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The selective detection of dopamine at a polypyrrole film doped with sulfonated β-cyclodextrins

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ABSTRACT

A highly selective dopamine sensor was fabricated by doping polypyrrole with a sulfonated β-cyclodextrin. This composite material enabled the selective sensing of dopamine in the presence of a large excess of ascorbic acid and prevented the regeneration of dopamine through the homogeneous catalytic reaction of the ascorbate anion with the dopamine-o-quinone. A single redox wave, corresponding to the oxidation of dopamine, was observed in dopamine/ascorbate mixtures, giving a truly selective dopamine sensor. The limit of detection was measured as 3.2×10^{-6} M for dopamine.

1. Introduction

Dopamine is one of the most important catecholamine neurotransmitters in the mammalian central nervous system. Abnormalities in dopamine concentrations have been linked with several neurological disorders such as the debilitating ailment Parkinson's disease and the mental disorder schizophrenia [1,2]. Dopamine is also believed to play a central role in Huntington's disease, a fatal genetic neurodegenerative movement disorder and has also been associated with drug addiction and attention disorders [3–5].

Monitoring the concentration of dopamine is particularly challenging using electrochemical methods because dopamine coexists with many interfering compounds in biological samples. These interfering compounds are usually present at concentrations much higher than dopamine and, moreover, they are oxidised at similar potentials to dopamine at most solid electrodes. This is particularly true of ascorbic acid, the main interfering compound in the determination of dopamine. The concentration of the ascorbate anion is typically 10^{-3} M, while the concentrations of dopamine are considerably lower, in the range of 10^{-8} to 10^{-6} M. Ascorbic acid is easily oxidised having a range of $E_{1/2}$ values between −100 and 400 mV vs. SCE on most solid electrodes. This lies in the same potential region as dopamine, which has a range of $E_{1/2}$ values between 100 and 250 mV vs. SCE for various electrode substrates [6]. Furthermore, ascorbic acid reacts with the oxidised dopamine product (dopamine-o-quinone) which is generated through the electrochemical oxidation of dopamine. This reaction leads to the regeneration of dopamine making it available for further electrochemical oxidation, complicating the analysis [7,8].

A number of modified electrodes have been used in an attempt to resolve these problems. The most popular strategies include polymer, self-assembled monolayer, metal nanoparticle, carbon nanotube and surfactant modified electrodes [9–13]. In particular, there has been much interest in the development of sensors based on electrodes modified with polymeric films. Electropolymerised films of pyrrole, aniline, 3-methylthiophene, acridine red, sulfosalicylic acid, 3,5-dihydroxy benzoic acid and acid chrome K have all been reported [14–18]. Overoxidised polymer modified electrodes have also been employed to sense dopamine and ascorbic acid [19]. However, the most common approach is to use Nafion®, a perfluorinated polymer. Nafion® has terminal sulfonate groups that can repel the negatively charged ascorbate anion from the electrode surface, enabling the discrimination of the ascorbate and dopamine oxidation waves [20].

Cyclodextrins are naturally occurring macrocyclic oligosaccharides built from α-1,4-linked D-glucopyranose units. Cyclodextrins are well-known to bind with suitable guest molecules in aqueous solutions to form inclusion complexes [21]. They also exhibit excellent biocompatibility and as a result have been incorporated into various dopamine sensors. For example, Izaoumen et al. [22] and Bouchta et al. [23] have used polymer films modified with neutral cyclodextrins and doped with perchlorate anions for the sensing of dopamine, while Alarcon-Angeles et al. [24] have modified multiwall carbon nanotubes with β-cyclodextrins for the sensing

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of dopamine. The electrochemical synthesis of polypyrrole doped with sulfonated β-cyclodextrins has been reported by Temsamani et al. [25], Bidan et al. [26] and Reece et al. [27]. However, there are no reports, to the best of our knowledge, on using these materials in the selective sensing of dopamine. The modified sensor used here differs from the majority of all other publications on cyclodextrin modified dopamine sensors, as the anionic cyclodextrin is introduced into the polymer matrix as an immobile dopant. Furthermore, it is the sole dopant, as no other anions are used in the electropolymerisation step.

In this paper, we show that polypyrrole films doped with sulfonated β-cyclodextrins are readily formed and that these materials have excellent selectivity in the determination of dopamine concentrations, facilitating the oxidation of dopamine, but inhibiting the oxidation of ascorbate. In addition, there is no evidence of the regeneration of dopamine through the ascorbate/dopamine-o-quinone reaction. Also, the exceptional biocompatibility properties of the materials used make the cyclodextrin-doped polypyrrole sensor considerably more suitable for *in vivo* detection compared to some of the more complex electrodes already considered in the sensing of dopamine.

2. Experimental

2.1. Materials

Dopamine, ascorbic acid, pyrrole, citric acid, disodium hydrogen phosphate and sulfonated β-cyclodextrin were obtained from Sigma–Aldrich or its subsidiary company, Fluka. All chemicals were used as supplied except for the pyrrole monomer which was distilled before use and stored at −4 °C. All solutions were prepared freshly before each experiment and were deoxygenated with nitrogen. Platinum rod (99.95%, 4 mm in diameter) and glassy carbon (4 mm in diameter) were supplied by Goodfellow or Alfa Aesar. A 250 mL citrate phosphate buffer solution (pH 6.0) was prepared by mixing 150 mL of 0.2 M disodium hydrogen phosphate and 100 mL of 0.1 M citric acid.

2.2. Apparatus

The performance of the sensor was evaluated using both cyclic voltammetry measurements and constant potential amperometry. All data were recorded using a Solartron 1285A potentiostat at room temperature in a 0.10 M Na_2SO_4 supporting electrolyte, pH 6.0. The constant potential amperometry was performed by rotating the electrode at 2000 rpm using a rotating disc electrode assembly, EG&G Model 363. A platinum rotating disc electrode was used as the working electrode. In each case, the modified electrodes were first cycled in the background electrolyte, between −0.10 V vs. SCE and 0.90 V vs. SCE for 10 cycles to ensure the release of any pyrrole or oligomers from the surface.

A standard three-electrode electrochemical cell configuration was employed for all electrochemical experiments. A platinum or glassy carbon rod electrode was used as the working electrode. These were embedded in epoxy resin in a Teflon holder with electrical contact being achieved by means of a wire threaded through the holder to the rod substrate. A platinum wire was used as an auxiliary electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Tencor analysis was carried out on a Tencor Veeco Dektac 6M Stylus Profilometer in the Tyndall National Institute, University College Cork.

2.3. Fabrication of polymers

Prior to each experiment, the platinum electrode was polished to a mirror finish, using successively smaller sizes of diamond paste, down to a 1 μm sized diamond paste, rinsed with distilled water and finally cleaned in an ultrasonic bath. The cyclodextrin doped polypyrrole films were prepared at the platinum electrode from a 0.20 M pyrrole and 0.01 M sulfonated β-cyclodextrin solution[1] at a constant potential of 0.80 V vs. SCE until a charge of 0.24 C cm^{-2} was passed (approximately 35 s). The polypyrrole sulfonated β-cyclodextrin modified electrode was finally washed with distilled water and dried.

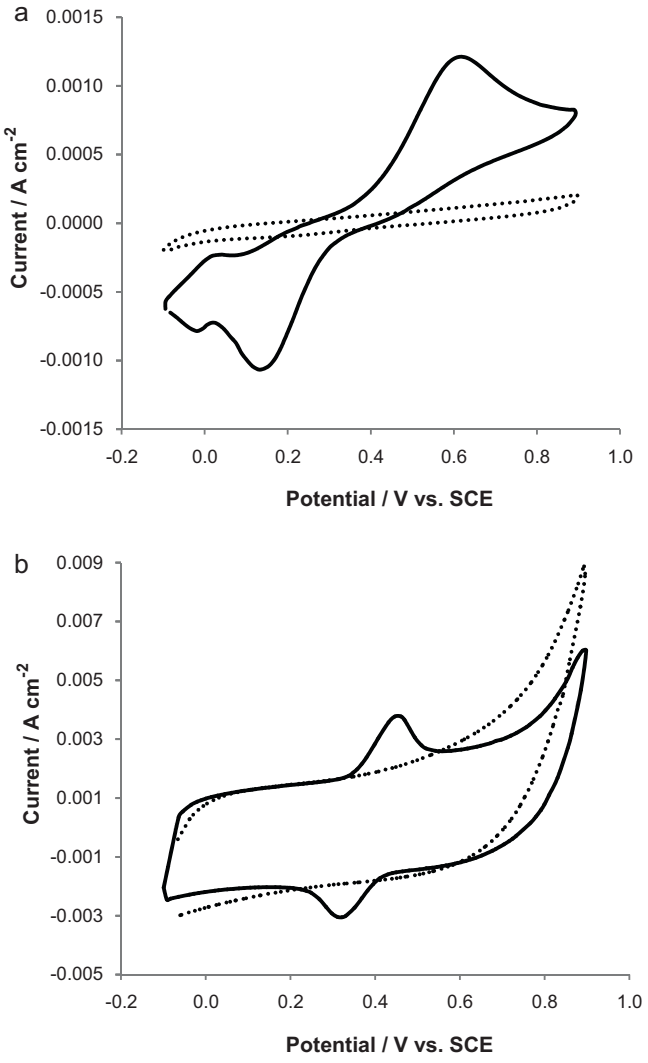


Fig. 1. Cyclic voltammograms of (a) bare platinum electrode and (b) a polypyrrole sulfonated β-cyclodextrin modified electrode in (···) a 0.10 M Na_2SO_4 solution and in (–) a 1.0×10^{-3} M dopamine/0.10 M Na_2SO_4 solution. Scan rate = 100 mV s^{-1}.

3. Results and discussion

3.1. Oxidation of dopamine at the polypyrrole sulfonated β-cyclodextrin film

The dopamine response at the bare platinum electrode and at the polypyrrole sulfonated β-cyclodextrin film was examined using cyclic voltammetry, Fig. 1(a) and (b), respectively. The electrodes were cycled in a 1.0×10^{-3} M dopamine solution dissolved in a

[1] Commercially available sulfonated β-cyclodextrin has approximately 7–11 sulfonated groups per cyclodextrin. A mean value of 9 sulfonated groups was assumed when calculating the molecular weight.

0.10 M Na_2SO_4 supporting electrolyte, between −0.10 V and 0.90 V vs. SCE at a scan rate of 100 mV s^{-1}. It can be seen in Fig. 1(a) that the oxidation of dopamine at the bare platinum electrode exhibits two pairs of redox peaks. The pair of redox peaks observed at the higher potentials corresponds to the oxidation of dopamine to dopamine-o-quinone, whereas the redox couple observed at the lower potentials relates to the oxidation of leucodopamine to dopaminochrome. These redox peaks are consistent with the electrochemical oxidation of dopamine at unmodified substrates [28].

The electrochemistry of dopamine at the polypyrrole sulfonated β-cyclodextrin film is very different (Fig. 1(b)). Only one pair of redox peaks, corresponding to the oxidation of dopamine (0.46 V vs. SCE) and the reduction of the dopamine-o-quinone (0.27 V vs. SCE), is observed and the peaks currents are considerably higher. This marked increase in the peak current can be attributed to the polymer and not the metal surface. Indeed, this is further supported by the fact that the oxidation potential of dopamine at the polymer-modified electrode is some 150 mV lower than that observed at the bare platinum electrode. In addition, the presence of this polymer on the platinum electrode has decreased the potential difference between the oxidation and reduction peaks of dopamine, making the reaction more reversible than that observed at a bare platinum electrode. The peak potential separation (ΔE_p) is approximately 190 mV at the polymer modified electrode, compared to 480 mV at the bare platinum electrode, indicating a significant increase in the reversibility of the system. This increase may be attributable to improved kinetics, however, the rate constant, k, was found to be 3.9×10^2 M^{-1} s^{-1} at the polymer modified electrode. This was determined using rotating disc voltammetry and the Koutecky–Levich equation, $1/i_L = 1/nFAC_o k\Gamma + 1/0.62nFAD^{2/3}\nu^{-1/6}C_o\omega^{1/2}$, where, i_L is the measured limiting current, n is the number of electrons transferred, F is the Faraday constant, A is the electrode area, C_o is the dopamine concentration, k is the rate constant, Γ is the surface coverage, D is the diffusion coefficient, ν is the kinematic viscosity and ω is the rotation speed. If a linear Koutecky–Levich relationship exists between the inverse of the limiting current and the inverse of the square root of the rotation speed then k can be determined from the intercept of this line. This value for k is reasonably high, indicating a fairly fast electrocatalytic process. However, higher rate constants have been reported in the literature [29,30]. Therefore, the obvious increase in the reversibility may not be solely due to the polymer film having a catalytic effect on the oxidation of dopamine.

Another aspect that must be taken into consideration is the porous nature of the polymer film. The thickness of the polypyrrole sulfonated β-cyclodextrin film was determined as 505 ± 50 nm using a Tencor profilometer. The thickness of the films was also theoretically calculated as 600 nm from the total charge passed using a relationship derived by Diaz et al. [31] that assumes that 1 C cm^{-2} is equivalent to 2.5 μm of polymer growth. This is slightly higher than the experimental analysis however, it is important to highlight that the relationship quoted by Diaz et al. [31] was for a simple chloride dopant, which has been shown to form thicker films than polypyrrole films doped with tosylate and polystyrene sulfonate when the same amount of charge has been passed [32]. The values obtained from both the experimental and theoretical analyses indicate that the polypyrrole sulfonated β-cyclodextrin films are porous and may exhibit thin film diffusion. Henstridge et al. [33] have shown that a reduction in the overpotential of a voltammetric signal at a porous film is due to planar diffusion and thin film diffusion rather than a faster rate of electron transfer. Therefore, the more reversible electrochemistry of dopamine at the polypyrrole sulfonated β-cyclodextrin film may be also connected with this phenomena.

Another characteristic of the voltammograms recorded by the polymer film is that the dopamine oxidation peak is more symmetric in comparison to the bare electrode. This may be connected to the capacitance of the polymer film. As evident in Fig. 1(b), the background current in the cyclic voltammograms is large, indicating a high charging capacitance. Indeed, the capacitance of the polypyrrole sulfonated β-cyclodextrin film was found to be 1.2×10^{-3} F cm^{-2} which is significantly higher than the capacitance associated with the bare platinum electrode. This higher capacitance may be responsible for the more symmetric shape of the dopamine oxidation wave. Indeed, it has been shown that the cyclic voltammograms of dopamine can become more symmetric in shape as the capacitance increases [34].

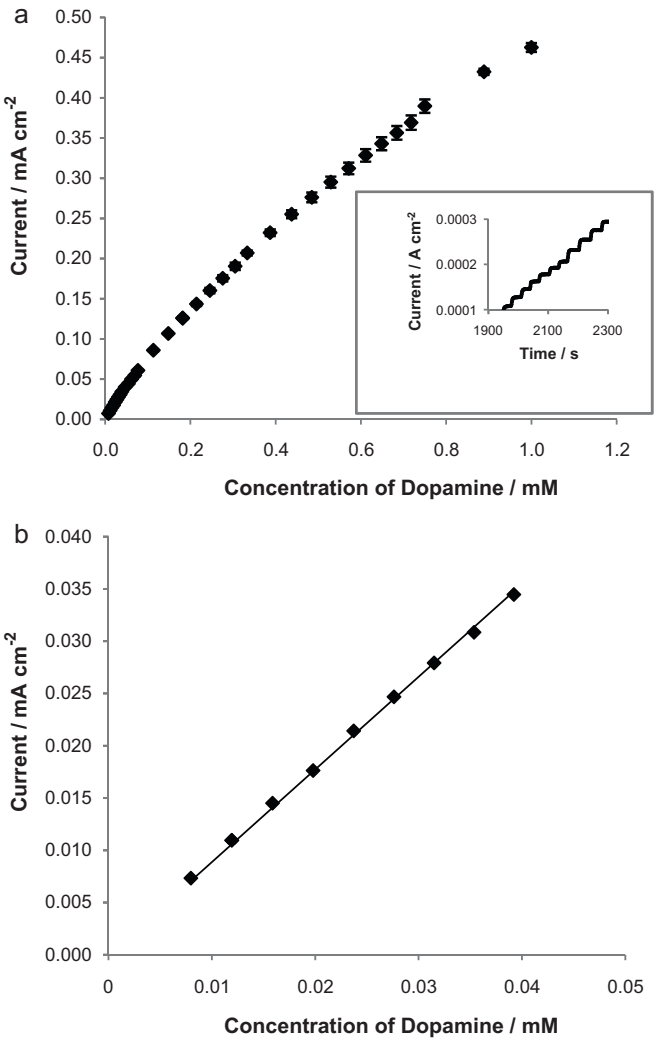


Fig. 2. (a) Steady-state currents from constant potential amperometry, recorded at a rotating disc electrode at 2000 rpm at 0.65 V vs. SCE, plotted as a function of the dopamine concentrations ($n = 4$). Inset shows the constant potential amperometry with current plotted as a function of time and as a function of successive additions of dopamine aliquots ranging from 50 μL to 5 mL. (b) The linear response of dopamine at low concentrations.

3.2. Sensitivity of the polypyrrole sulfonated β-cyclodextrin film

In order to obtain information on the sensitivity of the sensor, constant potential amperometry data were measured. A typical plot is presented in the inset of Fig. 2(a), showing the amperometric response of the cyclodextrin-doped polypyrrole film to successive additions of dopamine. The solution was agitated by rotating the electrode at 2000 rpm, while a constant potential of 0.65 V vs. SCE was applied. The response time (time for the signal to increase from

10% to 80%) was less than 3.3 s, which indicates a reasonably quick response of the modified electrode to dopamine. This compares very well with the typical response times of dopamine at other modified electrodes [35].

The relationship between the measured current and the concentration of dopamine is shown in Fig. 2(a). A curve is obtained over a wide concentration range, while a clear linear region is observed at lower concentrations, as shown in Fig. 2(b). The regression equation was $I_{pa} = 0.886c_{DA}$, with a correlation coefficient of 0.999. This gives a current to concentration ratio of 0.886 μA μM^{-1}. This sensitivity is reasonable given the fact that the sensitivities of the majority of polymer modified dopamine sensors are similar, if not, lower than this. For example, Gopalan et al. [36] obtained a sensitivity of 0.22 μA μM^{-1} in the presence of ascorbic acid using a poly(4-aminothiophenol) modified electrode embedded with gold nanoparticles while Balamurugan and Chen [37] acquired a sensitivity of 1.0 μA μM^{-1} for dopamine using an poly(3,4-ethylenedioxythiophene-co-(5-amino-2-naphthalenesulfonic acid)) modified electrode.

Using the linear calibration curve, the limit of detection was found to be 3.2×10^{-6} M dopamine. This was obtained using the expression $C_m = 3S_b/m$, where C_m is the detection limit, S_b is the standard deviation of the blank response and m is the slope of the linear calibration curve. Although this concentration is not sufficiently low for a viable *in vivo* dopamine sensor, it may be possible to reach lower detection limits by using pulsed techniques, such as differential pulse voltammetry, or by miniaturising the electrode. Interestingly, a limit of detection of 4.0×10^{-5} M dopamine, obtained by Ferreira et al. [38], was sufficient to detect dopamine in a pharmaceutical product. Therefore, the polypyrrole sulfonated β-cyclodextrin modified electrode may have potential in this area.

3.3. Effect of ascorbic acid on the sensing of dopamine

In Fig. 3(a), the cyclic voltammograms of the cyclodextrin doped polypyrrole films cycled in 1.0×10^{-3} M dopamine and in 1.0×10^{-3} M ascorbate are compared. In both cases, the potential is cycled in the potential range where dopamine and ascorbate are likely to oxidise. No oxidation wave is observed for the ascorbate system at the polypyrrole sulfonated β-cyclodextrin film. When ascorbic acid and dopamine are simultaneously mixed in the same solution, only the dopamine peak is detected at the polypyrrole sulfonated β-cyclodextrin electrode, giving very good selectivity, Fig. 3(a).

The influence of ascorbate on the dopamine signal is summarised in Fig. 3(b) and (c), where the magnitude of the oxidation peak currents and potentials obtained with pure dopamine, are compared to the values measured when 1.0×10^{-3} M ascorbate is present. The concentration ratio of ascorbic acid to dopamine in the combined solution was varied from 1.0 (1.0×10^{-3} M ascorbic acid and 1.0×10^{-3} M dopamine) to 16.7 (1.0×10^{-3} M ascorbic acid and 6.0×10^{-5} M dopamine). The values reported are averaged over at least three determinations (the errors in the measurements are less than 1.5%). It can be seen that the dopamine signal is not affected by the presence of ascorbic acid. Also, regardless of the concentration of dopamine, there is no evidence of any increase in the dopamine oxidation current as a result of the solution reaction between dopamine-o-quinone and ascorbic acid (Scheme 1).

In fact, no interference was observed when the concentration of ascorbic acid was increased to 1.0×10^{-2} M. At this high concentration the oxidation peak from ascorbic acid should be sufficient to overcome the background current. The mean I_p and E_p values for 1.0×10^{-3} M dopamine at the polymer film were 3.65×10^{-3} A cm^{-2} and 0.459 V vs. SCE, respectively ($n = 3$). Surprisingly, mean I_p and E_p values of 3.64×10^{-3} A cm^{-2} and 0.459 V vs. SCE were obtained in the presence of 1.0×10^{-2} M ascorbate

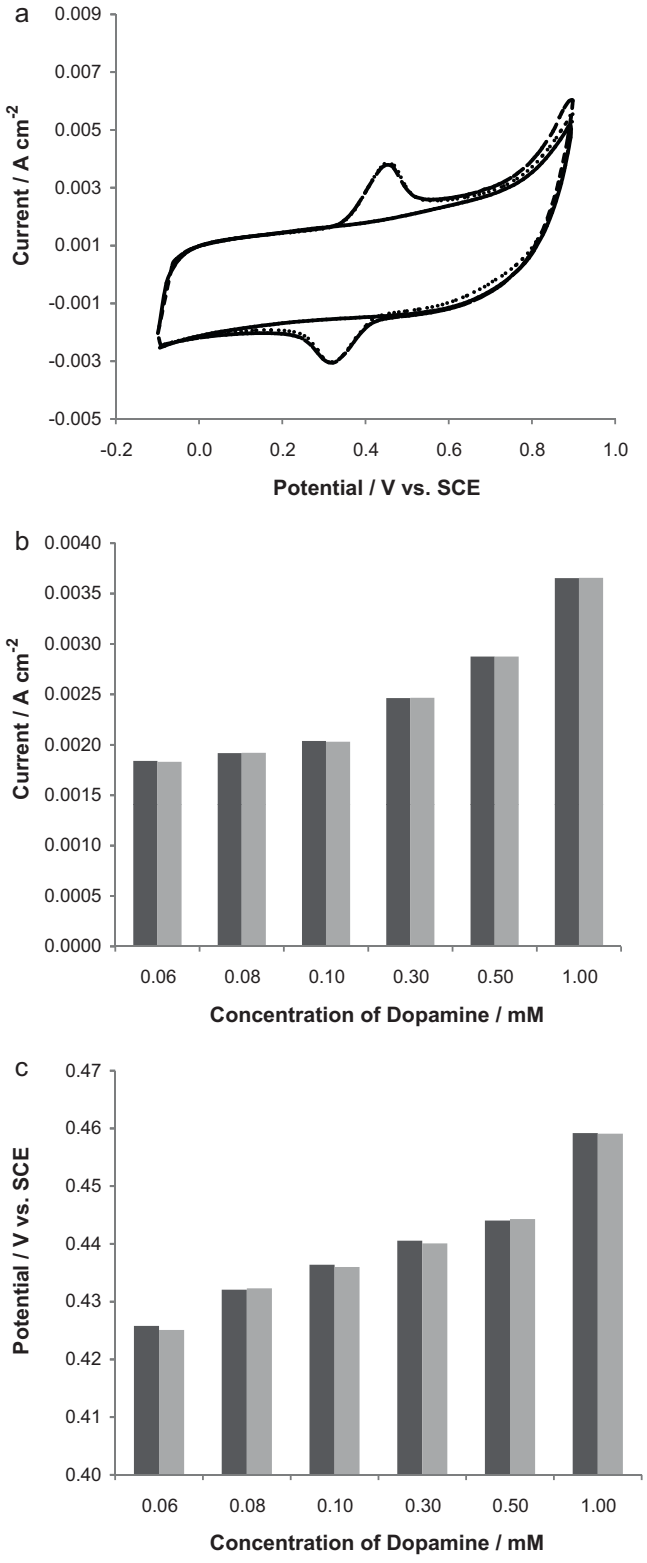
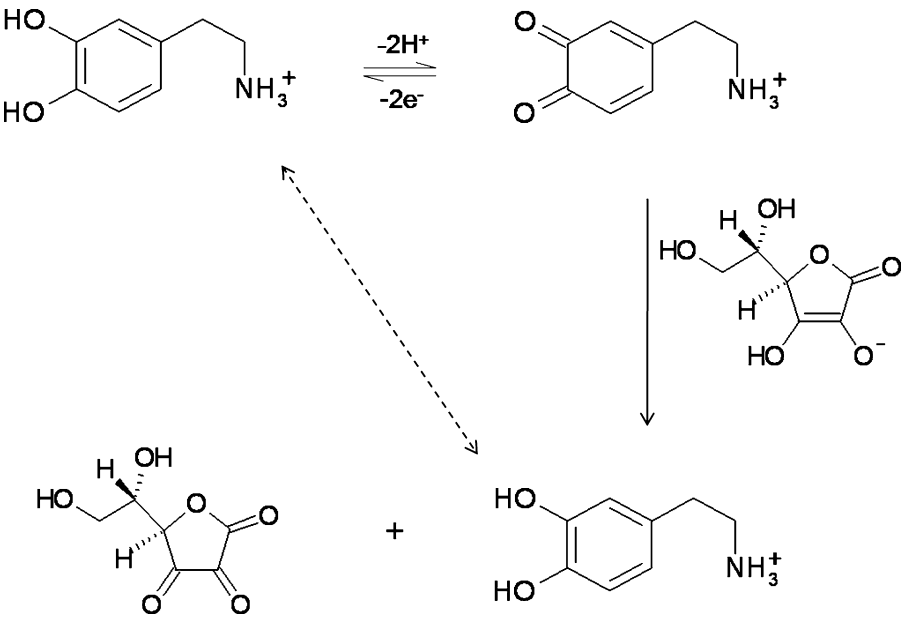


Fig. 3. (a) Cyclic voltammograms of a polypyrrole sulfonated β-cyclodextrin modified electrode in (- -) a 1.0×10^{-3} M dopamine/0.10 M Na_2SO_4 solution, (–) a 1.0×10^{-3} M ascorbic acid/0.10 M Na_2SO_4 solution and (···) a 1.0×10^{-3} M ascorbic acid/1.0×10^{-3} M dopamine/0.10 M Na_2SO_4 solution. Scan rate = 100 mV s^{-1}. (b) Peak currents and (c) potentials, from the cyclic voltammograms, of dopamine as a function of the concentration of dopamine in the (■) presence ($n = 3$) and (■) absence ($n = 4$) of 1.0×10^{-3} M ascorbic acid in a 0.10 M Na_2SO_4 supporting electrolyte. The concentration ratio of ascorbic acid to dopamine in the combined solution was varied from 1.0 (1.0×10^{-3} M ascorbic acid and 1.0×10^{-3} M dopamine) to 16.7 (1.0×10^{-3} M ascorbic acid and 6.0×10^{-5} M dopamine).



Scheme 1. Mechanism of the electrocatalytic oxidation of ascorbic acid by dopamine.

($n = 3$). The fact that this high concentration of ascorbic acid does not interfere is remarkable given that it is significantly higher than the typical concentrations of ascorbic acid found in most biological samples.

These results show clearly that both 1.0×10^{-3} M and 1.0×10^{-2} M ascorbate do not interfere with the detection of dopamine, with the polypyrrole sulfonated β-cyclodextrin films eliminating the signal of ascorbic acid. This is somewhat rare given that the majority of reports for modified electrodes in the literature are related to the simultaneous determination of dopamine and ascorbic acid [39].

3.4. Mechanism of sensing

The data presented in Section 3.3 clearly show that the cyclodextrin-doped polypyrrole films have excellent selectivity. The sulfonated β-cyclodextrin is highly charged, with 7 to 11 $-SO_3^-$ groups. An important consideration is the number of sulfonated groups on each cyclodextrin that takes part in the doping process. If all the sulfonated groups on the β-cyclodextrin were involved in charge balance there would be considerable steric strain in the polymer matrix. Therefore, it is highly probable that some free sulfonated groups are present within the polymer. Furthermore, Naoi and co-workers [40], in studying the doping of polypyrrole with mono-, di- and tri-sulfonated naphthalene, concluded that the polypyrrole-trisulfonate doped films possessed free sulfonated groups without any charge compensation. This is consistent with the lack of any signal from the oxidation of the ascorbate anion, as the anion will be repelled from the negatively charged surface. On the other hand, the protonated dopamine ($pK_a = 8.87$) will be attracted to the interface. In addition, this local negative charge is sufficient to maintain the ascorbate ($pK_a = 4.10$) at a sufficient distance from the interface, enabling the reduction of the dopamine-o-quinone back to dopamine during the reduction cycle of the voltammogram, avoiding any, or little, regeneration of the dopamine through the ascorbate catalysed reaction.

In order to see if there was any binding interaction between the dopamine and the polypyrrole sulfonated β-cyclodextrin film, the Michaelis–Menten equation, $V = V_{max}[S]/K_m + [S]$, was applied to the constant potential amperometry data (Fig. 2(a)). The Michaelis–Menten equation describes the relationship between the rate of substrate conversion by an enzyme and the concentration of the substrate, where, V is the rate of substrate conversion, V_{max} is the maximum rate of substrate conversion, $[S]$ is the substrate concentration and K_m is the Michaelis constant. Even though the polypyrrole sulfonated β-cyclodextrin film is not an enzyme, the Michaelis–Menten equation can be applied to this system to gauge if there is any binding interaction between it and the dopamine. This is because cyclodextrins can mimic enzyme-catalysed reactions and this has been well documented in the literature [41]. For this case, V is equal to the current I, and subsequently V_{max} is equal to I_{max}. The curve in Fig. 2(a) obeys the Michaelis–Menten equation with a correlation coefficient of 0.999. The K_m and I_{max} were determined from this curve with values of 1.53×10^{-3} M and 1.17×10^{-3} A cm^{-2} obtained, respectively. As this value of K_m is relatively high this would suggest that the dopamine [DA] interacts weakly with the polypyrrole sulfonated β-cyclodextrin film [PPy-SCD] to give the complex [PPy-SCD-DA], which can easily dissociate into the polypyrrole sulfonated β-cyclodextrin film [PPy-SCD] and the oxidised dopamine product, dopamine-o-quinone [DA-O-Q]. This can be summarised by

$$[\text{PPy-SCD}] + [\text{DA}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{PPy-SCD-DA}] \xrightarrow{k_2} [\text{PPy-SCD}] + [\text{DA-O-Q}]$$

where k_1 and k_{-1} are rate constants for the association and dissociation of dopamine and polypyrrole sulfonated β-cyclodextrin, respectively. The rate constant for the dissociation of converted dopamine (dopamine-o-quinone) is k_2.

The results acquired from the Michaelis–Menten kinetics indicate that there is an interaction between the dopamine and the polypyrrole sulfonated β-cyclodextrin film. The interaction could be purely electrostatic, with the negatively charged sulfonated groups on the cyclodextrin attracting the cationic dopamine to give an ion pair. Alternatively, it could be a combination of both an electrostatic interaction and the dopamine forming an inclusion complex with the sulfonated β-cyclodextrin.

Cyclic voltammetry was used to investigate the nature of this binding interaction between the dopamine and the sulfonated β-cyclodextrin in solution. These data were recorded with a fixed concentration of dopamine, 5.0×10^{-4} M, at a glassy carbon electrode in a buffered citrate-phosphate, pH 6.0, solution. The concentration of the sulfonated cyclodextrin was varied from

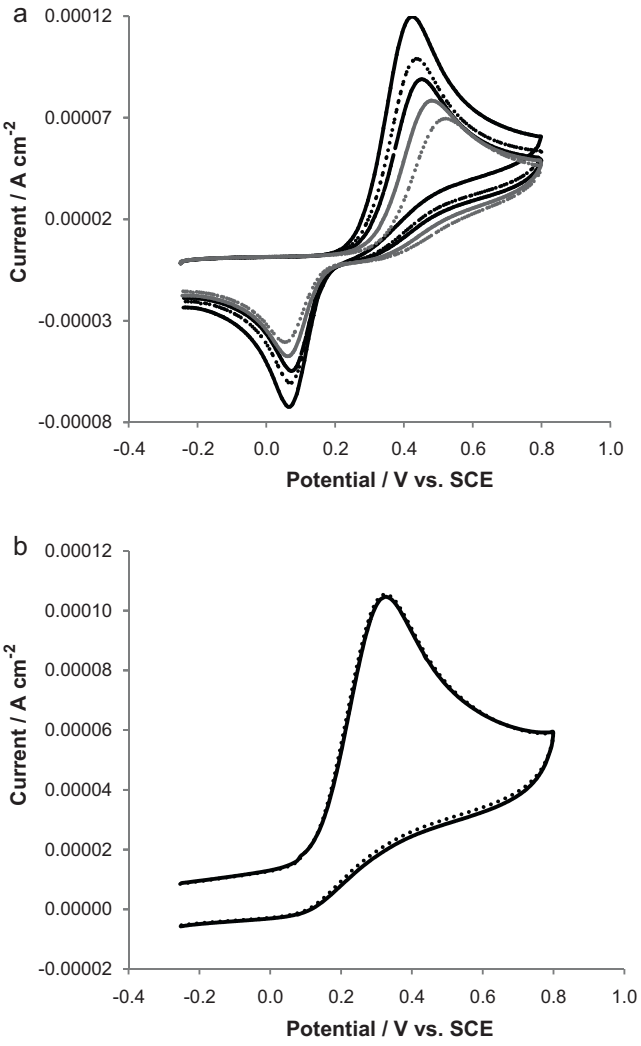


Fig. 4. (a) Cyclic voltammograms of a bare glassy carbon electrode in (–) 5.0×10^{-4} M dopamine and in 5.0×10^{-4} M dopamine/(...) 2.0×10^{-2} M, (▬) 1.0×10^{-2} M, (- -) 5.0×10^{-3} M and in (···) 2.5×10^{-3} M sulfonated β-cyclodextrin. All solutions were made up in a 0.30 M citrate phosphate buffer solution (pH of all solutions ~6.0). Scan rate = 50 mV s^{-1}. Electrochemical window: −0.25 V to 0.80 V vs. SCE. (b) Cyclic voltammograms of a bare glassy carbon electrode in (–) 5.0×10^{-4} M ascorbic acid and in (···) 5.0×10^{-4} M ascorbic acid/1.0×10^{-2} M sulfonated β-cyclodextrin. All solutions were made up in a 0.30 M citrate phosphate buffer solution (pH of all solutions ~6.0). Scan rate = 50 mV s^{-1}. Electrochemical window: −0.25 V to 0.80 V vs. SCE.

2.0×10^{-2} M to 2.5×10^{-3} M to give dopamine-containing solutions with an excess of the anionic sulfonated β-cyclodextrin, while the 0.3 M buffer solution provided a near constant ionic strength. The voltammograms recorded for the pure dopamine solution are compared to the data recorded in the presence of the sulfonated β-cyclodextrin in Fig. 4(a). On addition of sulfonated β-cyclodextrin to the dopamine solution, there is a clear anodic shift in the peak oxidation potential and a decrease in the peak oxidation current. In contrast, no evidence of any interaction was observed between the ascorbate anion and the sulfonated β-cyclodextrin when a similar analysis was carried out (Fig. 4(b)). This reduction in the peak current and the anodic shift of the peak potentials for the oxidation of the analyte are consistent with the formation of an inclusion complex [42,43]. The increase in the oxidation potential is connected to the fact that it is more difficult to oxidise the included dopamine, while the decrease in the peak currents is consistent with a lower diffusion coefficient of the included dopamine compared to that of free dopamine. The sulfonated β-cyclodextrin is large and bulky and this will give rise to a measurable decrease in the diffusion coefficient of the encapsulated dopamine. Although these data are consistent with the formation of an inclusion complex the driving force for this inclusion event may be the electrostatic attraction between the anionic sulfonated β-cyclodextrin and the cationic dopamine. Indeed our studies show that there is no apparent interaction between the neutral β-cyclodextrin and dopamine in solution.

Interestingly, there is no change in the potential at which the dopamine-o-quinone is reduced and converted back to dopamine, Fig. 4(a). For example, the peak potential is 0.064 V vs. SCE in the absence of the sulfonated β-cyclodextrin and 0.060 V vs. SCE in the presence of the 2.0×10^{-2} M sulfonated β-cyclodextrin. These observations illustrate that once the included dopamine is converted to dopamine-o-quinone, it is expelled from the cavity, enabling the detection of dopamine in subsequent cycles, corroborating the Michaelis–Menten analysis.

Assuming that the cavity is accessible when the cyclodextrin is doped within the polypyrrole matrix, then an inclusion complex between the dopamine and the cavity is likely. Interestingly, Bidan et al. [26] showed that N-methylphenothiazine (NMP) was encapsulated within the cyclodextrin cavity by simply immersing the polypyrrole-sulfonated β-cyclodextrin film in an acetonitrile (CH_3CN) solution containing NMP, indicating that the cavities are available for suitable guest molecules.

4. Conclusions

A sulfonated β-cyclodextrin doped polypyrrole film was formed at 0.80 V vs. SCE in a 0.20 M pyrrole and 0.01 M sulfonated β-cyclodextrin solution. This polymer has excellent selectivity for the detection of dopamine in the presence of ascorbate. The ascorbate anion is not detected. A linear calibration curve was obtained to give a sensitivity of 0.886 μA μM^{-1} and a detection limit of 3.2×10^{-6} M for dopamine.

Acknowledgments

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