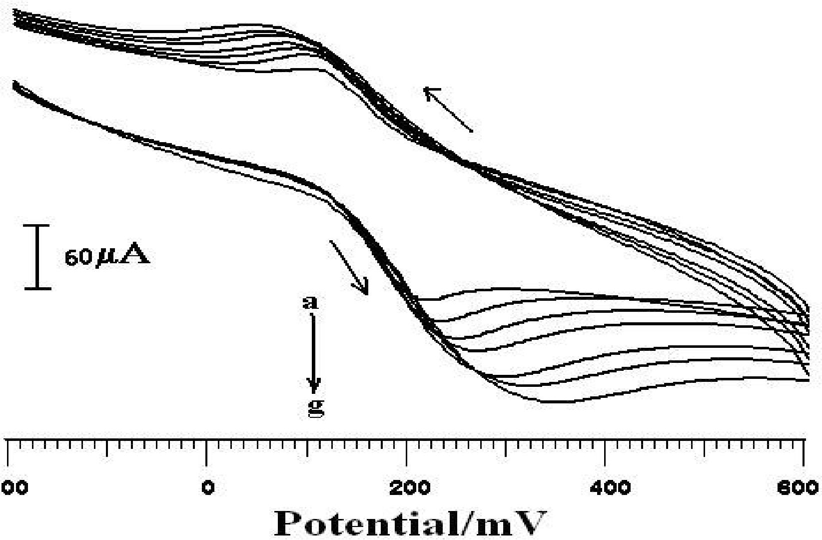

Figure 9a. Effect of concentration variation (CV) of dopamine at BMPTB modified carbon paste electrode [a = 1.0, b = 1.5, c = 2.0, d = 2.5, e = 3.0, f=3.5, g=4.0 mM]. Supporting electrolyte 0.1 M phosphate buffer at scan rate 100 mVs^{-1}

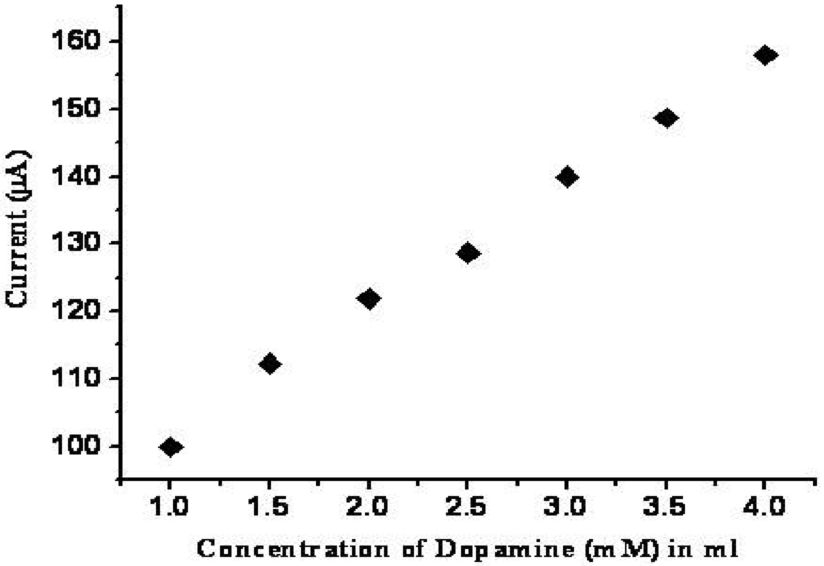

Figure 9b. Effect of concentration variation of dopamine at BMPTB modified carbon paste electrode. Supporting electrolyte 0.1 M phosphate buffer at scan rate 100 mVs^{-1}

3.11. Effect of scan rate

Fig.10a shows the cyclic voltammograms of 1 mM dopamine on BMPTB/CPE at different scan rate, with the increase of scan rate the peak currents increased linearly. Fig. 10b shows the relationship of square root of scan rate and anodic peak current of dopamine for the range of 50- 400 mV/s shows the good linearity. The electrochemical behavior was diffusion controlled for dopamine at modified BMPTB since linear co-relation constant was found 0.99932 [30-32,25].

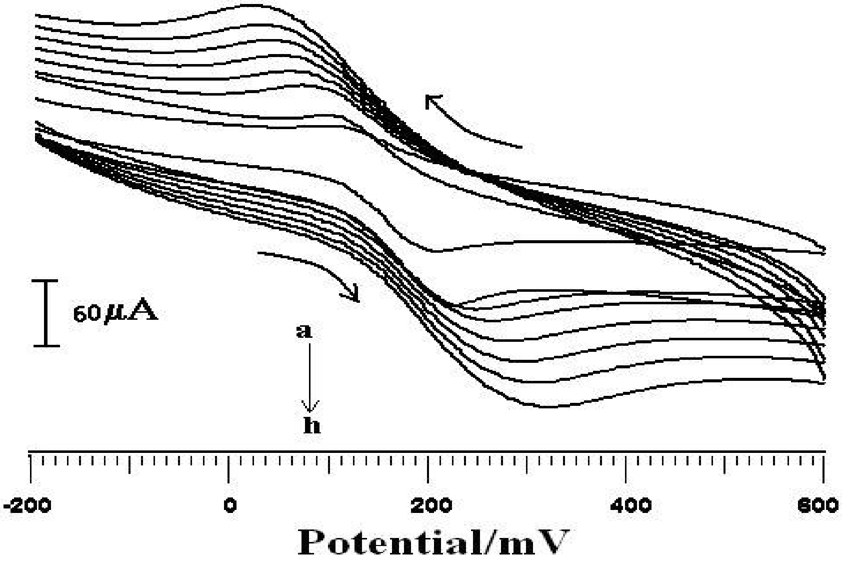

Figure 10a. Effect of scan rate variation (CV) of 1 mM dopamine at BMPTB modified carbon paste electrode [a = 50, b = 100, c =150, d = 200, e = 250, f = 300, g =350, h = 400 mV]. Supporting electrolyte 0.1 M phosphate buffer

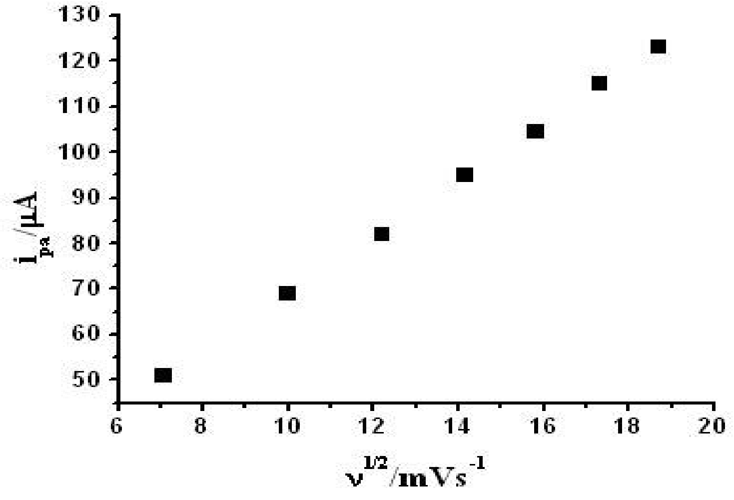

Figure 10b. Effect of scan rate variation of 1 mM dopamine dopamine at BMPTB modified carbon paste electrode. Supporting electrolyte 0.1 M phosphate buffer

3.12. Effect of BMPTB on peak current and peak potential

Fig. 11a and 11b shows the effect of BMPTB concentration on the peak current and peak potential of 1.0 × 10^{-3} M dopamine. When the BMPTB concentration was higher than the 1.25 μL at room temperature both ipa and Epa increases rapidly with increase of BMPTB concentration. However, the signals of dopamine apparently increased in the range of 1.25 to 10 μL

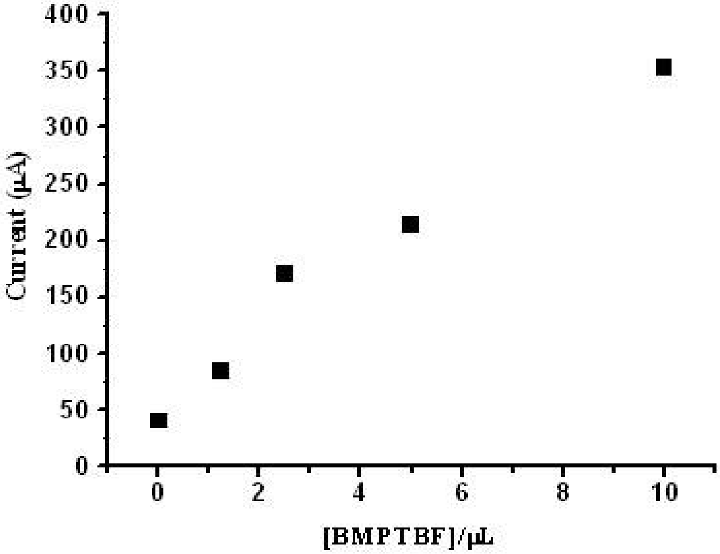

Figure 11a. Effect of modifier concentration on peak current for 1 mM dopamine at BMPTB modified carbon paste electrode supporting electrolyte 0.1 M phosphate buffer at scan rate 100 mV s^{-1}

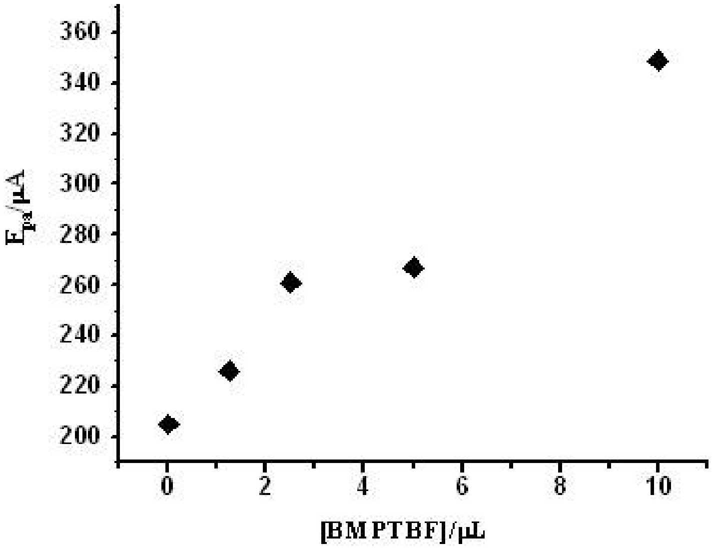

Figure 11b. Effect of modifier concentration on peak potential for 1 mM dopamine at BMPTB modified carbon paste electrode in 0.1 M phosphate buffer at scan rate 100 mV s^{-1}

3.13. Effect of BMPTB concentration on peak potential difference (ΔEp)

As the concentration of BMPTB increases the peak potential difference goes on increasing from 100 to 300 mV for 1.25 to 10 µL BMPTB and then there is increase in the ΔEp as shown in Fig. 12.

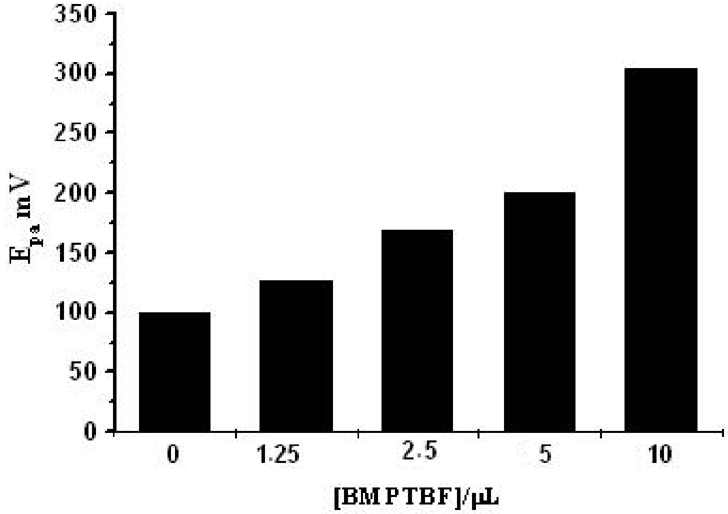

Figure 12. Effect of peak potential difference for 1 mM dopamine at BMPTB modified carbon paste electrode in 0.1 M phosphate buffer at scan rate 100 mV s^{-1}

3.14. Detection limit of BMPTB /CPE

Cyclic voltammograms in 0.1 M phosphate buffer of BMPTB/CPE in a series of dilute dopamine solutions at BMPTB /CPE no apparent peaks were appeared in 1× 10^{-5} M dopamine. This suggests the strong detection limit is upto 1×10^{-5}M dopamine at BMPTB /CPE modified electrode.

4. CONCLUSION.

From the CV data's modified BMPTB electrode shows quasi-reversible to reversible nature for both potassium ferricyanide and dopamine with the enhancement in current signal with different shape of cyclic volatmmograms. This modified electrode shows high sensitivity, selectivity, and low detection limit together with very easy preparation and surface regeneration of the modified electrode.

The reproducibility of the CV response makes the prepared modified system very useful in the construction of simple devices for potassium ferricyanide and dopamine. The application of this electrode creates a new approach to determine the importance neurotransmitter dopamine sensitivity and it acts as good sensor.

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