Electrochimica Acta 55 (2010) 4421–4427

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Studies based on the electrochemical response of 2-(2-nitrophenyl)-1H-benzimidazole at chemically modified electrodes with over-oxidized poly-1-naphthylamine

Fabiana D'Eramo[a,*], Marcela Beatriz Moressi[a,*], Héctor Fernández[a], María Alicia Zón[a], Alejandro Heraldo Arévalo[a], Leonides Edmundo Sereno[a], Alejandro Álvarez-Lueje[b]

[a] Departamento de Química, Facultad de Ciencias Exactas, Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Agencia Postal No. 3, 5800 Río Cuarto, Córdoba, Argentina
[b] Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Olivos 1007, Santiago, Chile

ARTICLE INFO

Article history:
Received 30 December 2009
Received in revised form 16 February 2010
Accepted 20 February 2010
Available online 4 March 2010

Keywords:
2-(2-Nitrophenyl)-1H-benzimidazole
Chemically modified electrodes
Poly-1-naphthylamine
Over-oxidation
Electroanalysis

ABSTRACT

The development of a simple and efficient method to 2-(2-nitrophenyl)-1H-benzimidazole (NB) electrochemical determination using a polymer film coated chemically modified electrode is described. A glassy carbon (GC) electrode was modified employing an electro-polymerized film of 1-naphtylamine (1-NAP) followed by an over-oxidation treatment in 0.2 M sodium hydroxide solution (poly-1-NAPox electrode).

The electrochemical behaviour of NB at the poly-1-NAPox electrode was investigated in a mixture of 10% ethanol + 90% buffer solution (pH 2) by cyclic voltammetry (CV) and square-wave voltammetry (SWV). The experimental results suggested that the poly-1-NAPox electrode had a good effect on NB electrochemical response because it avoided the electrode surface fouling as a consequence of the adsorption of NB reduction products, which was found when a bare GC electrode was employed as the working electrode. The NB cathodic current was dependent on the polymeric film over-oxidation degree (α).

NB could be determined in the range from 2×10^{-6} to 5×10^{-5} M. The NB detection and quantification limits were 5×10^{-7} and 1.7×10^{-6} M, respectively. The percent relative standard deviation of the peak current to 10-replicated measurement using 1.2×10^{-5} M NB solution was 1.4%. The method showed to be rapid, simple and with a good sensitivity.

1. Introduction

The objective of NB synthesis is to develop new compounds with potential biological activities. The benzimidazole nucleus presents a wide spectrum of biological activities such as antiparasitic, antibacterial, antiviral and especially, antitumoral amongst others [1,2]. In addition, NB has an aromatic nitro group in its molecular structure, which is widely used as pharmaceuticals, pesticides, etc. The presence of an aromatic nitro group in core 2 position allows NB physicochemical, electrochemical and spectroscopic characteristics different to the benzimidazole nucleus. These properties could be used to develop precise, accurate and selective new analytical methods to NB quantification and characterization.

NB has previously studied by spectroscopic and chromatographic methods as part of the characterization five nitroarylbenzimidazole derivatives with activity against Trypanosoma cruzi: [2] and recently, has been electrochemically studied using differential pulse polarography, tast polarography and cyclic voltammetry on dropping or hanging mercury electrodes, respectively. In addition, a differential pulse polarography method has been proposed for its quantification [4].

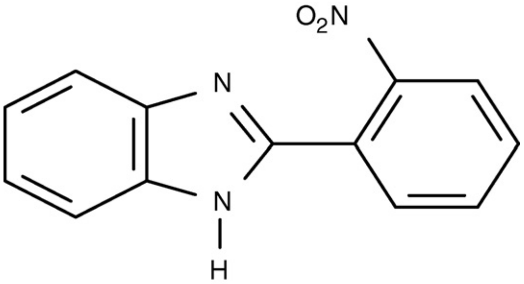
The electrochemistry has a well-defined role in drug analysis. Therefore, several electroanalytical methods have been developed for this purpose. Moreover, solid electrodes are particularly interesting due to their high sensitivity and versatility, with an useful large potential window and different materials, which allow to obtain several sensing units with distinct selectivity degree [5,6]. In addition, they can be modified easily by different compounds and technologies, which allow increasing their sensibility, selectivity and to avoid surface fouling problems due to the reaction product/s adsorption and favouring, in some cases, the reproducibility.

On the base of these results, our research group has suggested the possibility of using chemically modified electrodes by electrochemical polymerization of mono-nuclear or poly-nuclear aromatic amines [7–11]. The good electroactive properties of these polymers have allowed us to prepare sensors with a high degree of selectivity and with a good reproducibility [12–16].

---

* Corresponding authors. Fax: +54 358 4676233.
E-mail addresses: fderamo@exa.unrc.edu.ar (F. D'Eramo), mmoressi@exa.unrc.edu.ar (M.B. Moressi).

0013-4686/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2010.02.067



Scheme 1. Chemical structure of NB.

On the other hand, conducting polymers are a natural choice for preparing arrays of electrochemical sensors by considering that their electrochemical properties can be modulated by introducing chemical modifications on these sensitive materials. In addition, it is well known that the electrochemical properties of the obtained polymeric films strongly depend on the synthesis conditions. Therefore, different electrochemical options are available, which allow the rapid and simple modification of the electrochemical properties of the polymeric films [17].

We have recently reported a simple and effective method to modify a GC electrode to get the desired properties [15]. In that article, the determination of dopamine in the presence of ascorbic acid with a good sensitivity using a chemically modified over-oxidized poly-1-naphthylamine electrode (poly-1-NAPox electrode) was reported. The poly-1-naphthylamine (poly-1-NAP) film was deposited on the GC electrode surface by continuous electrooxidation of the corresponding monomer and then, it was over-oxidized in an alkaline solution. Over-oxidation of the polymer was the result of the attack of OH^- on the polymer units given a higher negative charged density in the polymeric film, which depend on the medium pH [15].

In this paper, the poly-1-NAPox electrode was used to NB determination. This methodology showed a fast experimentation time, good suitability to NB analysis and an acceptable electrode lifetime. The method analytical performance and the interaction between poly-1-NAPox electrode and NB were investigated using CV and SWV.

2. Experimental

2.1. Chemicals and reagents

NB (MW: 239.06 g mol^{-1}, MP: 277–278.5 °C), was prepared by following a previously reported procedure [3,4,18,19]. The compound purity was assessed by melting point, ^1H NMR, ^{13}C NMR and IR. Its chemical structure is shown in Scheme 1.

1-NAP from Merck p.a. was sublimated at 40 °C under reduced pressure and kept under vacuum [7]. All the other reagents were analytical grade and were used without further purification. The phosphate buffer solutions pH 2 were prepared by mixing 0.1 M KH_2PO_4 and 0.1 M H_3PO_4.

All solutions were prepared with ultrapure water from LABCONCO equipment model 90901-01 (HPLC grade water). Stock solutions of NB were prepared by dissolving the appropriate NB amount in 10 mL of ethanol. Working solutions were prepared by accurate serial dilution from the stock solutions of NB using a mixture of 10% ethanol + 90% phosphate buffer solution (pH 2).

The solutions used to obtain the poly-1-NAP were prepared by weighing given amounts of 1-NAP and dissolved in an acidic supporting electrolyte solution ($HClO_4$ solution at pH 1). Dissolved oxygen in the solution was removed by bubbling with high purity nitrogen and a nitrogen atmosphere was kept throughout experiments.

2.2. Apparatus and procedure

Electrochemical measurements were carried out using an AUTOLAB PGSTAT 30 potentiostat/galvanostat, run with GPES software, version 4.9 (Eco Chemie, Utrech, The Netherlands). A conventional three-compartment cell was used with a GC disk (BAS, $\phi = 3$ mm, $A = 0.071$ cm^2) as the working electrode, a Pt foil as the auxiliary electrode and an aqueous potassium saturated calomel electrode (SCE) as the reference electrode. The working electrode was polished with 0.3 μm alumina slurry, rinsed with a copious amount of triply distilled water and then sonicated for 5 min to remove any residual polishing material. Then, the GC electrode was activated electrochemically in 1 M NaOH aqueous solution by applying a potential step from 0 to +1.2 V over 5 min according to a procedure previously described by Anjo et al. [20].

In CV experiments, the scan rate (v) was varied from 0.01 to 5.0 V s^{-1}. The voltammograms were corrected for iR drop by positive feedback technique. The net charge and net current were calculated by subtracting from the total values the corresponding background values.

The working temperature was kept constant at 20 ± 0.1 °C for all measurements using a LAUDA K4R thermostat-cryostat.

3. Results and discussion

3.1. Cyclic voltammetry

Representative NB cyclic voltammograms in the mixture 10% ethanol + 90% buffer solution of pH 2 at a bare GC electrode is shown in Fig. 1a. It shows the usual reduction electron transfer reactions, which are characteristic of this class of compounds. According to molecular structure, the NB synthesized has a benzimidazole core and a nitrobenzene compound (Scheme 1). The imidazole does not show any reduction peak in aqueous media within the normally available potential range in our working conditions [21]. This lack of redox activity is associated with the aromatic nature of the five-member system, which can exist in several resonance structures. This behaviour could explain the high stability of imidazole to chemical reaction. On the other hand, NB follows reduction mechanism of nitro-aromatic compounds [22]. For comparison, nitrobenzene was examined in the potential range from 0.5 to −0.75 V (Fig. 1b) under the same experimental conditions. As it can be seen, both NB and nitrobenzene voltammograms were very similar.

Therefore, NB cyclic voltammograms show, during the first scan from positive to negative potentials, a single cathodic reduction peak (peak I) at about −0.20 V at all scan rates measured, which was similar to the behaviour found for nitrobenzene. The reduction wave is attributed to a four electrons/four protons nitro-reduction to produce the corresponding hydroxylamine derivate. Thus, the NB overall reduction process (peak I in Fig. 1a) could be represented by

$$C_7H_5N_2–C_6H_4–NO_2 \xrightarrow{4e^-, 4H^+} C_7H_5N_2–C_6H_4–NHOH + H_2O \qquad (1)$$

This was inferred by comparing the experimental current function of peak I (defined as $\Psi_I = ip_I/ACv^{1/2}$, where i_{pI} is the cathodic peak current of NB, C the NB bulk concentration, A the working electrode area) with that obtained for nitrobenzene in the same experimental conditions [23,24]. The experimental Ψ was calculated at $v > 1.5$ V s^{-1} because under this condition the amount of product formed is negligible and therefore the surface coverage of the electrode due to adsorption is insignificant (see below). The values