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Investigation of the Voltammetric Characteristics of Poly(1,4-diaminobenzene) Film as a Dopamine-Selective Polymer Electrode

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Electrochemical polymerization of 1,4-diaminobenzene in the KCl aqueous electrolyte at a potential of 0.600 V versus Ag/AgCl produces adherent poly(1,4-diaminobenzene) film on a gold electrode. The electrochemical behavior of dopamine and ascorbic acid at the polymer electrode prepared in this manner was examined by cyclic and differential pulse voltammetry. Voltammetry studies showed that polymeric film with a thickness corresponding to a 7-mC charge exhibited selective permeation for dopamine while retaining ascorbic acid. All the polymerization parameters affecting the permselective characteristics were systematically investigated and the optimum values were determined. The results showed that a polymeric membrane, owing to its permselective character, could be used as a dopamine-selective membrane.

Key Words: Poly(1,4-diaminobenzene), dopamine, ascorbic acid.

Introduction

Dopamine is an important neurotransmitter of catecholamines. Due to its electrochemical activity, its electrochemical detection is important in brain chemistry. However, the major problem is the interference of ascorbic acid, which coexists in biological fluids in very high concentration (100-500 mmol/L), while the dopamine level is much smaller (< 100 nmol/L).[1−7] Moreover, ascorbic acid can be oxidized at a potential close to that of dopamine; therefore, the addition of extra accumulation factors is necessary.[8,9] Significant advantages have been achieved by combining the electrocatalytic function of the catalyst with the charge-exclusion/pre-concentration features of Nafion. This problem can be circumvented using permselective polymeric membranes. Electrochemically generated conducting or non-conducting polymeric films have recently attracted increased interest due to their potential applications, such as in gas sensors[10−12] and biosensors,[13−19] and as permselective membranes.[20−22]

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In previous works,[23−28] we demonstrated that electrochemically synthesized films, such as poly(3-methylthiophene), polyaniline, polypyrrole, poly(*o*- toluidine), poly(1,3-phenylenediamine), and poly(*o*-phenylenediamine), could be used to differentiate dopamine and ascorbic acid. On the other hand, it was reported that poly(1,4-diaminobenzene) is a ladder polymer with phenazine rings. Poly(1,4-diaminobenzene)[29] films can be used to immobilize enzymes, and to prevent interference and fouling of the electrode surface. In addition, this polymeric film[30,31] has been used as a permselective membrane for halogenide ions. The present article[32] focuses on the electrochemical preparation, optimization, and voltammetric characteristics of the poly(1,4-diaminobenzene) film as a dopamine-selective polymeric membrane.

Experimental

Materials

1,4-Diaminobenzene was purchased from Merck (Darmstadt, Germany) and recrystallized from water before use (mp 139-142 °C). All the other chemicals used, such as dopamine hydrochloride, ascorbic acid, and KCl, were of analytical grade and purchased either from Sigma Chemical Company (St. Louis, MO, USA) or from Merck (Darmstadt, Germany). Aqueous solutions were prepared with double-distilled water. Ascorbic acid and dopamine solutions were prepared freshly for each experiment. Monomer solutions were purged with nitrogen gas for about 10 min before polymerization and the solution was blanketed with the same gas during electropolymerization. In voltammetric experiments, unless otherwise indicated, a 0.1-M aqueous Na_2SO_4 solution was used as the electrolyte.

Instrumentation

All electrochemical experiments were performed with a BAS 100 W (Bioanalytical Systems, Inc. West Lafayette, IN, USA) electrochemical analyzer in a 3-electrode cell, with a gold electrode (geometric area: 1.98 mm^2) as the working electrode, Ag/AgCl (BAS, MF-2063) as the reference electrode, and a Pt wire coil auxiliary electrode. In the cyclic voltammetry experiments the scan rate was 50 mV/s.

Preparation of poly (1,4-diaminobenzene) film

Prior to electropolymerization, gold disk electrodes, to be used as working electrodes, were cleaned according to the standard procedure,[33] and were polished with successively finer grades of diamond polishing compounds and aqueous alumina slurry (Johnson Matthey Catalog Comp., USA) down to 0.5 μm.

Electropolymerization was carried out in deaerated aqueous solution containing 1,4-diaminobenzene as the monomer and KCl as the supporting electrolyte. After polymerization, the resulting polymeric films were rinsed with deionized water for voltammetry measurement. Visual inspection revealed the formation of a thin and homogenous polymeric film of brownish color on the electrode surface. For the optimization of the polymerization parameters, differential pulse voltammetry (DPV) runs were performed in 0.1 M aqueous Na_2SO_4 (pH 6.0) containing 10 mM of dopamine or ascorbic acid.

Results and Discussion

In our preliminary experiments, cyclic voltammetry was used to determine the electrochemical polymerization potential of 1,4-diaminobenzene monomer in 0.1 M KCl solution. Cyclic voltammograms taken with a bare gold electrode, in the absence and presence of 1,4-diaminobenzene in KCl solution, are shown in Figure 1. On the voltammogram, irreversible oxidation currents appeared at 0.258 and 0.610 V peak potentials.

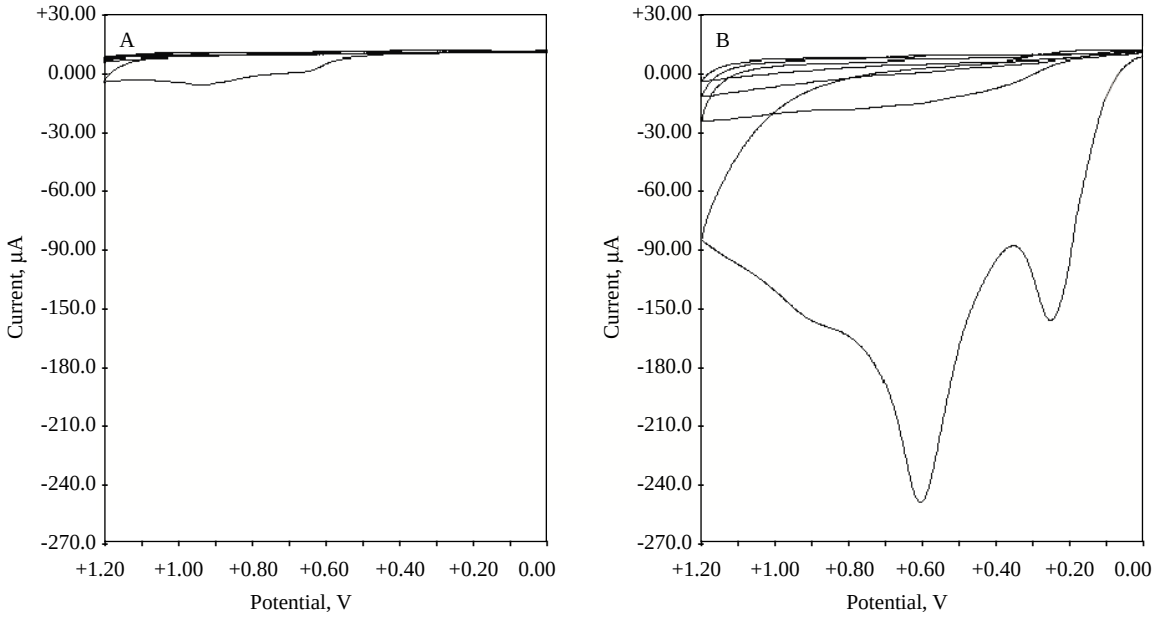

Figure 1. Cyclic voltammograms obtained with a bare Au electrode in 0.1 M KCl (A) and in 0.1 M KCl + 50 mM 1,4-diaminobenzene (B). Scan rate: 50 mV/s.

As discussed in our previous work[27,28] in which Au was employed as the working electrode, the decrease in the current magnitude with subsequent scans is indicative of the formation of a non-electroactive polymeric film. On the other hand, it has been known that non-electroactive polymeric films can be used as permselective membranes. Thus, in the present work, we considered the use of the poly (1,4-diaminobenzene) film as a permselective membrane, which could be selective for dopamine while preventing electroactive ascorbic acid permeation through the film. However, we observed that thin, stable, and insoluble polymeric films could be obtained in about 45 s at a constant potential of 0.600 V (versus Ag/AgCl) in 0.1 M KCl solution.

The effects of film thickness

In order to determine the optimum film thickness, the polymeric films at desired thickness were prepared at a potential of 0.600 V by varying the charge consumed during the electropolymerization process. Figure 2 shows the relationship between the peak currents and film thickness. The electroactive ascorbic acid current decreases with increasing film thickness and diminishes to zero for thicknesses > 7 mC. Once the optimum value for the studied parameter was determined, the effect of the next parameter was studied at optimum values of the already investigated parameters. As depicted in Figure 2, from the polymer electrode's responses to dopamine and ascorbic acid, it is seen that current due to ascorbic acid diminishes to zero for thicknesses

> 7 mC and that current for dopamine rises to a maximum value at a thickness of 7 mC. Therefore, the optimal film thickness for the polymer electrode was chosen as 7 mC.

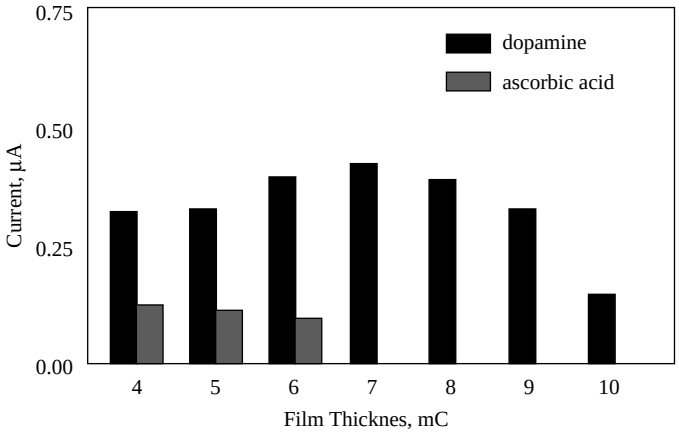

Figure 2. Effect of film thickness on the response.

The effect of polymerization potential on the response to dopamine

The polymerization potential dependence of the polymer electrode at optimum (constant) thickness was studied at 0.4-0.8 V. Currents due to dopamine obtained at different potentials are presented in Figure 3. As seen, peak currents increased with increasing potential and reached a maximum value at ca. 0.600 V, and then decreased. Thus, the optimal polymerization potential was found to be 0.600 V vs.Ag/AgCl.

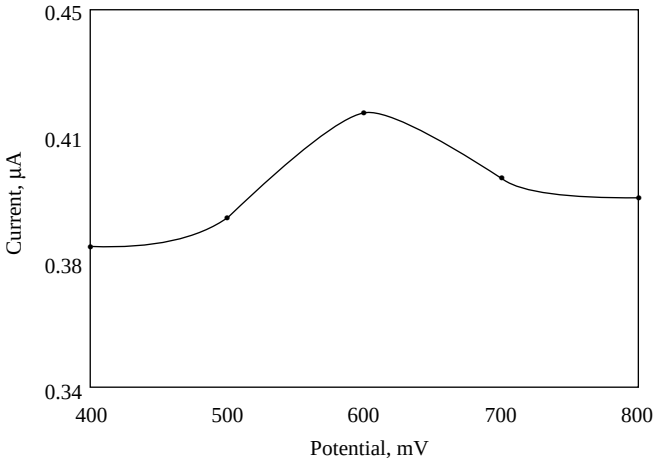

Figure 3. Effect of polymerization potential on the response.

Effects of monomer and electrolyte concentrations

Figures 4 and 5 reveal the effects of monomer and electrolyte concentration, respectively, used in the electropolymerization stage on the dopamine response of the polymer electrode at the optimal thickness. It is observed that the maximum voltammetric current response for dopamine was obtained in a solution containing 50 mM 1,4-diaminobenzene and 100 mM KCl. As expected, it was observed that the polymerization period decreased with increasing monomer concentration. Hence, the effect of the electrolyte type used in

DPV measurements was examined for Na_2SO_4, KCl, $NaNO_3$, NaCl, LiCl, $Mg(NO_3)_2$, $CaCl_2$, and $NaClO_4$ electrolytes, and the highest peak current for dopamine was obtained for Na_2SO_4. Therefore, the polymer electrode prepared under the optimum conditions was used in voltammetry studies.

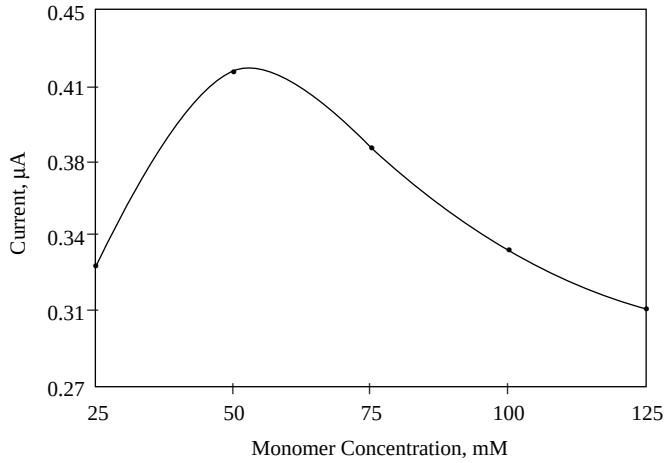

Figure 4. Effect of 1,4-diaminobenzene concentration on the response.

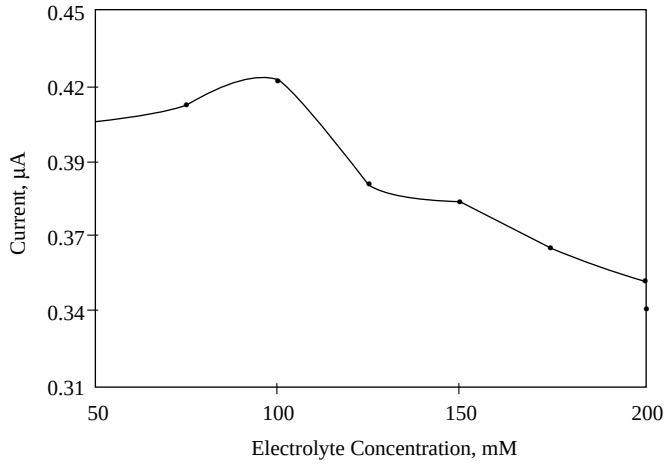

Figure 5. Effect of KCl concentration on the response.

Voltammetry Characteristics of the Optimized Poly(1,4-diaminobenzene) Films

DPVs of ascorbic acid at a bare gold and at the poly(1,4-diaminobenzene) electrodes are compared in Figure 6. An oxidation peak (at ca. 0.40 V) is observed at the bare electrode, whereas it disappears when a polymer electrode is used. This difference in the voltammograms confirms that the optimized polymeric film suppresses ascorbic acid oxidation. On the other hand, as expected and shown with DPVs in Figure 7, it is clear that the optimized poly(1,4-diaminobenzene) electrode permits greater penetration of dopamine when compared to a bare gold electrode.

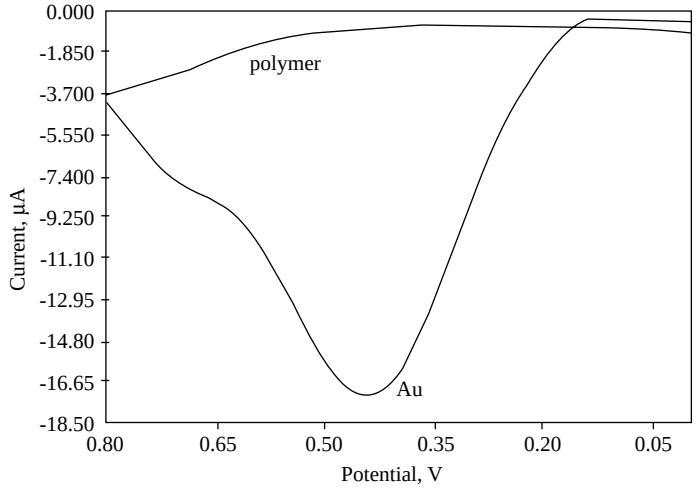

Figure 6. DPVs of 10 mM ascorbic acid at the bare and polymer electrodes.

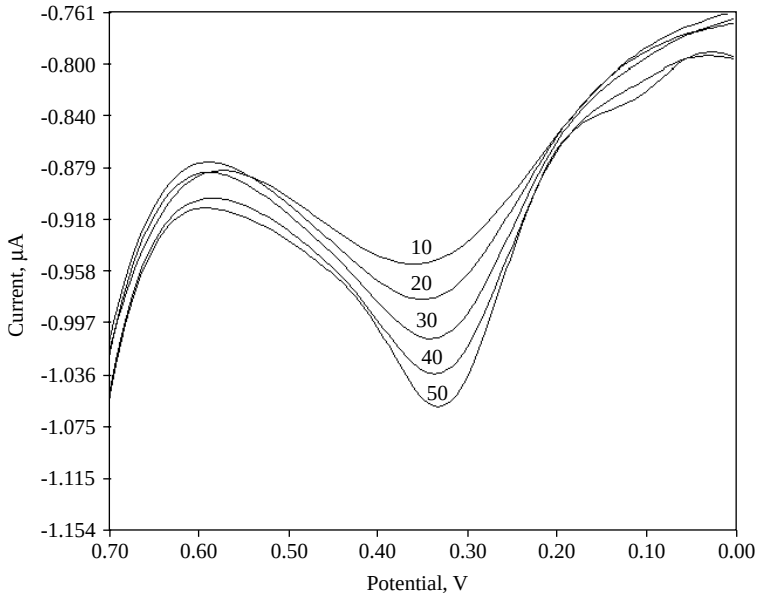

Figure 7. DPV of 10 mM ascorbic acid at various concentrations of dopamine (10-50 mM).

The voltammetric characteristics of the optimized polymeric film were also examined in ascorbic acid-dopamine mixtures, as indicated in Figure 8. The peak current due to dopamine was unaffected by increasing ascorbic acid concentration and peak currents increase linearly with increasing dopamine concentration, even in the presence of ascorbic acid. Moreover, from the successive runs of the optimized polymeric electrode in the binary mixture, it was observed that the voltammetric responses were almost invariable (not shown). This behavior reflects that the film was satisfactory.

In conclusion, we have shown in the present article that dopamine-selective poly(1,4-diaminobenzene) film could be easily prepared electrochemically from the relevant monomer in an aqueous solution (one-step procedure). The polymerization parameters affecting dopamine selectivity of the resulting polymeric film were systematically optimized. The excellent results obtained in the voltammetric studies showed that this polymeric film was selective for dopamine in the presence of ascorbic acid. Therefore, from a

technological point of view, it is claimed that this polymeric film can be used successfully as a dopamine-selective membrane.

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