

Effect of the Bathing Electrolyte on the Charge-Transport Process at Poly(o-aminophenol)-Modified Electrodes. An *ac* Impedance Study in Sulfate and Benzenesulfonate Solutions

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Abstract: The aim of this work was to study how charge-transport and charge-transfer processes at poly(o-aminophenol) film electrodes depend on the type and concentration of the external electrolyte solution in contact with the polymer film. To this end *ac* impedance measurements on poly(o-aminophenol) films contacting solutions of different anions such as sulfate and benzenesulfonate were carried out. These two different anions were chosen due to their differences in size and adsorbability. Impedance data were interpreted on the basis of a modified electron-hopping model, where the electron-transport rate within the polymer phase and the electron-transfer rate across the metal|polymer interface are represented by an effective diffusion coefficient (D) and a standard electrochemical rate constant (k_{sh}), respectively. It was found that both parameters are independent of the type and concentration of the electrolyte solution within the thickness range from 10 nm to 35 nm. However, these transport parameters depend strongly on both external variables within the thickness range from 38 nm to 70 nm. In this regard, the rate of charge conduction through thick poly(o-aminophenol) increases with the increase of the concentration of the electrolyte solution. The increase of poly(o-aminophenol) conductivity with the increase of film thickness was attributed to changes in the polymer morphology. It was assumed that the electrolyte incorporated into the open structure of a thick film reduces repulsive interactions between redox sites yielding a more compact distribution of redox centers as compared with that present in a thin film that does not incorporate the electrolyte. Lower distances between adjacent redox sites in a thick film facilitate the electron-hopping process, which in turn leads to a higher conductivity as compared with that of a thin film.

Keywords: Poly(o-aminophenol) Films, Sulfate, Benzenesulfonate, conductivity, morphology.

1. INTRODUCTION

It is well-known that without redox species in solution (“background electrolyte”) the charge-transport process of an electrode modified by an electroactive polymer film is affected by ionic transfer at the polymer|electrolyte interface, ionic and electronic charge carrier transport inside the polymer and an electronic transfer at the metal|polymer interface [1]. In this connection, counterions are able to cross the polymer film|solution interface to retain the bulk film electroneutrality. This process would only be dependent on the degree of oxidation of the polymer. However, it has also been suggested that the external supporting electrolyte contacting the polymer film could be incorporated into the polymer phase [2]. This internal electrolyte phase can play an important role in the charge-transport and charge-transfer processes of the polymeric material.

Poly(o-aminophenol) (POAP) is a typical electroactive polymer that has been employed as resistive and permselective material to build biosensors [3]. In this application, the resistive behavior of POAP films was only associated with the entrapment of nonconductive species into the polymer matrix [4], disregarding the effect of the external electrolyte

solution on the conductivity of the polymer. In the present work, *ac* impedance measurements on POAP film electrodes in contact with solutions containing different anions such as sulfate and benzenesulfonate (BS) anions were performed in order to detect changes in the polymer conductivity due to the different electrolyte composition. The experimental results were quantitatively interpreted on the basis of a modified electron-hopping model [5], which allowed bulk and interfacial transport parameter values obtaining. The aim of this work was twofold: firstly to demonstrate the crucial effect of the electrolyte composition on the charge-conduction process of the polymer and secondly, to compare conductivity values of POAP in these two electrolytes. To the best of my knowledge, no work employing *ac* impedance measurements on POAP films contacting these two electrolytes has been reported in the literature so far. This work could help those engaged in the development of sensors based on POAP because its operating characteristics can be favorably modified by selecting a suitable electrolyte.

2. EXPERIMENTAL

2.1. The Gold Film Electrodes

In order to obtain a specular surface to deposit POAP films, gold thin-film electrodes of constant thickness $\phi_m \sim 30$ nm were prepared by vacuum evaporation as was previously described [6]. The samples were inserted into an electrochemical cell similar to that shown in a previous paper [7]

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and employed as working electrodes. An electrode area of 0.56 cm^2 was exposed to the solution. A gold grid of large area was used as counterelectrode. All the potentials reported in this work are referred to the SCE.

2.2. The POAP-Coated Gold Film Electrodes

POAP-coated gold film electrodes were obtained by immersing the gold films described in the previous section in a 10^{-3} M *ortho*-aminophenol + 0.4 M NaClO_4 + 0.1 M HClO_4 solution and cycling the potential between -0.25 V and 0.8 V at a scan rate $\nu = 0.05 \text{ V s}^{-1}$. The POAP thickness was increased by increasing the number of potential cycles in the solution containing the monomer. In order to measure the polymer thickness, these POAP-coated gold film electrodes were then rinsed and transferred to the supporting electrolyte solution (0.4 M NaClO_4 + 0.1 M HClO_4). Then, the voltammetric reduction charge, Q_{Red} , in this solution was determined by integrating the cathodic current of the voltammetric response between -0.25 V and 0.5 V ($\nu = 0.05 \text{ V s}^{-1}$) [8]. Thus, Q_{Red} was considered as representative of the polymer thickness. Two POAP film thicknesses with Q_{Red} values of 0.42 mC cm^{-2} and 1.5 mC cm^{-2} were employed in this work. For this type of polymer, many researchers have correlated the charge obtained from the integration of the voltammetric profile with the ellipsometric thickness [9-12]. Although this procedure is reasonable within an order of magnitude, the ellipsometric thickness is usually obtained under the assumption of a homogeneous film, that is, by averaging the optical film properties across its thickness. Thus, the thicknesses of the POAP films (in nanometers) were determined from an ellipsometric working curve reported in our papers [6, 8]. The Q_{Red} values indicated above would correspond to polymer thicknesses (ϕ_p) of 19 nm and 70 nm , respectively. With these POAP-coated gold film electrodes, voltammetric responses (j - E) were recorded separately for each ϕ_p value, within the potential range from -0.2 V to 0.5 V at a scan rate $\nu = 0.01 \text{ V s}^{-1}$ in solutions containing SO_4^{2-} and benzenesulfonate ($\text{C}_6\text{H}_5\text{SO}_3^- = \text{BS}$) anions, respectively. In CV measurements a PAR Model 173 potentiostat and a PAR Model 175 function generator were used. An X1-X2-Y Hewlett-Packard Model 7046 B Plotter was used to record the j - E responses.

Impedance spectra of the POAP-coated gold film electrodes in contact with solutions containing SO_4^{2-} and benzenesulfonate ions were also recorded. Impedance spectra were measured following a 30-min application of the steady-state potential ranging from -0.2 V to 0.2 V . Impedance measurements in the frequency range from 0.01 Hz to 10 kHz were performed with a PAR 309 System. Impedance values were determined at seven discrete frequencies per decade with a signal amplitude of 5 mV . The validation of the impedance spectra was done by using Kramers-Kronig transformations.

AR grade chemicals were used throughout. *O*-aminophenol (Fluka) was purified as described elsewhere [13]. The solutions were prepared with water purified using a Millipore Milli-Q system. NaClO_4 , HClO_4 , H_2SO_4 , Na_2SO_4 , benzenesulfonic acid and sodium benzenesulfonate were employed to prepare the corresponding solutions.

3. RESULTS AND DISCUSSION

J - E responses for the 30 nm thick gold film coated with POAP films of different thicknesses ϕ_p ($= 19 \text{ nm}$ and 70 nm ,

respectively) were recorded in solutions containing SO_4^{2-} and BS anions. j - E responses at a given scan rate (ν) and POAP thickness in the presence of the different anions do not show big differences. This is shown in Fig. (1) for the 70 nm thick POAP film. In the inset of Fig. (1), the corresponding response for the thinner POAP film ($\phi_p = 19 \text{ nm}$) is shown.

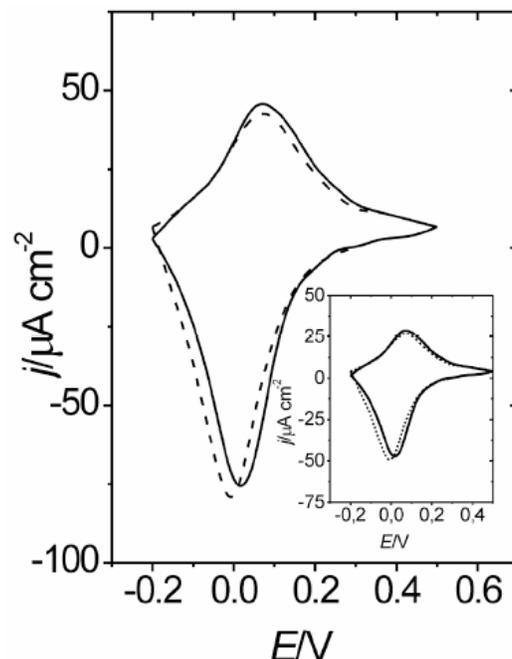


Fig. (1). Voltammetric (j - E) response of a 70 nm thick POAP film in contact with: (---) a 0.4 M Na_2SO_4 + 0.1 M H_2SO_4 solution and (—) a 0.4 M $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$ + 0.1 M $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ solution. Inset: The corresponding voltammetric responses for a 19 nm thick POAP film. Scan rate: $\nu = 0.01 \text{ V s}^{-1}$.

Impedance spectra of POAP films at different potentials within the potential range from -0.2 V to 0.2 V were recorded. Fig. (2) shows the impedance spectrum at $E = 0.1 \text{ V}$, corresponding to the 70 nm thick POAP films in contact with a 0.4 M Na_2SO_4 + 0.1 M H_2SO_4 solution, and Fig. (3) shows the spectrum of the same film but contacting a 0.4 M sodium benzenesulfonate + 0.1 M benzenesulfonic acid solution. In the presence of sulfate anions, POAP films exhibit a capacitive behavior towards the low-frequency limit and Warburg-type impedance at intermediate frequencies with a less than 45° slope. In the low-frequency range $\text{Im}[Z(\omega)]$ should increase indefinitely as $\omega \rightarrow 0$, whereas $\text{Re}[Z(\omega)]$ should remain frequency invariant. However, in the present case the impedance data display a noninfinite slope at low frequency. In the presence of a solution containing BS anions, impedance spectra are characterized by a pronounced semicircular form at high frequency (Fig. 3). At low frequency a capacitive rise is also observed. These high-frequency semicircles reflect distinct effects of BS anions on the charge-transport and charge-transfer processes of POAP as compared with sulfate anions. Although we only show impedance results corresponding to a 70 nm thick POAP film, the same impedance response was observed within the thickness range from 38 nm to 70 nm . Impedance spectra of the thinner POAP film ($\phi_p = 19 \text{ nm}$) contacting the same solutions indicated above do not practically exhibit any differences

(Fig. 4). Besides, spectra only consist of a high-frequency semicircle. This same impedance response shown in Fig. (4) was observed within the thickness range from 10 nm to 35 nm.

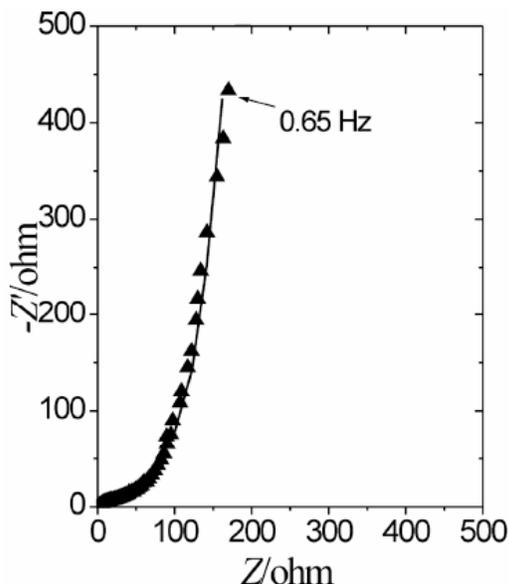


Fig. (2). Ac impedance diagram in the Nyquist coordinates ($-Z''$ vs. Z') obtained at $E = 0.1$ V for a 70 nm thick POAP film in contact with a 0.4 M $\text{Na}_2\text{SO}_4 + 0.1$ M H_2SO_4 solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].

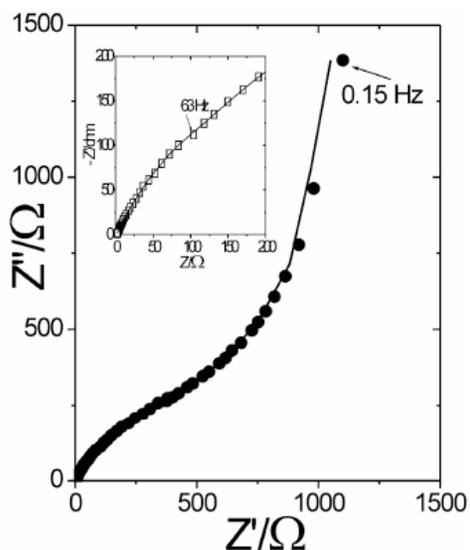


Fig. (3). Ac impedance diagram in the Nyquist coordinates ($-Z''$ vs. Z') obtained at $E = 0.1$ V for a 70 nm thick POAP film in contact with a 0.4 M $\text{C}_6\text{H}_5\text{SO}_3 \text{Na} + 0.1$ M $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5]. The inset is a magnification of the high-frequency region.

It is well-known that some impedance models consider a porous electrode with two superimposed phases where one (the polymer) transports electrons and the other (the electrolyte) transports ions [1]. In other models [14] the polymer is

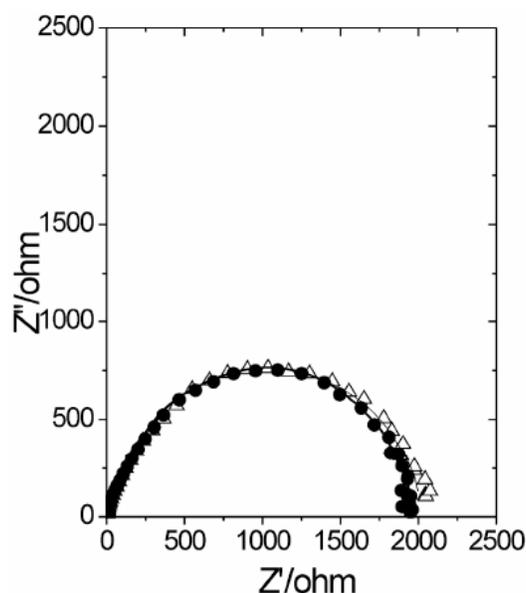


Fig. (4). Ac impedance diagrams in the Nyquist coordinates ($-Z''$ vs. Z') obtained at $E = 0.1$ V for a 19 nm thick POAP film in contact with: (Δ) a 0.4 M $\text{C}_6\text{H}_5\text{SO}_3 \text{Na} + 0.1$ M $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ solution and (\bullet) a 0.4 M $\text{Na}_2\text{SO}_4 + 0.1$ M H_2SO_4 solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].

considered as a single homogeneous phase where the transport of both carriers occurs by diffusion-migration in a single phase. The problem arises because the different models can fit the same experimental results and the parameters obtained by impedance analysis are susceptible to different interpretations depending on the applied model. In this regard, the treatment of the impedance data is often complicated by accompanying not only experimental but also theoretical difficulties. With regard to experimental conditions, by employing a gold film as base electrode as is described in the experimental section, it is expected to reduce surface defects of the base electrode on an atomic scale, in such a way that the polymer film is deposited on a smooth enough surface. Gold films deposited under high vacuum conditions ($\sim 10^{-7}$ Torr), as in the present work, result polycrystalline with crystallite sizes between 0.01 and 0.1 μm [6, 7]. Studying the “Size effects” [6] on these gold films, a value of the specularly parameter, $p \sim 0.91$, was estimated. Parameter p correlates with the roughness of the surface topography and the presence of surface defects. More precisely, this parameter represents the probability of an electron being reflected specularly or diffusely (due to the presence of defects) at the film surface. The p value ranges from 0 for complete diffuse scattering to 1 for complete specular scattering. Thus, imperfections should lead to experimental p values much lower than 1. In this connection p values of our gold films, are high enough ($p \sim 0.91$) to assume a low amount of surface defects on an atomic scale, as compared with the surface of a bulk electrode mechanically polished to deposit a polymer film. Concerning the POAP layer deposited on the metal electrode, it has been demonstrated that when a POAP film that is thick enough [15] covers a gold film, the internal structure of the polymer layer contacting the metal surface is highly compact. Then, the experimental arrangement used in this work, that is, a gold base electrode of low surface roughness

($p \sim 0.91$ after deposition of a thin gold film by evaporation) coated with a thick POAP film ($\phi_p > 10$ nm), could be a good approximation to the existence of a homogeneous (uniform) polymer layer on an electrode surface to apply a homogeneous electrochemical model in its study. Then, impedance spectra recorded in the work were analyzed by using the following impedance expression:

$$Z(\omega) = R_{Qt} + (RT/nF^2Ac) [k_f + k_b (K+1)/K] A(\omega) \quad (1)$$

Eq. (1) was derived from a physical model previously reported by Rodríguez Nieto and Tucceri [5], which considers effects of the degree of protonation of the polymer on the dynamics of the charge-transport process by electron hopping between redox sites. This model describes the charge-transport process within the polymer film by means of an effective diffusion coefficient, D , contained in $A(\omega)$ (see Eq. (1)), whose expression is

$$A(\omega) = \frac{\coth \left\{ \phi_p \left(\frac{j\omega}{D} \right)^{1/2} \right\}}{(k_f)(j\omega D)^{1/2}} + \frac{\coth \left\{ \left(\phi_p / D^{1/2} \right) \left[j\omega + \frac{k}{1+K} \left(1 - \frac{1}{1 + \frac{1+K}{kK} j\omega} \right) \right]^{1/2} \right\}}{k_b^{-1} \frac{D^{1/2} \left[j\omega + \left(\frac{k}{1+K} \right) \left(1 - \frac{1}{1 + \frac{1+K}{kK} j\omega} \right) \right]^{1/2}}{D^{1/2}}}} \quad (2)$$

Parameters k_f and k_b in Eqs. (1) and (2) are the forward and the backward electrochemical rate constants corresponding to the charge-transfer process, defined as

$$k_f = k_{sh} \exp [b_f (E - E^o)] \quad (3)$$

$$k_b = k_{sh} \exp [b_b (E - E^o)] \quad (4)$$

where E^o is the standard potential of the redox couple, b_f and b_b are the Tafel coefficients ($b_f = anF/RT$ and $b_b = (1-a)nF/RT$) and k_{sh} is the standard electrochemical rate constant for the interfacial charge-transfer process. K is an equilibrium constant depending on the external proton concentration through $K = K' 10^{-pH}$. K' is related to the pK_a of the polymer redox species. The parameter k ($= k_{1+} + k_{-1}$) in Eq. (2) is related to the forward (k_{1+}) and the backward (k_{-1}) electrochemical rate constants corresponding to a protonation chemical step coupled to the charge-transfer step, as proposed in [5]. Besides, Eq. (2) contains the angular frequency of the perturbation, ω , and the complex unit, j . R_{Qt} in Eq. (1) is a charge-transfer resistance related to the high-frequency semicircle in the impedance diagrams, whose expression is

$$R_{Qt} = (RT/nF^2Ac) [(k_f + k_b) (k_f k_b)^{-1} + (k_f K)^{-1}] \quad (5)$$

In both Eq. (1) and Eq. (5), A is the electrode area, c is the total redox site concentration and n is the number of transferred electrons of the redox process of POAP.

The fitting of impedance diagrams was made by using the aforementioned expression (1), provided that K , D and k_{sh} are adjustable parameters of the model. Figs. from (2 to 4) show the fittings (solid lines) of experimental Nyquist

diagrams (discrete points) by means of the expression given by Eq. (1). Also, the corresponding Bode diagrams were fitted by means of Eq. (1) (Fig. 5). In the simulations a value of $n = 0.44$ for the number of transferred electrons of the redox system of POAP [14] and a total concentration of redox sites in the polymer $c = 4.5$ M [13] were used. An electrode area of $A = 0.56$ cm² was used. A K' value around 8.5×10^2 cm³ mol⁻¹ was adequate to obtain the best fits. The last value leads to $pK_a = 2.93$. This value is of the order of that expected for the deprotonation reaction of the arylamine group of polyaniline [5]. With the K' value, and the pH of the solutions measured *in situ*, the K value for each solution was calculated. To fit experimental impedance diagrams a double-layer capacitance C_{HF} ($= 30 \times 10^{-6}$ F cm⁻²), in parallel with the charge-transfer resistance at high frequency, was also considered. At fixed polymer thickness and solution pH , D and k_{sh} were considered dependent on the type of anion contained in the supporting electrolyte. Table 1 shows that for the thicker POAP film ($\phi_p = 70$ nm) both parameters k_{sh} and D decrease following the sequence $SO_4^{2-} > C_6H_5SO_3^-$. While the diffusion coefficient value for BS anions is nearly two orders of magnitude lower than that for sulfate anions, the standard electrochemical rate constant for BS is almost 4 orders of magnitude lower than that for sulfate. However, Table 2 shows that for the thinner POAP film ($\phi_p = 19$ nm) both parameters remain nearly constant with the change of the electrolyte composition. Also, D and k_{sh} values for the thinner POAP film are several orders of magnitude lower than those corresponding to the thick one.

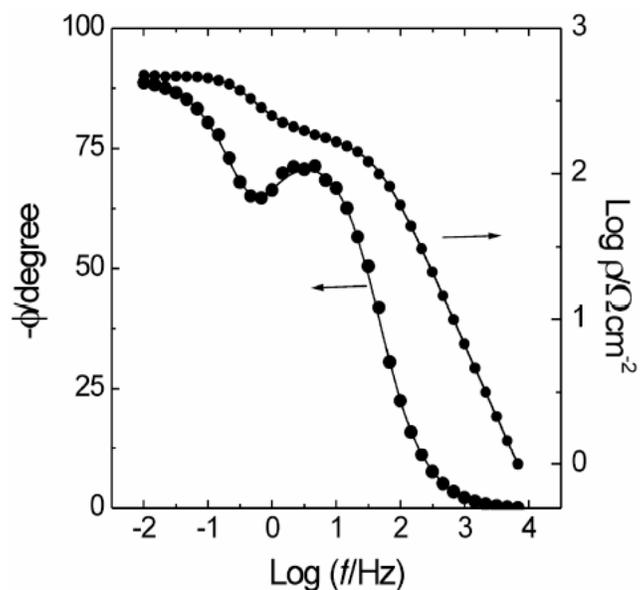


Fig. (5). Ac impedance diagrams in Bode coordinates (Phase and Quadrature vs. Logarithm of the frequency) obtained at $E = 0.1$ V for a 70 nm thick POAP film in contact with a 0.4 M $C_6H_5SO_3 Na + 0.1$ M $C_6H_5SO_3 H$ solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].

According to the impedance model used here [5], the significant decrease in both parameters D and k_{sh} for the 70 nm thick POAP film, in going from sulfate anions to BS anions, seems to indicate that the anion present in the supporting electrolyte affects both interfacial (gold film|POAP interface) and bulk transport processes at POAP films. However,

Table 1. Comparison of the Standard Electrochemical Rate Constant (k_{sh}) and Diffusion Coefficient (D) Values for a Thick POAP Film in the Presence of Sulfate and BS Anions. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

Anion	$10^2 k_{sh}/\text{cm s}^{-1}$	$10^8 D/\text{cm}^2 \text{s}^{-1}$	ϕ_p/nm
$^a\text{SO}_4^{-2}$	1.04	3.72	70
Anion	$10^2 k_{sh}/\text{cm s}^{-1}$	$10^{10} D/\text{cm}^2 \text{s}^{-1}$	ϕ_p/nm
$^b\text{C}_6\text{H}_5\text{SO}_3^-$	2.25	5.32	70

$c = 4.7 \text{ M}$, $K' = 8.5 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$, $C_{HF} = 30 \times 10^{-6} \text{ F cm}^{-2}$. Electrode potential: $E = 0.1 \text{ V}$. Electrolytes: $^a 0.1 \text{ M SO}_4\text{H}_2 + 0.4 \text{ M Na}_2\text{SO}_4$, $^b 0.1 \text{ M C}_6\text{H}_5\text{SO}_3\text{H} + 0.4 \text{ M C}_6\text{H}_5\text{SO}_3\text{Na}$.

for the thinner POAP film, the effect of the electrolyte solution on the charge-transport process seems to be negligible. As it has been indicated that electron hopping controls the charge-transport process at POAP [5, 14], the interpretation of electrolyte effects on the charge conduction can be made on the basis of the electron-hopping model [14]. In the limit of a large excess of supporting electrolyte in the film and noninteracting sites, D has been expressed in terms of the mean distance between adjacent redox sites, according to $D = (a^2 k_0)$. Parameter k_0 is the intermolecular electron-transfer rate constant and a is the mean distance between two adjacent redox sites. The hopping rate k_0 exhibits an exponential dependence on a , through the energy $-U(x+a)$ of a state with an electron in the position x along the current direction (see Eq. (23) in Ref. [16]). That is, the principal effect of the hopping distance a on D proceeds from the exchange rate. In this sense, the effect of increasing the mutual separation a between adjacent redox centers is to decrease the exchange rate k_0 , which in turn should lead to a D_e decrease. Then, it could be suggested that at low POAP thickness the intrinsic electron hopping controls the rate of the charge-transport process because the low quantity of electrolyte contained in the polymer matrix is unable to reduce the electrostatic repulsion between charged redox sites [17]. Then, the redox sites adopt an extended configuration with a large a value (low D value) so as to minimize the coulombic repulsion. In this connection, in previous work [15] it was demonstrated that within the thickness range from 0.4 mC cm^{-2} to 0.82 mC cm^{-2} ($10 \text{ nm} - 35 \text{ nm}$), POAP exhibits a rather continuous and compact structure. Thus, it is possible that only very low amounts of electrolyte can be incorporated into the compact structure exhibited by a thin POAP film ($\phi_p = 19 \text{ nm}$), and then transport parameters of POAP become independent of the external electrolyte composition. However, for large POAP thicknesses it is possible that considerable amounts of electrolyte can be incorporated into the polymer matrix. The electrolyte solution incorporated into the polymer can shield the redox centers from interaction between them and so the existence of a more compact distribution of these centers, as compared with that present in thin films, would reduce the a value, thereby increasing the rate of the charge-transport process by intrinsic electron hopping. Besides, it is possible

that BS anions were more effective than sulfate anions to shield the redox centers from interaction between them; however, its larger size as compared with sulfate, should lead to a higher a value, and then to a lower D value as experimentally observed (Table 1).

The higher ability of the BS anion to shield redox centers, as compared with that of the sulfate anion, could be due to both its larger size (area of the BS anion between 0.44 and $0.54 \pm 0.03 \text{ nm}^2$, and that of sulfate 0.18 nm^2 [18]) and a stronger interaction (anion with charged and noncharged parts) with the redox site. In this regard, SEM images of a thick POAP film ($0.82 \text{ mC cm}^{-2} - 1.5 \text{ mC cm}^{-2}$) show an external structure that is able to incorporate electrolyte solution [15].

With regard to the standard electrochemical rate constant, k_{sh} , the electron injection at the metal|polymer interface must be accompanied by ion injection at the polymer|solution interface to maintain charge neutrality within the polymer phase. The ion motion across the film is not expected to affect the overall charge-transfer reaction. However, for thin PAOP films (see Table 2) the resistance to counterion motion through the polymer phase (low content of electrolyte) seems to reduce the apparent rate of charge injection (large high-frequency semicircle) as compared with values for thick films (Table 1) where higher amounts of electrolyte could be incorporated. On the assumption that the external electrolyte can be incorporated into open structures of a thick POAP film, the lower rate of charge injection (k_{sh}) at the gold|POAP interface in the presence of BS anions as compared with sulfate anions could be due to a more pronounced blocking effect of BS anions towards the electron exchange between redox sites and the gold surface [15]. However, at present we have no clear explanation about the dependence of this interfacial charge-transfer parameter on the content of electrolyte in a POAP film.

As was above-indicated, impedance diagrams were recorded at various potentials. Both parameters obtained from the model (D and k_{sh}) are independent of the net oxidation state of the polymer within a large potential range. However, they decreased slightly at low degrees of oxidation.

Table 2. Comparison of the Standard Electrochemical Rate Constant (k_{sh}) and Diffusion Coefficient (D) Values for a thin POAP Film in Contact with Sulfate and BS Solutions. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

Anion	$10^4 k_{sh}/\text{cm s}^{-1}$	$10^{11} D/\text{cm}^2 \text{s}^{-1}$	ϕ_p/nm
$^a\text{SO}_4^{-2}$	1.04	1.72	19
$^b\text{C}_6\text{H}_5\text{SO}_3^-$	1.22	1.83	19

$c = 4.7 \text{ M}$, $K' = 8.5 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$, $C_{HF} = 30 \times 10^{-6} \text{ F cm}^{-2}$.

Electrode potential: $E = 0.1 \text{ V}$. Electrolytes: $^a 0.1 \text{ M SO}_4\text{H}_2 + 0.4 \text{ M Na}_2\text{SO}_4$, $^b 0.1 \text{ M C}_6\text{H}_5\text{SO}_3\text{H} + 0.4 \text{ M C}_6\text{H}_5\text{SO}_3\text{Na}$.

In order to analyze in more detail the effects of electrolyte incorporation on the charge-conduction process of POAP, the ionic strength of the electrolyte solution was varied while the proton concentration remained constant. Impedance diagrams for the 70 nm thick POAP film in contact with solutions of different concentration of sulfate and benzenesulfonate anions are shown in Fig. (6) and Fig. (7), respectively. As can be seen, impedance plots depend on the electrolyte concentration. However, for the 19 nm thick POAP film impedance spectra do not depend on the electrolyte concentration (not shown).

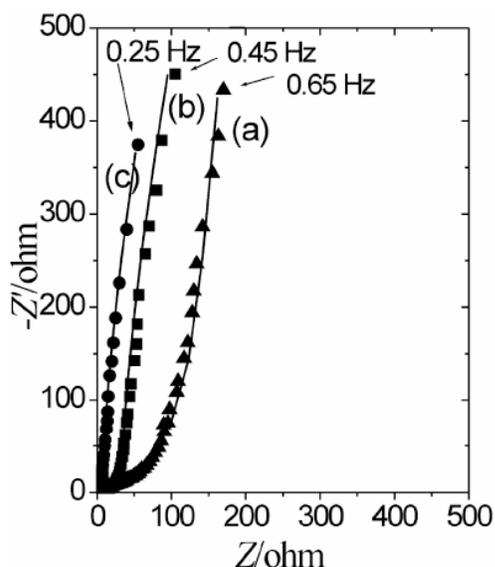


Fig. (6). *Ac* impedance diagrams in the Nyquist coordinates ($-Z''$ vs. Z) obtained at $E = 0.1$ V for a 70 nm thick POAP film in contact with x M $\text{Na}_2\text{SO}_4 + 0.1$ M H_2SO_4 solutions. Values of x : (\blacktriangle) 0.4; (\blacksquare) 0.8 and (\bullet) 1.5. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].

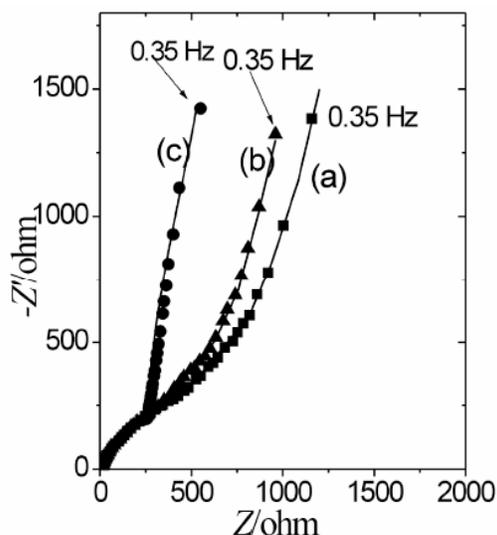


Fig. (7). *Ac* impedance diagrams in the Nyquist coordinates ($-Z''$ vs. Z) obtained at $E = 0.1$ V for a 70 nm thick POAP film in contact with x M $\text{C}_6\text{H}_5\text{SO}_3\text{Na} + 0.1$ M $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ solutions. Values of x : (\blacksquare) 0.4; (\blacktriangle) 0.8; and (\bullet) 1.5. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].

The fitting of these impedance diagrams (also the corresponding Bode plots) gives the parameter values collected in Tables 3 and 4, respectively. As can be seen, both parameters (D and k_{sh}) increase with the increase of the anion concentration. On the assumption that the external electrolyte was incorporated into the polymer phase, it would be expected that an increase in the ion concentration in the solution would cause an increase in the ion concentration within the film (inner solution). If these ions (sulfate and benzenesulfonate) reduce the repulsive interaction between redox sites, an increase in their concentration within the film would cause a decrease in the resistance to the charge conduction by electron hopping through it. That is, an increase in the electrolyte concentration should cause an increase of the diffusion coefficient. Again, by comparing the adsorption capability of both anions ($\text{BS} > \text{sulfate}$) lower k_{sh} values are observed in the presence of benzenesulfonate anions as compared with sulfate ones. However, k_{sh} values in the presence of both anions increase with the increase of the ionic strength of the solution.

4. CONCLUSIONS

Charge-transport and charge-transfer parameters of poly(*o*-aminophenol) films were obtained by impedance measurements in solutions containing sulfate and benzenesulfonate anions, respectively. Experimental impedance spectra were interpreted on the basis of a modified electron-hopping model. The model gives an effective diffusion coefficient whose value represents the electron-transport rate within the polymer phase. Also, a standard electrochemical rate constant is obtained from the model, which describes the electron-transfer rate across the metal|polymer interface. While for film thicknesses within the range from 10 nm to 35 nm both transport parameters are independent of the type and concentration of the anion present in the external solution, in the thickness range from 38 nm to 70 nm, the parameter values increase with the increase of the electrolyte concentration. Besides, within the former thickness range, parameter values are nearly two orders of magnitude lower than within the latter thickness range. This indicates a resistive behavior of thin poly(*o*-aminophenol) films. However, at constant film thickness and electrolyte concentration, in the thickness range from 38 nm to 70 nm, parameter values are higher in the presence of sulfate ions than in the presence of benzenesulfonate ones. The influence of the type and concentration of the electrolyte on the charge-transport and charge-transfer rates at thick poly(*o*-aminophenol) films was explained in terms of the incorporation of the electrolyte into their open structures, which facilitates the electron-hopping process by reducing the repulsive interactions between redox sites. Strong repulsive interactions between redox centers should operate in thin poly(*o*-aminophenol) films whose compact structures hinder the incorporation of the electrolyte. These considerations on the basis of different structures of thin and thick films, respectively, are confirmed by SEM images. Although the simple impedance model employed in this work gives satisfactory results, more work is in progress to obtain a more complete series of charge-transport parameters, electron and ion diffusion coefficients, interfacial resistances and capacitances as a function of the type and concentration of ions present in the electrolyte solution in contact with poly(*o*-aminophenol) films. To this end the theory of

Table 3. Comparison of the Standard Electrochemical Rate Constant (k_{sh}) and Diffusion Coefficient (D) Values for a 70 nm thick POAP Film in Contact with Sulfate Solutions of Different Concentration. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

Anion	$10^2 k_{sh}/\text{cm s}^{-1}$	$10^8 D/\text{cm}^2 \text{s}^{-1}$	X
$^a\text{SO}_4^{-2}$	1.04	3.72	0.4
	3.02	6.27	0.8
	5.22	9.83	1.5

$c = 4.7 \text{ M}$, $K^* = 8.5 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$, $C_{HF} = 30 \times 10^{-6} \text{ F cm}^{-2}$. Electrode potential: $E = 0.1 \text{ V}$. Electrolytes: $^a 0.1 \text{ M SO}_4\text{H}_2 + x \text{ M Na}_2\text{SO}_4$.

Table 4. Comparison of the Standard Electrochemical Rate Constant (k_{sh}) and Diffusion Coefficient (D) Values for a 70 nm Thick POAP Film in Contact with Benzenesulfonate Solutions of Different Concentration. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

Anion	$10^2 k_{sh}/\text{cm s}^{-1}$	$10^{10} D/\text{cm}^2 \text{s}^{-1}$	x
$^a\text{C}_6\text{H}_5\text{SO}_3$	2.25	5.32	0.4
	3.17	6.93	0.8
	7.22	9.91	1.5

$c = 4.7 \text{ M}$, $K^* = 8.5 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$, $C_{HF} = 30 \times 10^{-6} \text{ F cm}^{-2}$. Electrode potential: $E = 0.1 \text{ V}$. Electrolytes: $^a 0.1 \text{ M C}_6\text{H}_5\text{SO}_3\text{H} + x \text{ M C}_6\text{H}_5\text{SO}_3\text{Na}$.

Vorotyntsev *et al.*, reported in Ref. [19], will be applied to study this system in more detail.

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REFERENCES

- Inzelt, G.; Pineri, M.; Schultze, J.W.; Vorotyntsev, M.A. Electron and proton conducting polymers: recent developments and prospects. *Electrochim. Acta*, **2000**, *45*, 2403-2421.
- Cai, Z.; Martin, R. Electrochemical investigations of electronically conductive polymers. Part VI. Mechanism of the redox reactions for the electronically conductive form of polypyrrole. *J. Electroanal. Chem.*, **1991**, *300*, 35.
- Tucceri, R. Practical applications of poly(o-aminophenol) film electrodes. *Open Phys. Chem. J.*, **2009**, *3*, 46-62.
- Chen, X.; Chen, J.; Deng, C.; Xiao, C.; Yang, Y.; Nie, Z.; Yao, S. Amperometric glucose biosensor based on boron-doped carbon nanotubes modified electrode. *Talanta*, **2008**, *76*, 763-767.
- Rodríguez Nieto, F.J.; Tucceri, R. The effect of pH on the charge transport at redox-modified electrodes: an ac impedance study applied to poly(o-aminophenol) film electrodes. *J. Electroanal. Chem.*, **1996**, *416*, 1-24.
- Tucceri, R. A review about the surface resistance technique in electrochemistry. *Surf. Sci. Reports*, **2004**, *56*, 85-157.
- Tucceri, R.I.; Posadas, D. A surface conductance study of the anion adsorption on gold. *J. Electroanal. Chem.*, **1985**, *191*, 387.
- Tucceri, R.I.; Barbero, C.; Silber, J. J.; Sereno, L.; Posadas, D. Spectroelectrochemical study of poly-o-aminophenol. *Electrochim. Acta*, **1997**, *42*, 919.
- Barbero, C.; Zerbino, J.; Sereno, L.; Posadas, D. Optical properties of electropolymerized orthoaminophenol. *Electrochim. Acta*, **1987**, *32*, 693.
- Rubinstein, I.; Sabatani, E.; Rishpon, J. Electrochemical impedance analysis of polyaniline films on electrodes. *J. Electrochem. Soc.*, **1987**, *134*, 3078.
- Greszczuk, M.; Poks, P. Analysis of charge transport impedance in the reduction of thin films of conducting polyaniline in aqueous trichloroacetic acid solutions. *J. Electroanal. Chem.*, **1995**, *387*, 79.
- Greef, R.; Kalaji, M.; Peter, L. M. Ellipsometric studies of polyaniline growth and redox cycling. *Faraday Discuss. Chem. Soc.*, **1989**, *88*, 277.
- Barbero, C.; Silber, J. J.; Sereno, L. Electrochemical properties of poly-ortho-aminophenol modified electrodes in aqueous acid solutions. *J. Electroanal. Chem.*, **1990**, *291*, 81.
- Rodríguez Nieto, F.J.; Posadas, D.; Tucceri, R.I. Effect of the bathing electrolyte concentration on the charge transport process at poly(o-aminophenol)-modified electrodes. An ac impedance study. *J. Electroanal. Chem.*, **1997**, *434*, 83-91.
- Tucceri, R. Blocking effect of poly(o-aminophenol) towards adsorption processes at a gold film surface. A comparison with its performance as biosensor and electrocatalyst material. *Open Phys. Chem. J.*, **2009**, *3*, 63-71.
- Chidsey, C.E.D.; Murray, R.W. Redox capacity and direct current electron conductivity in electroactive materials. *J. Phys. Chem.*, **1986**, *90*, 1479.
- Barbero, C.; Silber, J.J.; Sereno, L. Formation of a novel electroactive film by electropolymerization of orthoaminophenol. Study of its chemical structure and formation mechanism. Electropolymerization of analogous compounds. *J. Electroanal. Chem.*, **1989**, *263*, 333-352.
- Dutkiewicz, E.; Skoluda, P. Adsorption of benzenesulphonate anions at an Au(111) electrode: application to study of the reconstruction phenomenon of the Au(100) surface. *J. Chem. Soc. Faraday Trans.*, **1996**, *92*, 3763.
- Vorotyntsev, M.A.; Deslouis, C.; Musiani, M.M.; Tribollet, B.; Aoki, K. Transport across an electroactive polymer film in contact with media allowing both ionic and electronic interfacial exchange. *Electrochim. Acta*, **1999**, *44*, 2105.

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