

Electrochemical and Spectroscopic Studies of Redox Mechanisms in Poly-Benzidine Film Formation

F. D'Eramo, A.H. Arévalo, J.J. Silber and L. Sereno*

Departamento de Química y Física, Universidad Nacional de Río Cuarto,
Estafeta Postal Nº 9, Río Cuarto 5800, Córdoba, Argentina

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Neste trabalho é relatada a oxidação eletroquímica da benzidina (Bz) para obter um filme eletroativo de poli-benzidina (poly-Bz). As condições ótimas de formação do filme foram estudadas por voltametria cíclica variando-se de temperatura, pH e concentração inicial de Bz. Estudos cinéticos da reação de polimerização foram realizados combinando-se técnicas eletroquímicas e espectroscópicas. Um mecanismo de reação é proposto e os parâmetros cinéticos para os eventos iniciais da polimerização são calculados.

The electrochemical oxidation of benzidine (Bz) to obtain an electroactive film of poly-benzidine (poly-Bz) is reported. The optimal conditions of the film formation were studied by cyclic voltammetry and the variation of the temperature, pH and initial concentration of Bz. Kinetic studies of the polymerization reaction were performed by combining electrochemical and spectroscopic techniques. A reaction mechanism is proposed and the kinetic parameters for early events of polymerization are calculated.

Keywords: benzidine, poly-benzidine, modified electrodes

Introduction

The deliberate modification of an electrode surface by organic polymeric compounds provides new and interesting properties for electrochemistry and some other sciences. This type of electrode has been widely studied during recent years¹⁻³. These surface polymers are receiving growing attention due to their potential application in microelectronic devices⁴, analytical sensors⁵, electrocatalysis⁶, electrooptic displays^{7,8}, and rechargeable non-aqueous and aqueous secondary batteries⁹⁻¹¹.

Electrooxidation of aromatic amines is well known, and different aspects of their mechanism have been elucidated^{12,13}. The electrochemical oxidation of polynuclear amines on platinum electrodes in non-aqueous media has been studied in our laboratory. Their products are generally dimers more easily oxidizable than the parent substances¹⁴⁻¹⁷. When some of the dimers are oxidized, as in the case of naphthidine (NAP), they follow a complex reaction to give a polymer that adheres to the electrode surface^{18,19}. This new electrode shows a behavior similar to that of other organic polymers, such as polypyrrole²⁰, polythiophene²¹, polyanilines²²⁻²⁴ and poly-o-aminophenol²⁵⁻²⁷. These polymers adhered to a base metal are conductors and their doping grade can be controlled. This kind

of polymerization reaction and studies on the electrochemical response of conducting polymers has been previously reviewed²⁸⁻³⁰.

In an earlier paper¹⁹ we reported the preparation and some electrochemical properties of polynaphthidine on Pt electrodes in non-aqueous systems. This film is homogeneous, electroactive and strongly adherent, as demonstrated by its stability during repetitive oxidation-reduction cycles. It shows electrochromic properties in its electroactive potential range. To better understand the complex properties of this polymer, we decided to study a smaller homologue of naphthidine, such as benzidine (Bz).

The electrooxidation of Bz in a non-aqueous solution was previously reported³¹, but no details of the electrooxidation mechanism or film formation were reported. A more recent study³² shows some aspects of the electropolymerization of Bz and other substituted polymers. However, the electropolymerization mechanism and the chemical structure of the polymer are still not defined.

In this work we report electrochemical and spectroscopic studies of the oxidation of Bz in aqueous media in order to obtain more insight into the mechanism of the formation of polybenzidine film (poly-Bz). Quantitative relationships of the electropolymerization reaction are es-

tablished to determine the optimal conditions for film formation.

Experimental

Benzidine (Fluka, p.a.) was used as received. HClO_4 and NaClO_4 were reagent grade and used without further purification. Water was first purified by distillation over KMnO_4 in an alkaline medium to eliminate organic contaminants and distilled twice.

To obtain the film, the solutions of Bz were prepared by weighing the Bz and dissolving it in a previously deoxygenated solvent-supporting electrolyte solution. During the measurements the solutions were maintained free of oxygen. The solutions of Bz at $\text{pH} = 1$ obey Lambert and Beer's Law ($\lambda_{\text{max}} = 250 \text{ nm}$, $\log \epsilon = 4.2$). These properties were used to determine the concentration of the working solutions. The pH was measured *in situ* with a glass electrode. A standard three-electrode electrochemical cell was used for voltammetric experiments²⁶.

The spectroelectrochemical cell was a rectangular prism to which two glass slides were attached at opposite ends. The lid of the cell supported the reference and auxiliary electrodes and had a provision for bubbling nitrogen gas. The working electrode used was a Pt plate (1.28 cm^2). This electrode was polished with 0.3 m alumina slurry, rinsed with copious triply distilled water and sonicated for 15 min to remove residual polishing material. The counter electrode was a Pt foil (20 cm^2) used without pre-treatment. A conventional potassium chloride saturated electrode (SCE) was used as the reference electrode. All the measurements were performed with a PAR 273 potentiostat/galvanostat with ohmic drop compensation, in combination with a sweep generator. The output signal was recorded on an HP7015B XY recorder. The UV-Visible spectra were taken in a Hewlett Packard 8452A spectrophotometer.

Results and Discussion

A typical voltammogram of Bz in aqueous solution on a Pt electrode is shown in Fig. 1a. One peak (I) is observed in the first anodic hemicycle. When the scan is reversed, peak (I) shows a complementary cathodic peak (II). An exhaustive study of the peak system (I-II) shows that the peak potential separation is $\Delta E_p = (E_{pI} - E_{pII}) = 0.029 \pm 0.003 \text{ V}$. This E_p is predicted by the theory for a reversible EE system where $\Delta E^0 = (E_{pII}^0 - E_{pI}^0) > -0.180 \text{ V}$ ³³ at room temperature. There are no shifts of E_p with a sweep rate (v) at least in the v range studied, that is, between 0.010 and 0.250 V. These results are consistent with two successive charge transfers to give a benzidine dication (Bz^{2+}).

The i_{pII}/i_{pI} current peak ratio is close to unity. This means that although Bz^{2+} is quite stable, it is involved in a slow follow-up reaction¹⁶. The product of this reaction is detected by a wave at 0.30 V. The current at 0.30 V increases by continuously cycling the potential between 0

and 0.800 V vs. SCE, and a new peak system is defined (III-IV) (Fig. 1b). This peak system shows the characteristic behavior of a deposited electroactive substance. Moreover, if the solution is stirred while cycling, no variation is observed, as expected for an irreversible adsorbed electroactive substance. The yield of the electropolymerization reaction, and consequently of the film formation, depends on the temperature and the pH of the solution. Therefore, systematic studies were performed in order to obtain the optimum conditions for the reaction. The procedure used to prepare the film consisted of cycling the potential ten times at the same potential interval, as in Fig. 1a, but changing the conditions of the electrolyte solution, temperature and pH. In every case, the last potential cycle was stopped for several minutes at a potential of 0.0 V to allow the film to be completely reduced³⁴. The results are shown in Table 1.

On the other hand, if the ratio i_{pII}/i_{pI} is measured as a function of the pH, it continuously decreases as the pH increases, indicating that the dication concentration decreases when the pH increases³⁴. However, the yield of polymerization reaches a maximum at $\text{pH} \sim 2.5$. Thus, it can be assumed that the dication takes part in the electropolymerization reaction, but it is not the unique species. On the other

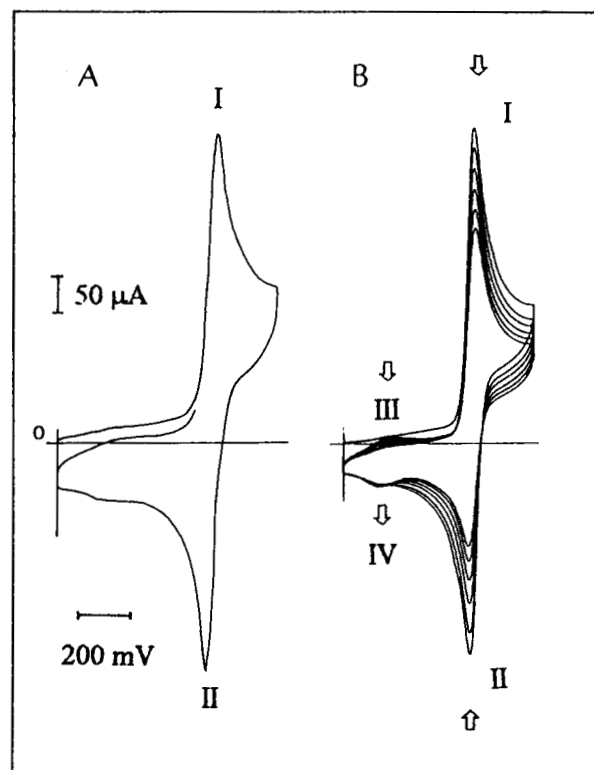


Figure 1. A) Cyclic voltammogram for the oxidation of $5 \times 10^{-4} \text{ M}$ Bz in 0.3 M NaClO_4 - 0.1 M HClO_4 solution at a platinum electrode. $v = 0.1 \text{ V.s}^{-1}$. First scan. B) Repetitive cyclic voltammogram in the same conditions.

Table 1. Optimum conditions for film formation.

[Benzidine] mol.l ⁻¹	[NaClO ₄] mol.l ⁻¹	Electrochem. technique	Temperature °C	pH
5 x 10 ⁻⁴	0.3	C.V.	25 - 35	2.0 - 2.5

hand, the direct dimerization of the dication is probably difficult due to steric hindrance and charge repulsion.

Another important conclusion is that, at sufficiently high acidic media (for example HClO₄ 2 M) the Bz²⁺ is stable. This fact has been confirmed by controlled potential electrolysis (CPE) in this medium (see below).

The mechanism of the electropolymerization reaction

In order to obtain some insight into the electropolymerization mechanism, CPE was performed. Solutions of Bz at pH = 1 were electrolyzed at 0.750 V on a large area Pt electrode (16 cm²). The electrolyzed solutions were analyzed by cyclic voltammetry with an auxiliary Pt electrode (0.1 cm²)³⁵ and UV-Visible spectroscopy at different conversion stages.

As the degree of conversion of the monomer was increased, the following facts were observed:

i) The rest potential shifted to more positive values with respect to a non-electrolyzed solution.

ii) The i_{pI} decreased and the $i_{pII}/i_{pI} > 1$.

iii) The peaks (III-IV) were detected in the first scan, as i_{pIII} continuously increased, i_{pI} decreased.

iv) When the CPE was transferred to another cell with a substrate-free solution, the expected electrochemical response of the film was obtained.

v) The number of Faradays per mole of electroactive material (n_{app}) was obtained by plotting $\ln i$ vs. t . A linear relationship was observed only to 15% of conversion, giving an $n_{app} \approx 2$. At higher conversion, the plot was not linear, as the current was greater than the expected, indicating an $n_{app} > 2$. This shows that a slow chemical reaction coupled to the first charge transfer process may occur.

vi) When CPE was performed in HClO₄ 2 M at 100% of conversion (that is, when the current was nearly 1% of the initial value), the absorption band at $\lambda = 426$ nm corresponding to Bz²⁺ was stable for several hours. By taking this fact into account and assuming that the Bz²⁺ concentration was equal to the initial Bz concentration, the molar absorption coefficient ($\log \epsilon_{Bz^{2+}} = 4.7$) can be calculated at this λ . The value obtained is similar to other dications of aromatic amines¹⁶.

vii) The UV-Visible spectra of the partially electrolyzed solution showed two absorption bands, one at 250 nm corresponding to Bz and the other at 426 nm for Bz²⁺, Fig. 2. If the spectral response of this solution is followed through time, the band at 426 nm slowly disappears and the band at 250 nm increases. No other changes were observed in the spectra.

On the other hand, when Bz was added to a partially electrolyzed solution the absorbance at 426 nm decreased and at 250 nm increased, more rapidly than without the addition of Bz. This result suggests that Bz²⁺ may react with Bz to give a dimer and initiate the polymerization reaction. Moreover, during electrolysis dark insoluble particles precipitate. If these particles are collected, washed and pressed in a clean Pt electrode they present a similar response to that shown by the film when it is obtained by repetitive cycling of potential sweeps.

To explain the results hitherto presented, and considering some aspects of the stability of dimeric amines in aqueous media solutions, we propose the following mechanism for film formation

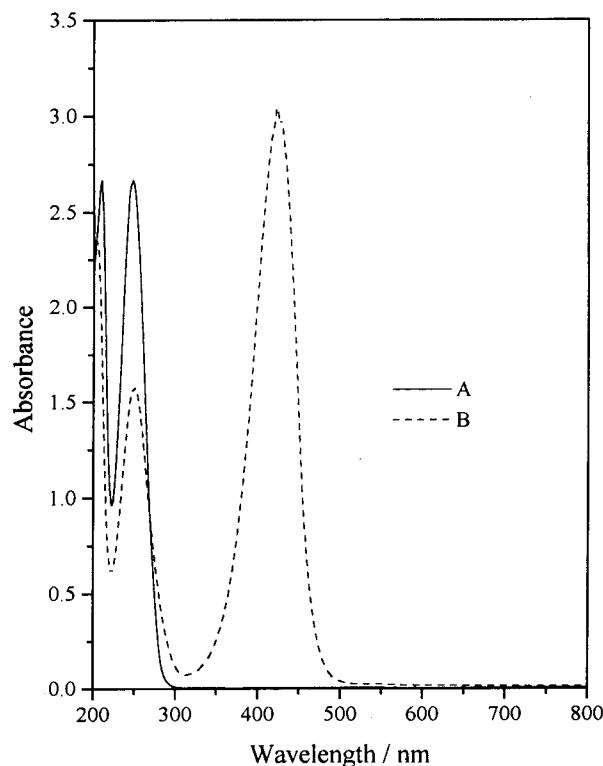
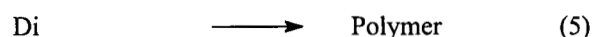
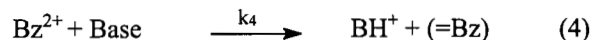


Figure 2. Absorption spectra of Bz-NaClO₄-HClO₄ solutions. A) Non-electrolyzed solution, B) Partially electrolyzed solution.



Reaction 1 is an acid-base reaction ($\text{p}K_{a1} = 9.04$)³⁶. The proton transfer in aqueous solution is usually fast, and thus no effects on the electrochemical reaction are detected unless fast electrochemical techniques are used. Reaction 3 is the coupling between the dication and parent molecule to give first a dimer (Di) and then the polymer (Reaction 5). To obtain a polymer of heavy molecular weight this structure probably needs to be electrooxidized. Reaction 4 is the deprotonation of the dication by any base present in the medium, for example water or the parent compound. This reaction which gives a diimine structure (= Bz) competes with Reaction 3, but is only important at $\text{pH} > 2$. Taking into account that the electropolymerization yield decreases, continuously, at $\text{pH} > 2$, it is assumed that (= Bz) does not yield any polymer.

Reactions 3 and 4 are competitive and slow in the time scale of voltammetric experiments. Thus at $0 < \text{pH} < 1$, $i_{pII}/i_{pI} \approx 1$. At $1 < \text{pH} < 2.5$ Reaction 3 prevails and the polymer yield increases, and the ratio $i_{pII}/i_{pI} \approx 0.7$. On the other hand, for $2.5 < \text{pH} < 4$ Reaction 4 becomes more important ($i_{pII}/i_{pI} \ll 1$) and the polymer yield decreases. More quantitative data can be obtained for Reaction 3 by studying the Bz solutions at $\text{pH} = 1$ where Reaction 4 is not important and Reaction 5 is very slow.

The following procedure was used: a solution of Bz 1.5×10^{-4} M at $\text{pH} = 1$ was electrolyzed at 0.750 V at ca. 40% of conversion in a spectrophotometric cell. At this point, (which is considered $t = 0$) a spectrum was recorded and followed through time. Two wavelengths were used for the calculation of the concentration of Bz, Bz^{2+} and Di after the electrolysis was interrupted. By assuming that Lambert and Beer's Law was obeyed, and the principal product formed by the chemical reaction was a Di, the initial absorbance at 250 nm is

$$A^{t=0}_{250 \text{ nm}} = \epsilon_{\text{Bz}} \delta [\text{Bz}] + \epsilon_{\text{Di}} \delta [\text{Di}] \quad (6)$$

where ϵ_{Bz} and ϵ_{Di} are the extinction coefficients of Bz and Di. $[\text{Bz}]$ is the concentration of Bz, $[\text{Di}]$ the concentration of Di produced during the electrolysis, and δ is the optical path. At the same time the absorbance at 426 nm is only due to Bz^{2+} and is equal to:

$$A^{t=0}_{426 \text{ nm}} = \epsilon_{\text{Bz}^{2+}} \delta [\text{Bz}^{2+}] \quad (7)$$

The mass balance for all the species is:

$$C_T = [\text{Bz}] + [\text{Bz}^{2+}] + 2 [\text{Di}] \quad (8)$$

where C_T is the analytical concentration of Bz. At any other time Eqs. 6, 7, and 8 are modified as:

$$A^{t=t}_{250 \text{ nm}} = \epsilon_{\text{Bz}} \delta [\text{Bz} - x] + \epsilon_{\text{Di}} \delta [\text{Di} + x] \quad (9)$$

$$A^{t=t}_{426 \text{ nm}} = \epsilon_{\text{Bz}^{2+}} \delta [\text{Bz}^{2+} - x] \quad (10)$$

$$C_T = [\text{Bz} - x] + [\text{Bz}^{2+} - x] + 2 [\text{Di} + x] \quad (11)$$

where x is the quantity of Di formed at time t and can be calculated by subtracting Eq. 7 from Eq. 10

$$x = \{A^{t=0}_{426 \text{ nm}} - A^{t=t}_{426 \text{ nm}}\} / \epsilon_{\text{Bz}^{2+}} \delta \quad (12)$$

Removing $(\text{Bz} - x)$ from Eq. 11 and inserting this value in Eq. 9 Eq. 13 is obtained.

$$A^{t=t}_{250 \text{ nm}} = \delta \{ \epsilon_{\text{Bz}} [C_T - \text{Bz}^{2+} - 2 \text{Di}] + \epsilon_{\text{Di}} [\text{Di}] \} + \delta (\epsilon_{\text{Di}} - \epsilon_{\text{Bz}}) (x) \quad (13)$$

The first term on the right of Eq. 13 is the value of $A^{t=0}_{250 \text{ nm}}$, thus:

$$A^{t=t}_{250 \text{ nm}} = A^{t=0}_{250 \text{ nm}} + \delta (\epsilon_{\text{Di}} - \epsilon_{\text{Bz}}) (x) \quad (14)$$

Inserting the value of Eq. 12 in Eq. 14, Eq. 15 is obtained:

$$A^{t=t}_{250 \text{ nm}} = A^{t=0}_{250 \text{ nm}} + \{ (\epsilon_{\text{Di}} - \epsilon_{\text{Bz}}) / \epsilon_{\text{Bz}^{2+}} \} A^{t=0}_{426 \text{ nm}} - (\epsilon_{\text{Di}} - \epsilon_{\text{Bz}}) / \epsilon_{\text{Bz}^{2+}} A^{t=t}_{426 \text{ nm}} \quad (15)$$

Plotting $A^{t=t}_{250 \text{ nm}}$ vs. $A^{t=t}_{426 \text{ nm}}$ a good straight line is obtained throughout the whole reaction time (approximately 4 h), Fig. 3. This indicates that Step 3 may be the principal reaction detected. From the slope of the plot, ϵ_{Di} can be calculated ($\log \epsilon_{\text{Di}} = 4.4$). With this value and Eqs. 6 - 8, the concentration of Bz, Bz^{2+} and Di can be calculated at any time.

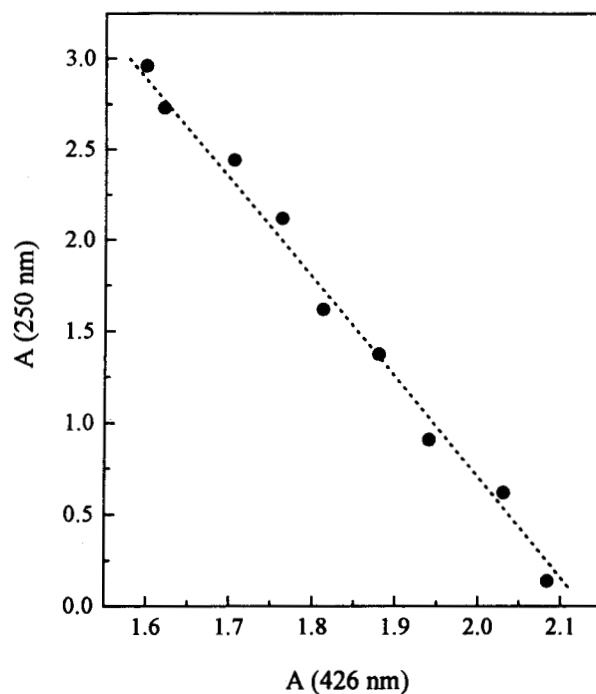


Figure 3. Plot of Eq. 15, for ϵ_{Di} determination.

In order to calculate the rate coefficients for the reactions of Bz^{2+} , the procedure previously described was followed. When the electrolysis is stopped, at 40% of conversion, the concentrations of species are calculated and immediately a 2×10^{-2} M solution of Bz is added to accelerate the kinetic process, and the initial concentration is recalculated. The reaction evolution is followed with the 426 nm band, and the Bz^{2+} concentration is calculated with Eq. 12. The data obtained fit a second order reaction Eq. 16:

$$\ln\left\{\frac{(Bz^0 - x) / (Bz^{2+0} - x)}{-\ln(Bz^{2+0} / Bz^0) + k(Bz^0 - Bz^{2+0})t}\right\} = \quad (16)$$

where Bz^0 and Bz^{2+0} are the concentration at $t = 0$, and x is the quantity of the product formed according to Eq. 12.

A typical result is shown in Fig. 4. The slope gives a value for a kinetic constant (Eq. 3) $k_3 = 0.32 \text{ s}^{-1} \text{ M}^{-1}$. This result gives good evidence that the mechanism proposed may represent early film formation.

Conclusions

The electrooxidation of Bz in acid media leads to the formation of the dication, Bz^{2+} , by an EE process. The Bz^{2+} is stable at $\text{pH} < 1$ at room temperatures. At higher pH, Bz^{2+} reacts to give a polymer film, probably through the proposed mechanism. The spectroscopic results show that Bz^{2+} reacts with Bz, following a second order kinetic to form a dimer which may induce the polymerization reaction. At $\text{pH} > 2.5$ the reaction of deprotonation of the dication becomes important and competes with the coupling reaction, thus lowering the polymerization yield.

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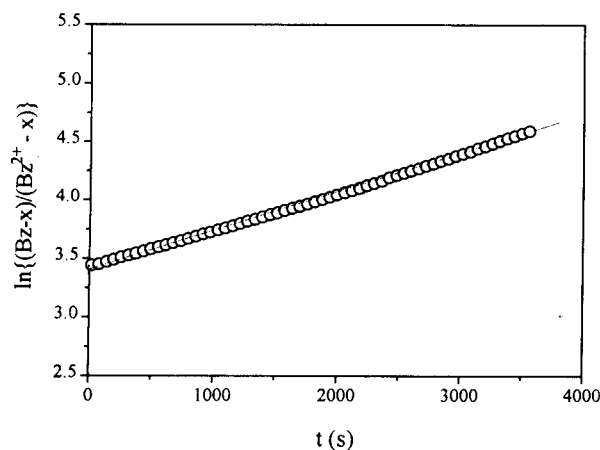


Figure 4. Plot of Eq. 16 with the experimental data obtained from spectroelectrochemical experiments.

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