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Selective detection of dopamine using a functionalised polyaniline composite electrode

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Abstract

The behaviour of a poly (aniline boronic acid) (PABA) modified glassy carbon electrode (GCE) for the detection of dopamine (DA) in the presence of excess of ascorbic acid (AA) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques is investigated. On bare GCE, both DA and AA are oxidized at ~0.16 V, whereas on PABA modified GCE they are oxidized at 0.2 and 0.054 V, respectively. Though PABA favours DA oxidation through ester formation with boronic acid motif, the AA oxidation is also promoted by polyaniline backbone through the involvement of AA in the redox of polyaniline. Since both DA and AA undergo oxidation at closely spaced potentials at a PABA electrode, Nafion®-incorporation into the PABA film was examined for selective determination of DA in the presence of AA. The selectivity was due to accumulation of DA on the electrode surface through ester formation with the boronic acid group and suppression of AA oxidative current through charge discrimination by Nafion.

1. Introduction

Identification and determination of catecholamine neurotransmitters electrochemically has been a subject of interest over the past few decades [1, 2]. Dopamine (DA) is an important neurotransmitter in mammalian central nervous systems [3] and its deficit results in brain disorders such as Parkinson's disease [4] and Schizophrenia [5]. Determination of DA electrochemically by direct oxidation at conventional electrodes is difficult because of (i) fouling of the electrode surface due to sticking of oxidation products [6], (ii) interference due to the co-oxidation of ascorbic acid (AA) present in biological fluids in the same potential window [7], (iii) concentration of AA is relatively higher than that of DA in biological samples (10^3 times higher than DA) giving poor selectivity and sensitivity [8]. Hence, the detection of DA in the presence of AA is a challenge in electroanalytical research. Various attempts based on polymer modified electrodes, pretreated electrodes, carbon fiber electrodes and self-assembled monolayers have been reported to overcome the limitations and achieve reliable estimation of DA [9–14]. However, these methods have their own limitations from the practical point of view. Among the various approaches, polymer-modified electrodes offer several advantages in terms of ease of preparation of stable and adherent films and the possibility of manipulating selectivity and sensitivity through incorporation of functional groups.

Among the electronically conducting polymers, polyanilines are the preferred electrode modifiers for chemical sensor applications because of their low cost, ready film-forming ability, chemical and electrochemical stability and scope for incorporation of functional groups [15]. It is well known that while polyaniline favours catalytic oxidation of AA [16, 17] and its sensing, it is silent towards DA. Hence, it is challenging to induce dopamine-sensitivity of polyaniline. This can be achieved by modification of the polymer backbone with suitable functional groups reactive towards DA.

Recently, there has been a great deal of interest in using boronic acid functionalized polyaniline modified electrodes for sensing applications [18, 19]. The boronic acid moiety is used as the recognition *motif* because of its high affinity towards diol-containing compounds and its strong interaction through reversible ester formation. Such strong binding allows boronic acids to be used as the recognition moiety in the construction of sensors for saccharides [20]. Strawbridge et al. [21] reported that boronate esters formed through the reaction of the diol compounds with phenyl boronic acids are electrochemically oxidized at potentials more positive than that necessary to oxidize the diol compound. However, addition of such free compounds (i.e., phenylboronic acid) leads to incompatibility of the solution medium with the physiological conditions. And hence, a polymeric sensing film with a boronic acid group can be an ideal choice to suit the physiological application.

Though the poly (aniline boronic acid) (PABA) conducting polymer has been reported as a sensing matrix for various analytes, it is found from literature that PABA modified electrodes have not been reported for the voltammetric sensing of DA in neutral PBS solution.

In the present paper, we report the results of studies on the electrodeposition of PABA films and voltammetric measurements on the oxidation of DA in presence of AA.

2. Experimental details

2.1. *Materials*

Aniline boronic acid (ABA)/3-Amino phenyl boronic acid monohydrate (98%) used as the monomer in the electropolymerisation and Nafion solution perfluorinated ion-exchange resin, (5 wt% lower aliphatic alcohol and 45% water) were purchased from Aldrich. DA (ACROS), AA (Merck), potassium dihydrogen phosphate, sodium hydroxide and sodium fluoride were used as received. Phosphate buffer solution (PBS 7.4) of pH 7.4 was prepared by mixing KH_2PO_4 and NaOH. All other reagents were of analar grade and were used as received. All solutions were prepared with water purified by a Milli-Q system (Millipore).

2.2. *Electrochemical measurements*

In the electrochemical experiments, a GC electrode (ϕ 1.5 mm, Cypress Systems, Inc.) and platinum foil were used as the working and auxiliary electrodes respectively, in a standard three-electrode configuration. A saturated calomel electrode (SCE) was used as the reference electrode and the potential values are reported against the SCE. All the electrochemical experiments were carried out using a Potentiostat-Galvanostat Autolab PGSTAT-30 (Eco-Chemie B.V., The Netherlands) at ambient temperature (25 ± 1 °C). To record differential pulse voltammograms (DPV), the following input parameters were used: scan rate 30 mV s^{-1}, sample width 17 ms, pulse amplitude 50 mV, pulse width (modulation time) 50 ms, pulse period (interval) 200 ms and quiet time 2 s. Peak currents were determined either after subtraction of a manually added baseline or as absolute peak heights above zero. Electrochemical impedance spectral (EIS) characteristics of the polymer film were measured using Solartron system (Electrochemical Interface SI 1287 + Impedance/Gain-Phase analyser SI 1260) in a frequency range of 0.1 MHz to 0.1 Hz.

2.3. *Fourier transform infrared spectroscopy (FT-IR)*

FT-IR spectra were recorded using FT-IR spectrometer (Thermo Nicolet Model 670) equipped with a DTGS detector. The infrared absorption spectrum was obtained by depositing the PABA/PABA-Nafion film on ITO glass employed as working electrode. The ABA monomer spectrum was measured in absorbance mode, in which the solid ABA was mixed with KBr and the KBr pellet was used for analysis. All spectra were collected for 256 interferrograms at a resolution of 4 cm^{-1}.

2.4. *Preparation of PABA film coated electrodes*

The GC electrode surface was polished first on fine emery paper (4/0 & 5/0) and then with 1.0 and 0.06 μm alumina powder and finally sonicated with Milli-Q water for 5–6 min. Prior to the electropolymerisation, the polished electrode was electrochemically pretreated in PBS 7.4 by scanning the electrode potential repeatedly between −0.2 and 1.3 V at 10 V s^{-1} for 20 min. The electropolymerisation procedure/conditions are reported elsewhere [22] and briefly described as follows: 87 mg 3-amino phenyl boronic acid (0.04 M) and 105 mg sodium fluoride (0.2 M) were dissolved in 12.5 ml of 0.2 M HCl solution. Polymerisation was effected by keeping the GC electrode, in this monomer solution under unstirred conditions and the electrode potential was scanned between 0.0 and 1.1 V until the charge in the cathodic scan reached 10 mC cm^{-2}. A deep bluish-green film was obtained and it was washed with water. Then it was kept in a 0.1 M HCl solution and cycled between 0.0 and 0.8 V to ascertain the redox behaviour of the modified electrode ensuring a stable redox response. The modified electrode was then rinsed with water followed with PBS solution and used for the further electrochemical experiments.

For the preparation of PABA-Nafion composite film electrode, a few microliters of 5% Nafion ionomer solution in alphatic alcohols (Aldrich) were placed on the electrodeposited PABA film. However, the PABA film was found to be disturbed/dissolved by the alcohols in the Nafion solution, rendering the coating mechanical unstable. Hence, a different procedure was employed to prepare a mechanically stable PABA-Nafion composite film. This composite film was formed by electrodeposition from a solution containing 0.04 M 3-amino phenyl boronic acid and 0.20 M sodium fluoride in 0.2 M HCl solution containing 2 ml of Nafion solution (4 mM). The above solution mixture was vigorously stirred and the deposition was carried out under the stirred condition only.

3. Results and discussions

3.1. *PABA modification of GC electrode*

The electrochemical deposition of PABA on a GC electrode was carried out potentiodynamically. Figure 1 shows the cyclic voltammograms recorded during the electro-polymerization of 3-amino phenyl boronic acid (ABA) from a 0.2 M HCl solution in the presence of 200 mM sodium fluoride. ABA was readily oxidized in

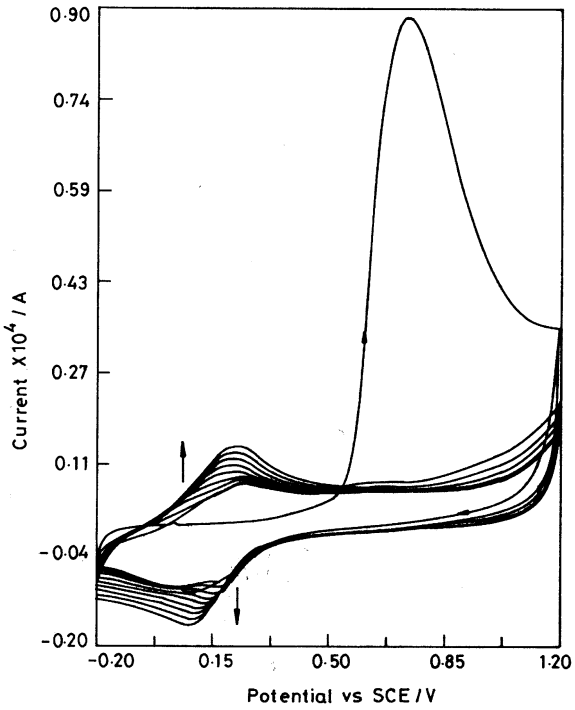


Fig. 1. Electropolymerisation of 3-amino phenyl boronic acid (40 mM) in 0.2 M HCl in presence of sodium fluoride (200 mM) on glassy electrode; scan rate = 100 mV s^{-1} (10 cycles).

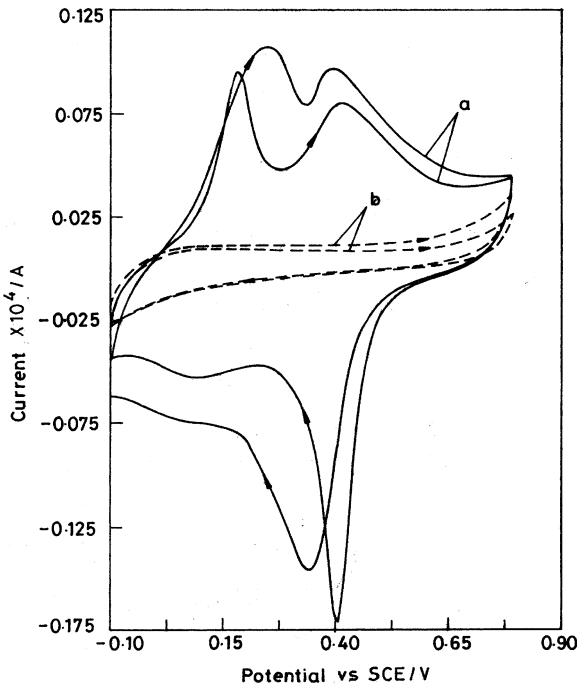


Fig. 2. Redox behaviour of PABA and PABA-Nafion modified electrode in (a) 0.2 M HCl (b) PBS 7.4 solutions.

the presence of fluoride at ~0.75 V and further potential cycling facilitates the growth of polymer film on the electrode surface [22, 23]. Similar features were observed when Nafion was co-deposited with the PABA deposition. The equilibrium reaction of boronic acid with fluoride is known to produce a tetrahedral anionic complex [23], which acts as the precursor for the fluoride-catalysed polymerization of APBA under acidic conditions [22].

Figure 2 shows the redox behaviour of PABA and PABA-Nafion modified GC electrodes in 0.2 M HCl solution. The cyclic voltammogram shows a response that consists of two sets of redox peaks at ~0.20 and 0.4 V similar to that of polyaniline, corresponding to leucoemeraldine/emeraldine and emeraldine/pernigraniline transformations. Incorporation of Nafion does not alter the redox activity of the PABA film. In PBS 7.4 solution, no redox peak was observed and hence the modified electrode provided an ideal potential window to investigate the electro-oxidation behaviour of DA and AA. The impedance spectrum of PABA film in a pH = 7.4 solution (Figure 3) shows a linear behaviour in the entire frequency range studied (0.1 MHz to 0.1 Hz). Nafion incorporated PABA film shows a semicircle in the high frequency range and a linear part in the low frequency range. A phase angle of 90° suggests that the Nafion incorporated PABA film is capacitive in nature.

Figure 4 shows the FTIR spectrum of the PABA and PABA-Nafion films together with the ABA monomer spectrum. The large descending baseline in the spectral region 4000–2000 cm^1 is attributed to free electron conduction in the doped polymer [24]. The absorption peak at 1260 cm^{-1} corresponds to the C–N stretching, the peak at 1123 cm^{-1} is due to the C–H *in plane* bending and that at 1260 cm^{-1} is related to the protonated C–N group. The characteristic peaks at 1489 and 1532 cm^{-1} are assigned to the C=C stretching modes of the benzenoid ring and quinonoid ring respectively. Both polymers present an absorption band at 827 cm^{-1}, characteristic of the C–H *out-of-plane* bending vibrations of 1,4-di-substituted benzene rings. In Nafion-incorporated PABA film, the peak at 1063 cm^{-1} corresponds to the $-SO_3^-$ group and the peaks at 1066 and 876 cm^{-1} correspond to the presence of vinyl fluoride group confirming the presence of Nafion in the polymer matrix.

3.2. *Oxidation of DA & AA at PABA/GC*

Figure 5a shows the cyclic voltammetric (CV) behaviour of DA at bare GC and PABA modified GC electrode respectively. It can be seen that at a bare GC electrode, the DA oxidation occurs at 0.156 V, whereas at a PABA-modified electrode it occurs at 0.208 V. It is also observed that the oxidation current significantly increases on the polymer-modified electrode. When compared to the response at the bare GC surface, the reversibility of DA oxidation becomes sluggish on the polymer surface. This suggests that there is considerable interaction between the polymer and DA or its oxidation products. AA oxidation (Figure 5b) shows a broad oxidation peak at 0.203 V at bare GC, and at 0.054 V on PABA modified electrode. An increase in oxidation current observed at the PABA modified electrode

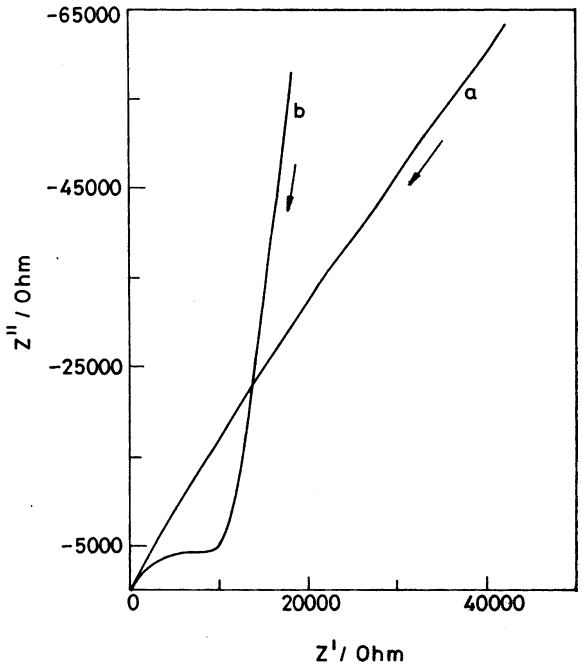


Fig. 3. Electrochemical impedance spectra of (a) PABA and (b) PABA-Nafion composite film in PBS 7.4 solution.

indicates the electrocatalytic character of the polymer. The peak potential for the oxidation of DA shifts in the positive direction (ca. ~50 mV), whereas for AA it is in the negative direction (ca. ~150 mV). Figure 5c shows the oxidation of DA and AA at PABA modified electrode in a solution containing both DA and AA.

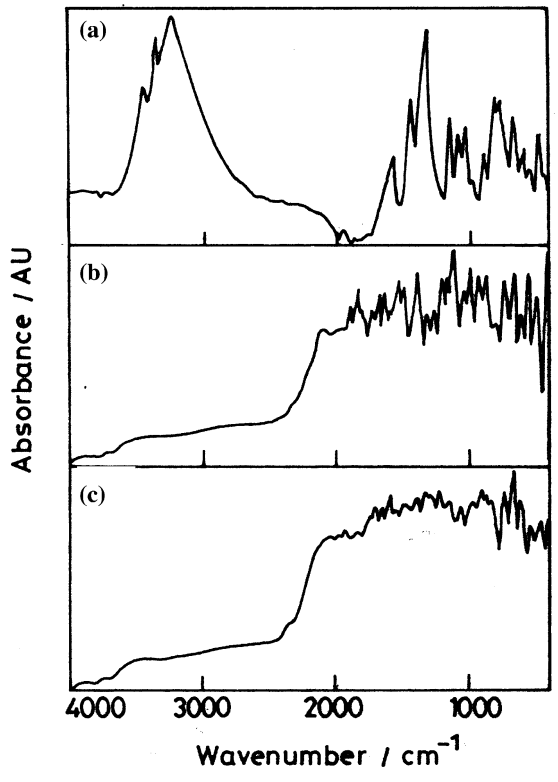


Fig. 4. FTIR spectra of (a) aniline boronic acid (ABA), (b) PABA & (c) PABA – Nafion composite films.

Both DA and AA oxidation peaks coalesce to yield a single broad oxidation peak. The causes for this behaviour are explained based on the interactions between (a) polyaniline matrix and AA; and (b) boronic acid and DA.

At neutral pH, DA exists as a cation with a positively charged amino group (pK_a 8.9) and AA exists as a negatively charged ascorbate species (pK_a 4.17) [25]. In the case of DA, it is known to form an ester with the boronic acid moiety [21]. The shift in oxidation potential is due to the ester formation with boronic acid in PABA film (Scheme I) and thus it needs more energy to oxidize and hence the oxidation potential was observed from the usual redox potential at a bare electrode. In the case of AA, it diffuses from the solution to the modified electrode surface and reacts with the oxidized polyaniline and it is converted to its reduced form [26]. Thus, the content of the reduced form of polyaniline increases in the film, resulting in an increase in the AA oxidation current.

$$\mathrm{PANI_{red}} + \mathrm{e^-} \rightarrow \mathrm{PANI_{ox}} \quad (1)$$

$$\mathrm{PANI_{ox}} + \mathrm{AH_2} \rightarrow \mathrm{PANI_{red}} + \mathrm{AH_2^+} + 2\mathrm{e^-} \quad (2)$$

On PABA, the boronic acid moiety is specific to DA through covalent interactions whereas the polyaniline backbone favours AA interaction through non-specific electrostatic interactions [27] (Scheme I). Though these interactions facilitate a shift in oxidation potential of DA and AA and these peaks merge to yield a single peak (Figure 5c) (an ill-defined hump appears before the main peak corresponding to ascorbic acid oxidation). Further, the oxidized DA product, dopamine-*o*-quinone mediates the oxidation of ascorbate at the film solution interface in the presence of both DA and AA in a solution [28]. It is also reported that these oxidation products adhere to the electrode surface, leading to attenuation of the analytical signal [29]. A combination of these factors contribute to the decrease in the voltammetric signal for DA. The beneficial effect of boronic acid in inducing electroactivity of DA on polyaniline electrode surfaces is countered by increased electroactivity of AA on polyaniline. It is now necessary to examine if the suppression of the AA signal can help enhancing the limits for DA detection. To overcome this problem, we herein attempt to explore the use of PABA in conjunction with an anion repelling matrix like Nafion. Nafion is known to filter out negatively charged species like ascorbate anion through electrostatic repulsion [30] and can be used to reduce the interference from the ascorbate anion in the detection of DA selectively. However, a Nafion film as a filter will cause a diffusional barrier for both molecules. Hence, co-deposition of PABA with Nafion is used, so that a thin layer of Nafion surrounds each PABA chain and hence minimizes the

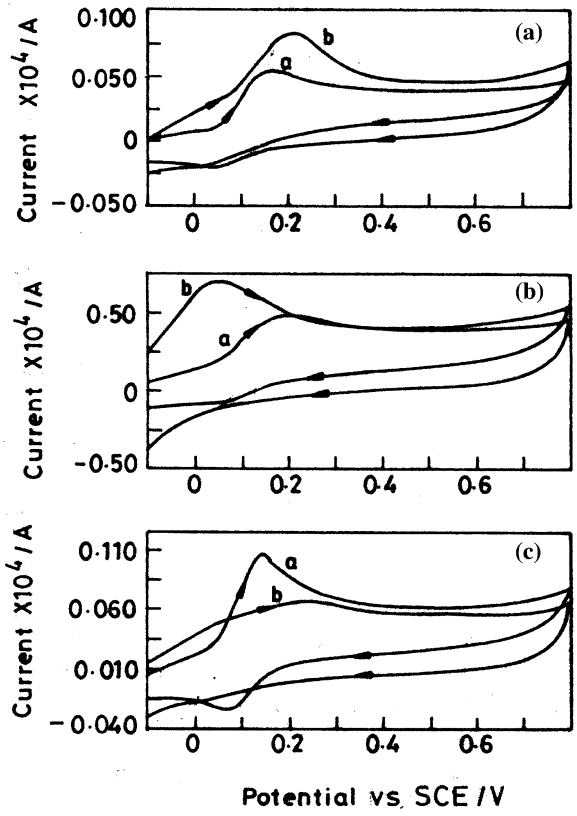


Fig. 5. Electrochemical behaviour of (a) 0.5 mM dopamine (DA); (b) 0.5 mM ascorbic acid (AA); (c) 0.5 mM dopamine + 0.5 mM ascorbic acid on (a) bare GC electrode and (b) PABA modified GC electrode in PBS 7.4; sweep rate = 100 mV s^{-1}.

diffusional barrier and at the same time provides mechanical stability and reduced interference by ascorbate anions. The detectability is further enhanced by the specific interaction between boronic acid in PABA film and DA. It is also observed that the background current for the PABA-Nafion composite film is much less than the Nafion-covered GC electrode. This is also likely responsible for the enhanced sensitivity in detecting DA.

3.3. *Oxidation of DA & AA at PABA-Nafion/GC*

Figure 6 shows the CV behaviour of DA and AA on PABA-Nafion coated GC electrode. The oxidation of DA occurs at ~0.210 V. It can be seen from Table 1 that the ratio of AA and DA oxidation current is 1.09 and 1.36 for bare and PABA modified GC electrodes respectively, whereas, a ratio value of 31.9 for the PABA-Nafion modified electrode was obtained. This proves the near-complete elimination of interaction with AA. The strong cation exchange of Nafion leads to an uptake of the positively charged DA and the anionic ascorbate interferent is electrostatically rejected from the surface because of the negatively charged Nafion (Scheme I).

The peak current associated with DA oxidation shows a linear relationship with square root of the scan rate in the range from 5 to 150 mV s^{-1}, which suggests that the oxidation of DA at the PABA-Nafion coated GC

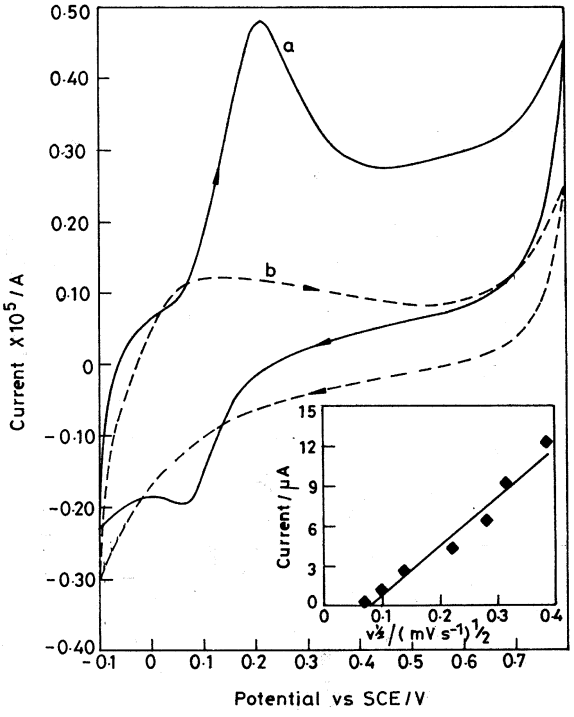


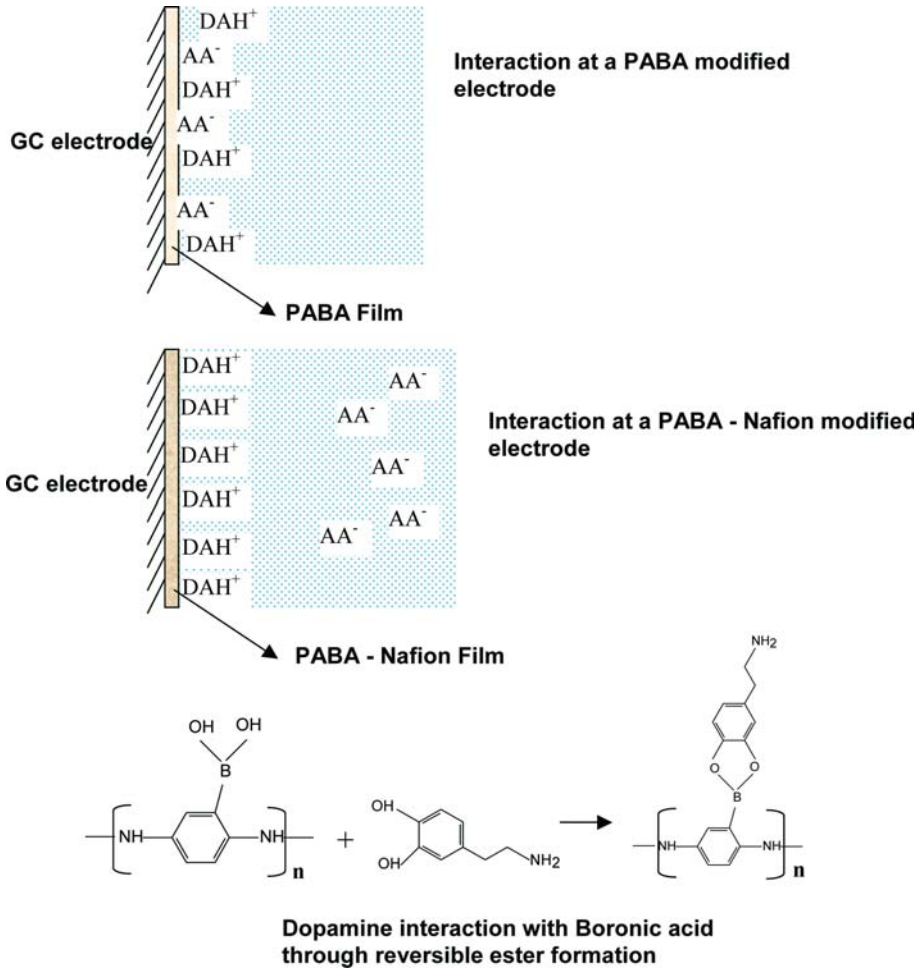
Fig. 6. Electrochemical behaviour of (a) 0.5 mM dopamine and (b) 0.5 mM ascorbic acid on PABA-Nafion modified GC electrode in PBS 7.4; sweep rate = 100 mV s^{-1} (Inset: Effect of sweep rate).

electrode is diffusion controlled [Figure 6, Inset]. Further, the diffusion coefficient for DA is calculated from the plots of peak current vs. square root of sweep rate, according to Randles–Sevick equation [31]. The diffusion coefficient calculated from the sweep rate dependence of the peak currents works out to be 1.032 (± 0.15) $\times 10^{-6}$ cm^2 s^{-1}. This value compares well with the values reported for DA in polymeric films that range from 1.4 to 7.9 $\times 10^{-6}$ cm^2 s^{-1} [28, 32–34].

Thus, selective oxidation of DA was achieved in the presence of ascorbic acid. As can be seen from the current magnitudes, although Nafion favours the selectivity, it affects the oxidation current (i.e. detectability). This is evidenced by the decrease in the oxidation current of DA and increased background current. In order to measure the DA oxidation current selectively and hence increase the sensitivity by overcoming the problems due to the presence of significant background current, pulse techniques are preferred to cyclic voltammetry [35].

Table 1. The ratio of AA and DA oxidation currents at various electrodes

Electrode characteristics	Oxidation current/μA		Oxidation current ratio ($I_{DA/AA}$)
	Dopamine	Ascorbic acid	
Bare GC	3.814	3.510	1.09
PABA modified GC	5.434	4.006	1.36
PABA-Nafion modified GC	3.203	0.1004	31.9



Scheme I

3.4. *Differential pulse voltammetry*

Figure 7 shows the differential pulse voltammograms (DPV's) of DA, AA and DA + AA in a solution at the PABA-Nafion modified GC electrode in PBS 7.4. DA shows a well-defined sharp oxidation peak at ~0.13 V with and without AA (1:1 ratio), whereas AA does not shows significant oxidation current in the entire potential window.

Further, DPVs were measured at different concentrations of DA in the presence of a fixed concentration of AA (ca. 5 mM). The DA oxidation current is found to increase linearly (correlation coefficient of 0.98 and sensitivity of 0.02 μA μ M^{-1} for DA) with increase in DA concentration (0.005–0.2 mM) [Figure7 Inset], while the presence of 5 mM of AA does not affect the DA oxidation. It can be noted from this result that in the presence of AA at mM level, the electrode can sense DA in the micromolar concentration range at neutral pH. Thus, selective and sensitive detection of DA in the presence of a high concentration of AA (10^3 times) is found to be achievable at a PABA-Nafion composite electrode.

The stability of the electrode was checked, by dipping in PBS 7.4 solution for one day and its response was measured for DA oxidation after one day. DA was found to undergo oxidation at the same potential and

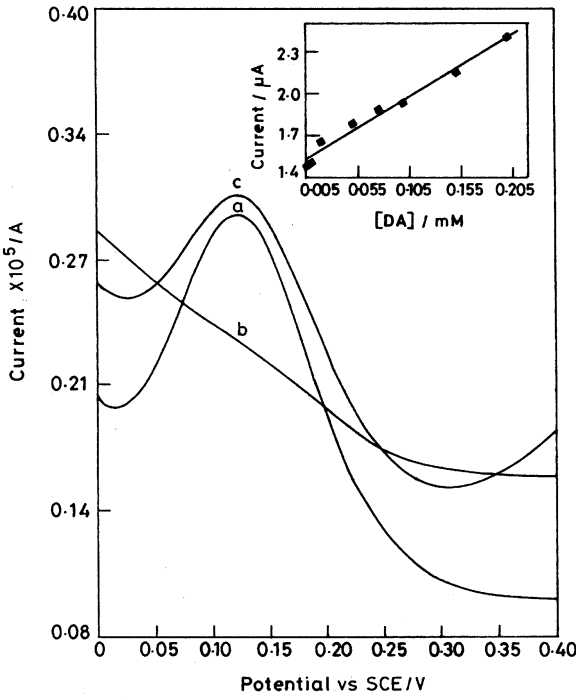


Fig. 7. Differential pulse voltammograms of (a) 0.5 mM DA, (b) 0.5 mM AA and (c) 0.5 mM DA + 0.5 mM AA a PABA-Nafion modified GC electrode in PBS 7.4 (Inset: Differential pulse voltammogram of DA (5 μm to 0.2 mm) in presence of 5 mM of AA in PBS 7.4 - Effect of concentration vs oxidation current).

the current response was found to be the same as that obtained at a freshly polymerized electrode. After each experiment with DA, the electrode appeared to lose its activity for subsequent measurements. However, the original response was found be regained after treatment in a 0.5 M HCl solution for a day.

Catalytic electrodes like PABA for DA detection [36] can be part of array electrodes that constitute a full sensor for a series of biological molecules while polyaniline can detect AA selectively. It is reasonable to expect the other arrays with materials like polypyrrole-tetradecyl sulfate [9], *o*-phenylene diamine [13] for sensing molecules such as uric acid, serotonin, L-Dopa, etc. Our future work will focus on these systems to arrive at comprehensive sensor arrays, along with approaches for chemical modification of polyaniline to overcome interference due to AA.

4. Conclusions

PABA polymer film has been electrochemically deposited on a GC electrode surface by continuous electrooxidation of aniline boronic acid catalysed by sodium fluoride. Electroanalysis of AA and DA has been performed at this PABA film modified electrode that can detect both AA and DA. Compared to a bare GC electrode, the oxidation of AA is shifted to less positive potentials, while that of DA is shifted to positive potentials. When both the analytes coexist in the electrolyte, the current peaks of DA and AA coalesce and appear as a single peak. While boronic acid favours separation of peak positions of DA and AA by selective interactions with DA, the polyaniline part of the film also shows a current response for AA, hindering the selective determination of DA. For the selective determination of DA, the AA response is suppressed using Nafion co-deposited with PABA. Limitation on the detectability due to higher background currents observed with Nafion-incorporated polymer films could be overcome using differential pulse voltammetry. The DA peak current is observed to increase linearly with concentration with a correlation coefficient of 0.98 and sensitivity of 0.02 μA μM^{-1} for DA. Thus, the composite electrode can sense DA in the micromolar concentration range at pH 7.4 in the presence of a high concentration of AA ($\sim 10^3$ times). Thus, any EC sensor that attempts to determine DA selectively should necessarily involve a composite coating like that presented in this paper.

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