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Electrode Modified with the Ionic Liquid [P$_{6,6,6,14}^+$]$_2$[MnCl$_4^{2-}$] for the Determination of Bisphenol A in Plastic Samples

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This paper describes a new and simple electrode for the determination of bisphenol A (BPA) in different plastic samples using carbon paste electrode (CPE) modified with a trihexyltetradecylphosphonium tetrachloromanganate(II) ([P$_{6,6,6,14}^+$]$_2$[MnCl$_4^{2-}$]) magnetic ionic liquid (MIL/CPE). Electrochemical characterization of MIL/CPE by cyclic voltammetry and electrochemical impedance spectroscopy indicated that MIL facilitated the electron transfer. Using squarewave voltammetry (SWV) under optimized conditions, the calibration curve showed a linear range for BPA from 2.0 to 53.0 µmol L^{-1}, with limit of detection (LOD) of 0.87 µmol L^{-1}. The proposed electrode demonstrated good precision with coefficients of variation of 4.5% (intra-day, n = 10), 2.0% (inter-day, n = 5) and 1.5% (electrode-to-electrode repeatability, n = 3). Recoveries of 93.0 to 101.1% demonstrated that the method is suitable for practical applications.

Keywords: ionic liquid, electrode chemically modified, bisphenol A

Introduction

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) is an estrogenic environmental toxin used in the production of polycarbonate (PC) and epoxy resins to produce plastics. This compound is highly resistant to chemical degradation and is present in a variety of products including packaging for food and drinks, baby nipples, water bottles and medical devices.[1,2] BPA is considered to be an endocrine disruptor because it is able to mimic or alter the normal hormonal activity of humans and animals, leading to negative health effects even in small concentrations.[1,3-5] It acts especially on the reproductive system, being able to cause disorders such as diminished sperm quality, birth defects and breast and prostate cancers.[2-4,6,7] For this reason, the development of sensitive methods capable of detecting BPA in lower concentrations is of paramount importance.

In recent years, many analytical methods have been described in the literature for the determination of BPA in different samples, including gas chromatography,[8-10] high-performance liquid chromatography,[11-13] spectrometric

methods[14,15] and electrochemical methods using different electrodes.[16-21] In this regard, the electrochemical methods stand out from the others because they present advantages, especially in relation to the low cost (equipment, maintenance and reagents), simple operation, rapid response and suitability for field-monitoring (miniaturization). In addition, the development of electrodes modified with different materials, such as enzymes, polymers, ionic liquids and nanomaterials, has contributed to improving the selectivity and sensitivity of this method.[7,17-25]

Ionic liquids (ILs) are compounds that have high conductivity and viscosity. They are widely used for the total or partial substitution of the non-conducting mineral oil used as a binder in carbon pastes.[26,27] The electrodes constructed with these materials present a higher and faster rate of electron transfer along with increased sensitivity and stability of the measurements.[28-32] Recently, a new subclass of ILs known as magnetic ionic liquids (MILs) has been the object of intense study, aimed at a number of innovative applications in chemistry, especially in analytical chemistry.[33-35] These magnetic compounds are produced by incorporating a paramagnetic component into the cation or anion present in the IL structure.[26,35,36] In general, they

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are ions of transition metals (most commonly manganese and cobalt) or lanthanides (neodymium, gadolinium, for example) and they have physicochemical properties similar to those presented by ILs.[35]

These materials have been introduced in analytical chemistry because of their outstanding properties, including multiple solvation capacity and high stability in different media. The applications include their use as sorbent phases in extraction and microextraction approaches, allowing the efficient determination of different analytes in several matrices. They can also be applied to membranes, gas absorption and density measurements.[33] In electrochemistry, this field is new and still little explored. However, studies for the determination of iron reported by Osborne *et al.*[37] and Fan *et al.*[38] have shown that these materials are sensitive and selective, providing an innovative technological tool and paving the way for new research in the field of electrochemistry and electroanalysis.

In this paper, we describe the simple and rapid construction of a sensitive electrode based on the modification of the internal material of a carbon paste electrode with the hydrophobic magnetic ionic liquid trihexyltetradecylphosphonium tetrachloromanganate(II) ($[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$) for the partial replacement of the non-conductive material. The proposed electrode, MIL/CPE (carbon paste electrode), was employed for the first time to determine BPA in real samples using square wave voltammetry (SWV). The method exhibited good accuracy and precision, as assessed through recovery studies and comparison with results provided by high performance liquid chromatography (HPLC) and spectrophotometric techniques.

Experimental

Reagents, solutions and samples

Trihexyltetradecylphosphonium chloride ($[P_{6,6,6,14}^+][Cl^-]$) (97.7%) and manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) (98.0%) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and they were used to synthesize MIL. Bisphenol A (BPA), boric acid (H_3BO_3), phosphoric acid (H_3PO_4), acetic acid (CH_3COOH), potassium ferricyanide ($K_3[Fe(CN)_6]$) and potassium ferrocyanide ($K_4[Fe(CN)_6]$) were purchased from Sigma-Aldrich. A BPA standard solution was daily prepared in a mixture of water:ethanol (7:3, v/v), and the reference solutions were prepared from stock solutions by appropriate dilution. Britton-Robinson buffer (0.1 mol L^{-1}, pH 3.0-12.0) was prepared by mixing H_3BO_3, H_3PO_4 and CH_3COOH and used as the supporting electrolyte in the method

development and determination of BPA. Acherson 38 graphite powder (Fischer) and mineral oil (Sigma-Aldrich) of high purity were used in the preparation of the carbon paste. All reagents were of analytical grade and used as received without further purification. Ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, USA) at a resistivity of 18.2 MΩ cm and was used in the preparation of all aqueous solutions. Different plastic samples (polypropylene (PP) cup, polystyrene (PS) plastic cup, polyvinylpyrrolidone (PVC) food package and baby nipple) were purchased in a supermarket located in Florianópolis City (Santa Catarina State, Brazil) and used in the determination of BPA using the method developed (electrochemical) as well as spectrophotometric and HPLC (for comparison purposes).

Instrumentation

Electrochemical impedance spectroscopy (EIS) analysis was performed on an Autolab PGSTAT128N potentiostat/galvanostat equipped with a FRA module for impedance (Eco Chemie, The Netherlands). Square wave voltammetry (SWV) and cyclic voltammetry (CV) analyses were performed on an Autolab PGSTAT101 potentiostat/galvanostat (Eco Chemie, The Netherlands), operating with data processing software (NOVA, version 1.10). Spectrophotometric measurements were taken on a Cary 60 UV-Vis spectrometer (Agilent Technologies, USA) with a quartz cell (optical path of 1.0 cm).

In the HPLC analysis, an Agilent 1260 Infinity HPLC system (Santa Clara, USA) equipped with a quaternary pump and diode array detector (DAD) was used for the determination of BPA. The HPLC system was equipped with a Rheodyne manual injector containing a loop of 20 μL and the separation was performed using a Zorbax Extend C18 column (5.0 μm, 4.6 × 250 mm). An isocratic method using acetonitrile:water (60:40) was adopted with a total flow rate of 1 mL min^{-1} and the analysis was performed at 200 nm. The characterization of MIL was carried out on a Varian Cary-50 UV-Vis (Varian Inc., Palo Alto, USA) spectrophotometer.

Synthesis and characterization of MIL

Trihexyltetradecylphosphonium tetrachloromanganate(II) ($[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$) was synthesized according to previously described procedures.[39,40] Briefly, for the synthesis of $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$, a mass of $[P_{6,6,6,14}^+][Cl^-]$ (1 equiv.) was mixed with $MnCl_2 \cdot 4H_2O$ (0.5 equiv.) in dichloromethane, and this mixture was reacted for 24 h at room temperature under constant

stirring. The product was then dried overnight at 60 °C in a vacuum oven. The characterization of MIL was carried out by UV-Vis spectroscopy and the results are shown in the Supplementary Information (SI) section (Figures S1 and S2). According to these results, characteristic peaks corresponding to the incorporation of manganese in the IL structure (region from 425-465 nm) are in agreement with data previously reported in the literature.[39,40]

Construction and electrochemical characterization of electrode

The construction of the proposed electrode is based on the internal modification of a carbon paste electrode with the magnetic ionic liquid. The manufacture of this electrode is simple, fast and of low cost. It consists of macerating 150 mg of graphite powder, 30 mg of MIL and 20 mg of mineral oil in a small mortar for 10 min. After homogenization, the paste formed was packed into a plastic syringe (1.0 mm internal diameter) and a copper wire was inserted to establish the external electrical contact. The obtained electrode was referred to as MIL/CPE and was used as the working electrode. This electrode was stored at room temperature when not in use. The other electrodes (unmodified CPE and MIL/CPE with different MIL:mineral oil proportions) were constructed similarly to MIL/CPE to evaluate the effect of the MIL:mineral oil proportions employed in this study.

Electrochemical electrode characterization was conducted by EIS and CV. CV measurements were recorded in a KCl solution (0.1 mol L^{-1}) containing 5.0 mmol L^{-1} [Fe(CN)$_6$]$^{3-/4-}$ cycling the potential between −1.0 and +0.8 V at a scan rate of 0.05 V s^{-1}. EIS measurements were performed using the same system (5 mmol L^{-1} [Fe(CN)$_6$]$^{3-/4-}$ in 0.1 mol L^{-1} KCl) in open-circuit mode, with an amplitude of 10 mV and a frequency range of 0.1 to 100,000 Hz.

Electrochemical measurements and electrodes

The electrochemical experiments were carried out at room temperature (ca. 25 °C) using a conventional three-electrode system: Ag/AgCl (3.0 mol L^{-1} KCl) as the reference electrode, a platinum plate as the auxiliary electrode and the proposed electrode (MIL/CPE) as the working electrode. All experiments were carried out in an electrochemical cell containing 10 mL of supporting electrolyte (0.1 mol L^{-1} Britton-Robinson, pH 7.0 or 0.1 mol L^{-1} KCl) and the required volume of analyte solution (standard solution or BPA sample).

CV measurements were recorded by cycling the potential from −0.3 to +1.2 V at a scan rate of 0.02-0.09 V s^{-1}. SWV measurements were performed by scanning the potential from +0.4 to +1.0 V at a frequency of 30 Hz, pulse amplitude of 80 mV and scan increment of 4 mV. All measurements were reported *vs.* Ag/AgCl (3.0 mol L^{-1} KCl) and a stirring time of 60 s was used to homogenize the solutions. The obtained peak currents, corresponding to the electrochemical oxidation of BPA, are proportional to the analyte concentrations in solution. The data reported for the optimization of the experimental conditions, the calibration curve and the determination in real samples are the average of three measurements (n = 3).

Preparation of plastic samples and determination of BPA

The plastic samples (PP cup, PS plastic cup, PVC food package and baby nipple) were purchased from a local supermarket and applied in the determination of BPA. The first step in the preparation of the samples was pre-cleaning in an ultrasonic bath with an ethanol:water (8:2, v/v) mixture for 15 min followed by successive rinsing with ethanol and Milli-Q water and drying at room temperature (ca. 25 °C). The samples were then cut into small pieces (2.0 g) and left under heating (80 °C) for 48 h in 50 mL of Milli-Q water. After cooling at room temperature and filtering, the residual water was stored under refrigeration at 4 °C for use in the determination of BPA. This procedure was based on the work published by Li *et al.*[41]
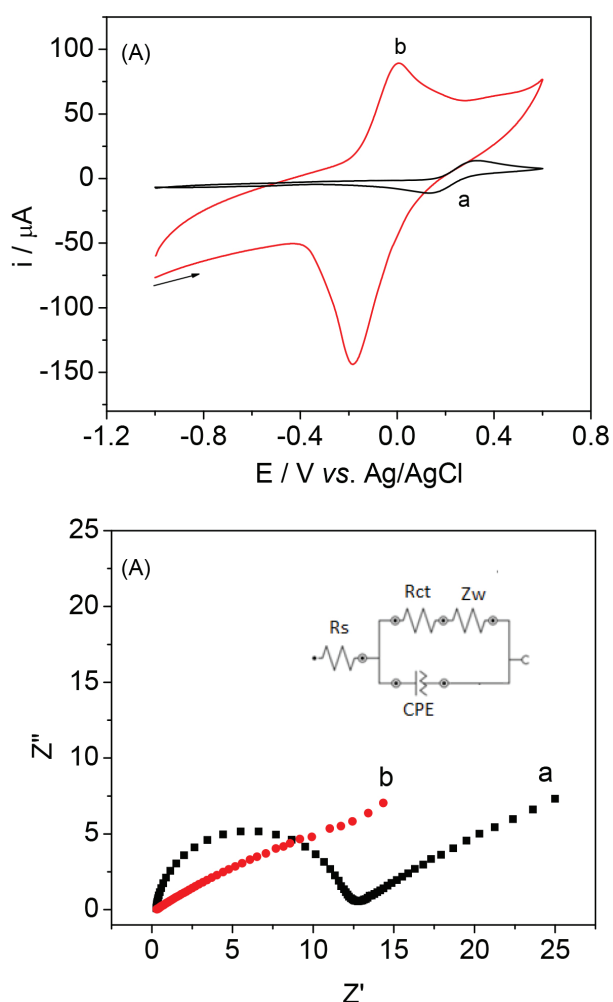
A standard addition method was used to evaluate the analytical performance of the electrode. Aliquots of the prepared sample were transferred to an electrochemical cell containing the supporting electrolyte (0.1 mol L^{-1} Britton-Robinson buffer, pH 7.0) and the BPA content was quantified using SWV after successive additions of a standard solution of BPA (1.0 mmol L^{-1}). All measurements were performed at room temperature (ca. 25 °C) and the quantification was based on the resulting peak currents (at a potential of approximately +0.765 V *vs.* Ag/AgCl), using the optimized SWV parameters (frequency of 30 Hz, amplitude of 80 mV and increment of 4 mV). For comparison purposes, the samples were also analyzed employing a spectrophotometric method (λ = 279 nm) and HPLC. The results were expressed as the mean value of three determinations.

Results and Discussion

Electrochemical characterization of MIL/CPE

The electrochemical characterization of the proposed electrode was performed in EIS and CV studies, using Fe(CN)$_6$$^{3-/4-}$ as the redox probe, to evaluate the effect of

the modification on the electrochemical behavior of the electrode. Figure 1A shows the cyclic voltammograms obtained for the unmodified electrode (a) and the electrode modified with MIL (b) in 0.1 mol L^{-1} KCl solution containing 5 mmol L^{-1} Fe(CN)$_6^{3-/4-}$ at a scan rate of 0.05 V s^{-1}. It can be observed that a pair of well-defined redox peaks related to the Fe(CN)$_6^{3-/4-}$ was obtained on employing the electrode b (proposed electrode). The strong increase in the peak current (decrease in the distance between the peak potentials (ΔE_p) and peak shift towards to lower potentials observed with the proposed electrode (compared to CPE)) indicates that the electron transfer reaction was favored both kinetically and thermodynamically in the presence of MIL.
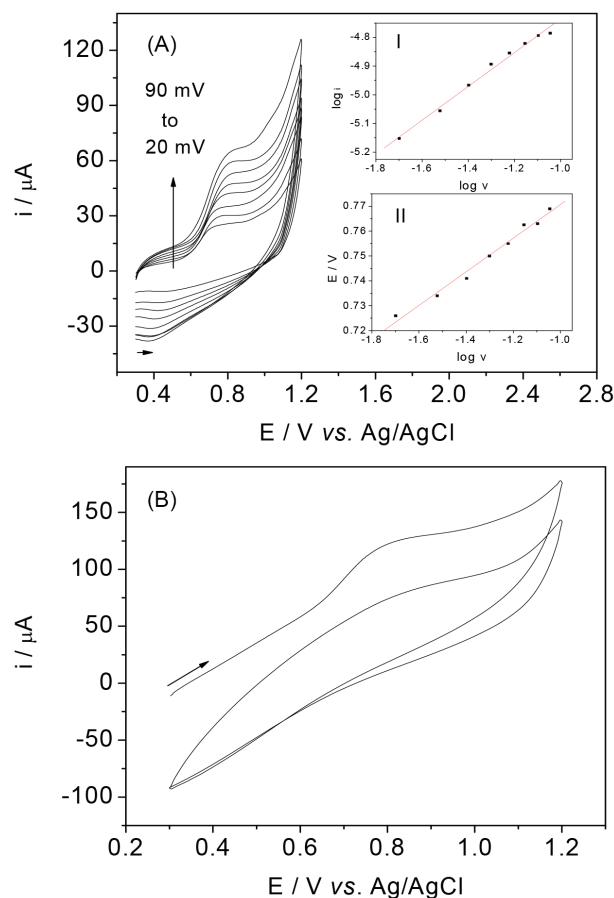
Nyquist plot and is related to the electron transfer kinetics of the redox probe at the surface of electrode. This study was performed under the same conditions and with the same electrodes as those employed in CV studies. Figure 1B shows the Nyquist plots obtained for the electrodes: (a) CPE and (b) MIL/CPE. It can be observed that a much faster electron transfer rate is obtained with the proposed electrode (R_{ct} of 0.026 kΩ) compared to the unmodified electrode (CPE, R_{ct} of 12.5 kΩ), indicating that MIL can facilitate the charge transfer process due to its high conductivity, reinforcing the results obtained by CV.

Electrochemical behavior of BPA at MIL/CPE

The electrochemical behavior of BPA on the surface of MIL/CPE was investigated by scan rate studies using CV (Figure 2). The measurements were performed in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) containing 35 µmol L^{-1} BPA, with scan rates varying from 0.02 to

Figure 1. (A) Cyclic voltammograms and (B) Nyquist plots obtained for (a) bare CPE and (b) MIL/CPE in 0.1 mol L^{-1} KCl solution containing 5 mmol L^{-1} Fe(CN)$_6^{3-/4-}$ at a scan rate of 0.05 V s^{-1} (CV) and open circuit mode, 10 mV amplitude and frequency range of 0.1-100 000 Hz (EIS).

Figure 2. (A) Cyclic voltammograms obtained using MIL/CPE in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) containing 35 µmol L^{-1} BPA, with scan rate varying from 0.02 to 0.09 mV s^{-1}; insert (I): plot of log i_p *vs.* log ν; insert (II): plot of E_{pa} *vs.* log ν. (B) Consecutive cycles for BPA oxidation process using MIL/CPE in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) containing 50 µmol L^{-1} BPA, with scan rate of 0.05 mV s^{-1}.

The electrochemical impedance study was performed in order to evaluate the effect of the electrode modification on the charge transfer resistance (R_{ct}). The R_{ct} value corresponds to the diameter of the semi-circle in the
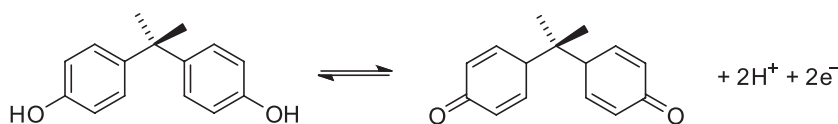
0.09 V s^{-1} (at intervals of 0.01 V s^{-1}). In this study, it was observed (see the voltammograms of Figure 2A) that the oxidation current of BPA increases with increasing scan rate. In addition, the plot of log i$_p$ *vs.* log ν (i$_p$ is the peak current and ν the scan rate, Figure 2A-II) presents a linear relationship with a slope of 0.589 (in agreement with a value reported in the literature),[42] suggesting that the oxidation of BPA on the electrode surface is a process controlled exclusively by diffusion.

The relationship between the anodic peak potential (E$_{pa}$) and log ν is also shown in Figure 2A-II. On observing the slope obtained from the linear relationship (equation: E = 8.38 × 10^{-1} ± 4.57 × 10^{-3} + 6.74 × 10^{-2} ± 3.46 × 10^{-3} log ν, r^2 = 0.992 (r^2 is the coefficient of correlation)) established by the Laviron equation,[43,44] it is possible to identify the number of electrons involved in the BPA oxidation (slope = 2.303 RT/αnF, where α = 0.5 for irreversible processes (α is the electron transfer coefficient, n is the electron transfer number, F is faraday constant, R is universal gas constant, T is temperature)).[45] According to the results obtained in this study, the number of electrons involved is two (n = 2, Scheme 1). Therefore, it was concluded that the BPA oxidation at MIL/CPE is an irreversible diffusion-controlled process involving the participation of two electrons.

Figure 2B shows two consecutive cycles for the BPA oxidation process using the same electrode (no surface renewal). It can be observed that in the second cycle there is a considerable loss of current (which is almost zero in relation to the first cycle). This is because in the oxidation of BPA, a polymeric product (non-electroactive) was formed, blocking the electrode surface. This has also been observed in other studies reported in the literature.[18,46,47] Thus, it is necessary to remove the contaminated surface after each measurement. In this regard, electrodes based on carbon paste have an important advantage over film electrodes because a new surface is created simply by removing some of the paste, while the electrode film needs to be discarded after each measurement.
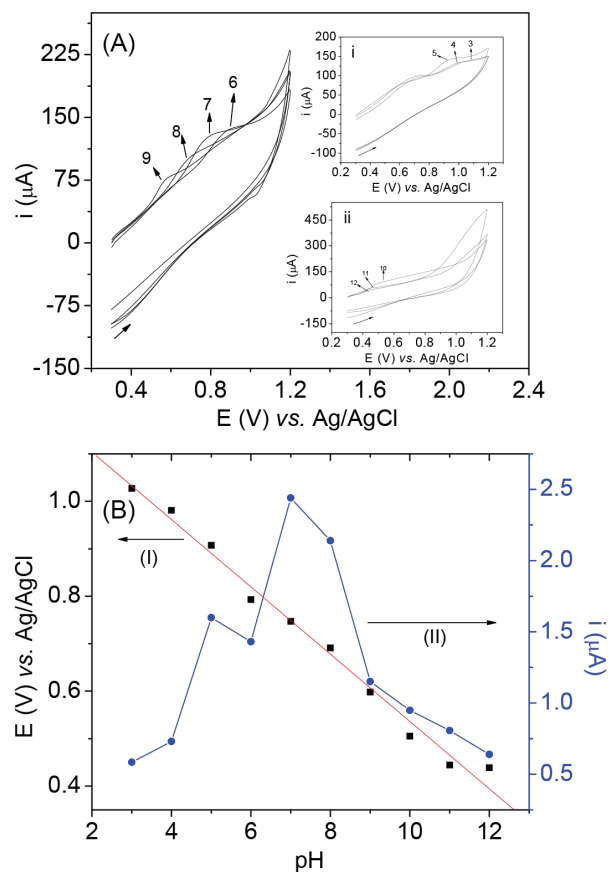
Influence of pH on the electrochemical behavior of BPA

The effect of the solution pH on the electrochemical behavior of BPA was studied by cyclic voltammetry employing MIL/CPE at a scan rate of 0.05 V s^{-1} in 0.1 mol L^{-1} Britton-Robinson buffer in the pH range of 3.0 to 12.0. Figure 3 shows that the peak potential and current of BPA are pH-dependent because they vary as the pH value of the electrolyte changes. The highest peak current for BPA was obtained at pH 7.0 and a decrease in the current can be observed above this pH. Thus, pH 7.0 was selected for subsequent analytical studies.

Figure 3. (A) Cyclic voltammetry for BPA (50 μmol L^{-1}) in 0.1 mol L^{-1} Britton-Robinson buffer (pH from 3.0 to 12.0) at 0.05 V s^{-1}, and (B) influence of pH value on the resulting peak current and peak potential of MIL/CPE.

In addition, Figure 3B shows the linear relation between the peak potential (E$_{pa}$) and the pH of the electrolyte support, according to the following equation: E$_{pa}$ = 1.24 ± 2.22 × 10^{-2} − 7.02 × 10^{-2} ± 2.77 × 10^{-3} pH (r^2 = 0.994). The oxidation peak potential of BPA shifted towards negative values with increasing pH, indicating that protons are directly involved in the BPA oxidation process. The slope of 70.2 mV pH^{-1} (close to the theoretical value


Scheme 1. Proposed reaction for BPA oxidation at the MIL/CPE surface.

of −59.2 mV pH^{-1} of the Nernst equation) indicates that the numbers of electrons and protons transferred in the electrochemical BPA reaction were the same. Therefore, the oxidation of BPA on the surface of MIL/CPE involved the transfer of two protons and two electrons (see Scheme 1).

Electrochemical behavior of BPA at different electrodes

Figure 4 shows the cyclic and square wave voltammograms of MIL/CPE (a) and bare CPE (b) in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) with 100 and 38.5 μmol L^{-1} BPA, respectively. It can be observed from the cyclic voltammograms (Figure 4A) that the oxidation current is higher at MIL/CPE, while no corresponding reduction peak is observed, indicating that the BPA redox reaction on the electrode surface is irreversible under these working conditions (as commonly found in BPA studies).[26,41,46] The BPA oxidation peak shifted towards higher potentials on using the modified electrode indicates that the reaction was not thermodynamically favored in comparison to the bare CPE. However, a considerable increase in the BPA oxidation peak current was also observed for this electrode, showing that kinetically this reaction is favored.

Figure 4B shows the square wave voltammograms obtained using MIL/CPE (a) and CPE (b). Similarly to the cyclic voltammetry results, a higher peak current was obtained for BPA using MIL/CPE in comparison with the unmodified electrode. The proposed electrode (curve a) provided a well-defined peak current, which was approximately 10 times higher than that observed for the bare CPE (curve b). These results suggest a faster oxidation process on the surface of the modified electrode due to the presence of MIL, which considerably increases the conductivity of the electrode (see EIS, Figure 1B) and presence of charges in its structure. The enhancement in the response also may occur due to the chemical interaction between the hydrophobic [P$_{6,6,6,14}$$^+$]$_2$[MnCl$_4$$^{2-}$] and BPA, since this compound exhibits low-polarity (log P around 3.6), which contributes to the extraction of analyte of the hydrophilic support electrolyte favoring its pre-concentration on the electrode surface.

Figure 4C shows the principle of the electrode functioning. In this process, BPA is attracted to the electrode surface by MIL, favoring the pre-concentration of the electroactive species on the electrode surface. BPA is then electrochemically oxidized at a potential of +0.765 V *vs.* Ag/AgCl, generating a current signal that is proportional to its concentration in the solution. This process is irreversible, as demonstrated by the cyclic voltammograms (Figure 4A).
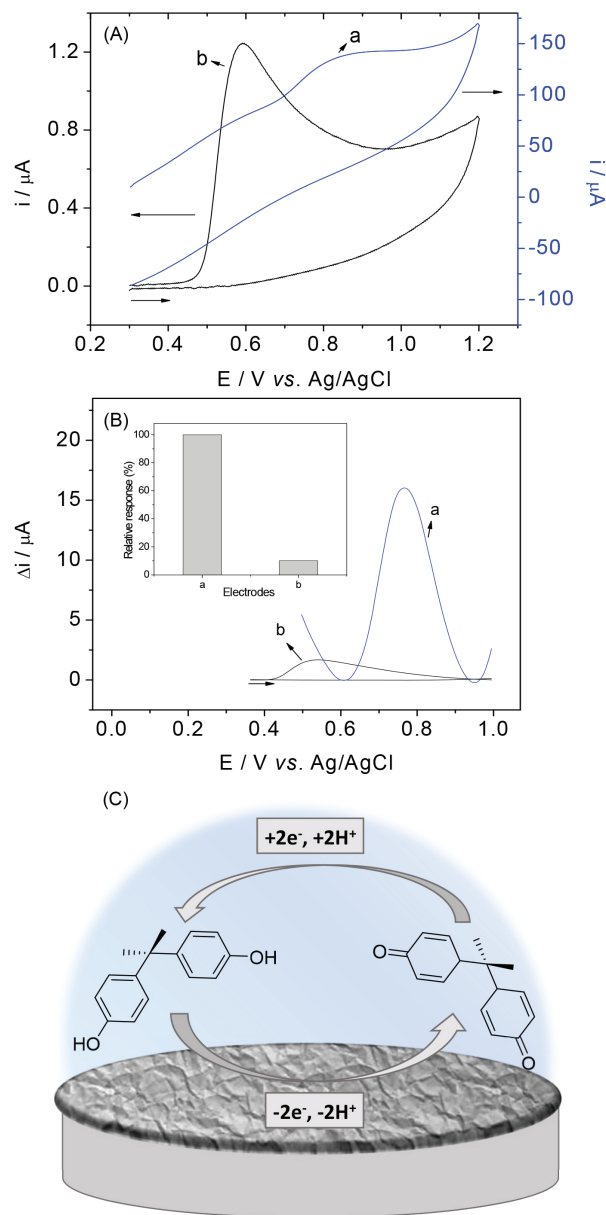
Figure 4. (A) Cyclic voltammograms obtained using (a) MIL/CPE and (b) CPE in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) containing 100 μmol L^{-1} BPA at a scan rate of 0.05 V s^{-1}; (B) square wave voltammograms obtained using MIL/CPE and (b) CPE in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) containing 20 μmol L^{-1} BPA. Inset: relative response (%); (C) schematic representation of the principle of the proposed electrode functioning.

Optimization of the electrode construction and operational parameters

In order to optimize the electrode construction and experimental conditions of the proposed method, the proportion of MIL, nature of the supporting electrolyte and parameters of the electroanalytical technique were investigated in triplicate. These variables were evaluated in order to obtain the best analytical performance (better

sensitivity and peak definition and a lower limit of detection (LOD)).

Initially, the effect of MIL was investigated through the construction of electrodes using different proportions of MIL (conductor material) and mineral oil (non-conductive material). The proportions investigated were: 0:50, 10:40, 20:30, 30:20, 40:10 and 50:0, MIL:mineral oil (m/m). The electrode performance was evaluated by SWV using 19.6 μmol L^{-1} BPA in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0). The combination that presented the highest synergism (best analytical response, as well as increased stability of the measurements) was the ratio of 30:20 MIL:mineral oil. Therefore, this proportion was selected for the construction of the working electrode.

Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0), phosphate buffer saline (0.1 mol L^{-1}, pH 7.4) and phosphate buffer (0.1 mol L^{-1}, pH 7.0) were evaluated as supporting electrolytes in the optimization studies. Britton-Robinson buffer provided the best electroanalytical response for BPA and thus it was selected as the supporting electrolyte. The effect of the pH of the supporting electrolyte on the analytical response for BPA was also investigated by CV, using Britton-Robinson buffer (universal buffer), in the pH range of 3.0-12.0. The highest oxidation peak current for BPA was obtained at pH 7.0, as previously observed by CV.

The SWV was the technique chosen for the analytical development of the method. The SWV parameters were studied with the aim of obtaining better sensitivity and peak definition in the BPA determination. The frequency (10-100 Hz), scan increment (1-10 mV) and pulse amplitude (10-100 mV) were investigated and the best analytical response was obtained with a frequency of 30 Hz, pulse scan increment of 4 mV and amplitude of 80 mV. Thus, these instrumental conditions were selected.

Analytical performance of the electrode

Calibration curve

Under the optimized conditions, the calibration curves for BPA (constructed from a plot of the resultant current peak *vs.* BPA concentration) were obtained by SWV, in triplicate, using the proposed electrode (MIL/CPE) and a bare CPE in the potential range of 0.45 to +1.0 V *vs.* Ag/AgCl, as shown in Figure 5. The calibration curve for MIL/CPE was linear from 2.0 to 53.0 μmol L^{-1} and presented the following regression equation: $\Delta i = 1.24 \times 10^{-6} \pm 1.26 \times 10^{-7} + 4.26 \times 10^{-1} \pm 4.06 \times 10^{-3}$ [BPA] (r^2 = 0.999), where Δi is the resultant peak current and [BPA] is the concentration of bisphenol A in mol L^{-1}. The LOD value, considered as three times the standard deviation of the intercept/slope,

was 0.87 μmol L^{-1}. The calibration curve obtained using the CPE was linear from 5.0 to 53.0 μmol L^{-1} and presented the following regression equation: $\Delta i = 8.75 \times 10^{-8} \pm 2.34 \times 10^{-8} + 2.30 \times 10^{-2} \pm 7.21 \times 10^{-4}$ [BPA] (r^2 = 0.996), with an LOD of 3.05 μmol L^{-1}. Compared with the unmodified electrode, the proposed electrode showed a significantly lower LOD and higher sensitivity (observed through the slope of the calibration curve), indicating an adequate analytical performance.
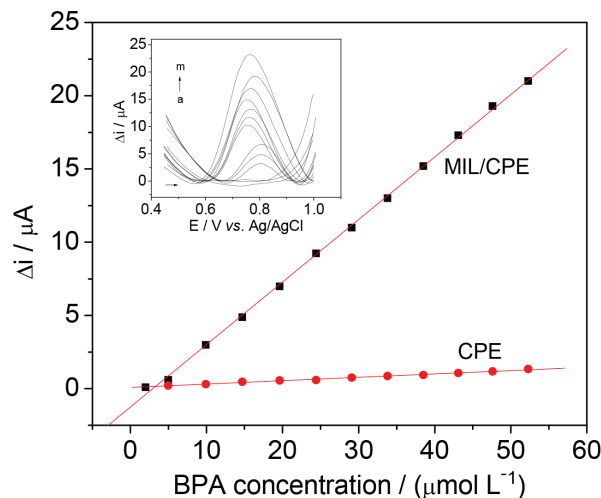
Figure 5. Calibration curves for BPA obtained using MIL/CPE and CPE. Insert: SWV of proposed electrode in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) at different BPA concentrations: 2.0, 5.0, 10, 14.7, 19.6, 24.4, 29.1, 33.8, 38.5, 43.1, 47.6 and 53.0 μmol L^{-1}.

Stability and precision studies

Intra-day and inter-day precision tests were carried out with MIL/CPE by SWV using 19.6 μmol L^{-1} BPA in Britton-Robinson buffer (0.1 mol L^{-1}, pH 7.0) under optimized experimental conditions. The intra-day precision (n = 10) showed a coefficient of variation of 4.5% and the inter-day precision (n = 5) had a coefficient of variation of 2.0%. These results indicate good repeatability for the measurements. The electrode-to-electrode repeatability, determined from the response of three electrodes prepared independently using the same procedure, was investigated to evaluate the construction step of the electrode. This study was performed using a 19.6 μmol L^{-1} BPA standard by SWV and the results also evidenced that the method is suitable for analytical purposes, with a coefficient of variation of 1.5% (n = 3). Results of the precision tests indicate good repeatability of the proposed method and acceptable fabrication reproducibility. The storage stability of MIL/CPE was also examined. It was found that after storage at 25 °C for 60 days the electrode retained 93% of its initial current response, suggesting acceptable storage stability.

Table 1. Analysis of BPA in different samples using different methods (n = 3)

Sample	Determined[a]	Added[a] / (μmol L^{-1})	Found[b] / (μmol L^{-1})			Recovery[c] / %
			Electrode	Spectrophotometric	HPLC	
PP cup	not detected	20.0	20.5 ± 0.02	19.4 ± 0.04	21.8 ± 0.5	94.6-101.1
PS plastic cup	not detected	20.0	19.5 ± 0.02	20.0 ± 0.01	21.4 ± 0.14	98.9-100.0
Baby nipple	not detected	20.0	20.8 ± 0.01	19.4 ± 0.01	20.8 ± 0.5	93.0-97.6
PVC food package	not detected	20.0	20.7 ± 0.03	19.1 ± 0.02	19.5 ± 0.5	95.3-99.5

PP: polypropylene; PS: polystyrene; PVC: polyvinylpyrrolidone. [a]Determined and added by electrode, spectrophotometric and high performance liquid chromatography (HPLC); [b]mean ± standard deviation (n = 3); [c]recovery by electrochemical method ((mean found value/added value) × 100).

Determination of BPA in plastic samples

In order to evaluate the performance of the proposed electrode in practical analytical applications, the determination of BPA in four different plastic samples (PP cup, PS plastic cup, PVC food package and baby nipple) was carried out in a recovery study according to the analytical procedure described in sub-section "Preparation of plastic samples and determination of BPA". The samples were analyzed by SWV with MIL/CPE, spectrophotometric and HPLC applying the standard addition method and BPA was not detected in any of the samples analyzed (Table 1). The percent recovery obtained for these samples ranged from 93.0 to 101.1%, demonstrating the satisfactory accuracy of the proposed electrode and low interference from the matrix (Table 1). These results indicate that the electrode can be used in practical applications.

Conclusions

A new electrochemical electrode for the determination of BPA based on the modification of the internal material of a carbon paste electrode with an MIL was developed. Due to the unique solvation properties, which can enhance the interaction with the analyte, and high conductivity of MIL, the oxidation peak current of BPA was significantly enhanced and the proposed electrode (MIL/CPE) exhibited satisfactory analytical features, including high sensitivity and low LOD (compared with an unmodified electrode). The proposed electrode showed good precision and excellent accuracy, as observed from recovery experiments (93.0 to 101.1%) and comparison with data obtained by other methods. In addition, this electrode also has advantages related to ease of manufacture and low cost.

Supplementary Information

Supplementary information (UV spectrum for the [P$_{6,6,6,14}^+$][Cl$^-$] IL and for the [P$_{6,6,6,14}^+$]$_2$[MnCl$_4^{2-}$] MIL) is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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