

Poly(*o*-aminophenol) film electrodes: synthesis and characterization and formation mechanisms — A review article

R. Tucceri, P.M. Arnal, and A.N. Scian

Abstract: This review, which is divided into three parts, concerns electrochemical synthesis, spectroscopic characterization, and formation mechanisms of poly(*o*-aminophenol) (POAP) film electrodes. The first part of this review is devoted to describing the electropolymerization process of *o*-aminophenol (*o*-AP) on different electrode materials and in different electrolyte media by employing both potentiodynamic and potentiostatic methods. The evolution of the voltammogram during the electrosynthesis of POAP and the assignment of the voltammetric peaks to different species, according to the formation mechanism formulated by each author, are described. The effects of some chemical substances and electrochemical pretreatments of the electrode surface, on the electropolymerization process of *o*-AP, are also considered in this part of the review. The synthesis of POAP in neutral media, which yields a nonconducting polymer, and its use as component of biosensors and protective layer in corrosion processes, are analyzed at the end of the first part. The second part of this review refers to spectroscopic studies carried out by different authors to both identify the products of the *o*-AP electro-oxidation and elucidate the chemical structure of POAP film electrodes. This second part of the review also describes the different spectroscopic methods employed to study the redox process of POAP, which allows the demonstration of the existence of transient species during the transition of the completely oxidized form of POAP to the completely reduced one. The third part of this review shows the different mechanisms formulated to interpret the POAP film formation from both acid and basic solutions of *o*-AP. Also, some electrochemical and spectroscopic data which allowed to propose the corresponding formation mechanisms, especially in basic media, are described.

Key words: poly(*o*-aminophenol) film electrodes, electrochemical synthesis, spectroscopic characterization, formation mechanisms, redox process.

Résumé : Cet article de revue est divisé en trois parties et il se rapporte aux synthèses électrochimiques, à la caractérisation spectroscopique et aux mécanismes de formation d'électrodes à base de films de poly(*o*-aminophénol) (POAP). La première partie de cette revue est utilisée pour décrire le processus d'électropolymérisation du *o*-aminophénol (*o*-AP) sur divers matériaux servant d'électrodes et dans divers milieux électrolytiques différents en faisant appel à des méthodes potentiodynamiques et potentiostatiques. On décrit l'évolution des voltampérogrammes au cours des électrosynthèses de POAP et l'attribution des pics voltampérométriques aux diverses espèces, suivant le mécanisme de formation formulé par les divers auteurs. Dans cette partie de la revue, on considère aussi les effets de diverses substances chimiques et de prétraitements électrochimiques de la surface de l'électrode sur le processus d'électropolymérisation du *o*-AP. À la fin de cette première partie, on procède à une analyse de la synthèse du POAP, en milieu neutre, qui conduit à la formation d'un polymère non-conducteur et de son utilisation comme couche protectrice dans les processus de corrosion. La deuxième partie de cette revue se réfère aux études spectroscopiques qui ont été réalisées, par divers auteurs, pour identifier d'une part le produit d'électrooxydation du *o*-AP et, d'autre part, pour élucider la structure chimique des électrodes de film de POAP. Dans cette deuxième partie de la revue, on décrit aussi les diverses méthodes spectroscopiques utilisées pour étudier le processus redox du POAP qui a permis de démontrer l'existence d'espèces transitoires au cours de la transition de la forme complètement oxydée du POAP à la forme complètement réduite. La troisième partie de cette revue présente les divers mécanismes formulés pour interpréter la formation des films de POAP tant à partir de solutions acides que basiques de *o*-AP. De plus, on présente des données électrochimiques et spectroscopiques qui ont permis de proposer les mécanismes de formation correspondants, particulièrement en milieu basique. [Traduit par la Rédaction]

Mots-clés : électrodes de film de poly(*o*-aminophénol), synthèse électrochimique, caractérisation spectroscopique, mécanismes de formation, processus redox.

Introduction

Oxidation of *o*-aminophenol (*o*-AP) on different electrode materials (gold, platinum, carbon, indium – tin oxide, etc.) in aqueous medium was shown to form poly-*o*-aminophenol (POAP). Like aniline, *o*-AP can be polymerized electrochemically in acidic, neutral, and alkaline solutions. However, while a conducting film is only formed in acidic media, POAP synthesized in neutral and alkaline media leads to a nonconducting film.

Electropolymerization of *o*-AP in acid medium yields an electroactive polymer that exhibits its maximal electroactivity within the potential range $-0.2 \text{ V} < E < 0.5 \text{ V}$ (vs SCE) at pH values lower than 3.^{1,2} The electroactivity of POAP is explained by a redox mechanism that involves an addition/elimination of protons coupled with a reversible electron transfer.² The charge-transport process at POAP films is studied by employing different electrochemical techniques.¹⁻⁷ In previous work⁸ we studied the electrochemistry of

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POAP in the presence of different active redox couples in solution, and it was demonstrated that external variables, such as film thickness, solution pH, and redox couple concentration in solution, affect both the permeation process of electroactive species and the electron motion through a POAP film. An interesting review concerning charge-transfer and charge-transport processes occurring over the course of redox reactions of POAP film electrodes can be found in ref. 9.

The properties of POAP synthesized in basic medium are favourable to its applications in the field of bioelectrochemistry and electrocatalysis. In this regard, a nonconducting material is obtained that exhibits several advantages with respect to other polymers. POAP can be synthesized on different electrode surfaces, and the polymer thickness can be controlled within 10–100 nm because of a self-limiting growth. Employed as material to build amperometric biosensors, POAP has been shown to be permselective. In this regard, the interference from electroactive species, such as ascorbic acid and uric acid that are generally encountered in the determination of physiological samples, was significantly reduced by the use of a POAP film. Also, POAP is able to immobilize biological macromolecules. It has been proven that large amounts of glucose oxidase can be immobilized at POAP films, which is essential for the good performance of an amperometric glucose sensor. In the field of electrocatalysis, an interesting characteristic of POAP is the presence of an electron-donating OH group next to the imine nitrogen that increases the electron density at the imine sites. In addition, OH by itself is also a potential coordinating site. These factors combine to provide a strong acceptor binding of POAP with several metal cations. In this regard, POAP has been employed to develop stable electrocatalysts for oxygen reduction. A review about practical applications of POAP is found in ref. 10.

In spite of the two reviews^{9,10} reported in the literature about charge conduction and practical applications of POAP film electrodes, respectively, according to our knowledge no review work has been reported until now about electrosynthesis and spectroscopic characterization of POAP films from both neutral and alkaline solutions of *o*-AP. It is expected that the present review, together with the other previously published reviews,^{9,10} will be helpful to the colleagues who would like to achieve a more complete knowledge about the particular properties of this polymer.

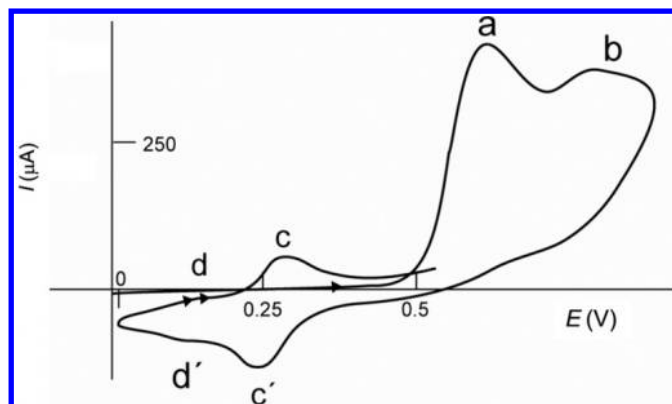
Electropolymerization of *o*-aminophenol on different electrode materials and in different electrolyte media – Formation of poly(*o*-aminophenol) film electrodes

Electropolymerization of *o*-aminophenol in acidic media

Barbero et al.¹¹ reported a study about the oxidation of *o*-AP and closely related compounds employing electrochemical, chemical, and spectroscopic measurements. The electro-oxidation of *o*-AP was studied on different electrode materials (Pt, Au, and glassy carbon (GC)) and different electrolyte media ($1 < \text{pH} < 7$). A typical voltammogram of a Pt electrode in contact with a 0.1 mol/L $\text{HClO}_4 + 0.4 \text{ mol/L NaClO}_4 + 1 \times 10^{-3} \text{ mol/L } o\text{-AP}$ aqueous solution (pH 1) is shown in Fig. 1.

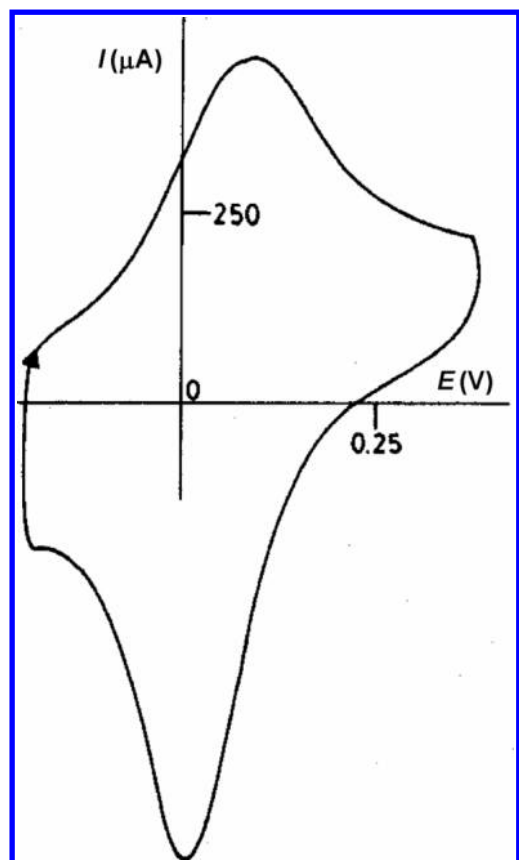
On the first positive sweep two peaks are defined (a) at 0.60 V (SCE) attributed to the oxidation of *o*-AP to the monocation radical ($o\text{-AP}^{+\bullet}$) and another peak (b) at 0.85 V, which was assigned to the oxidation of ($o\text{-AP}^{+\bullet}$) to dication. On the negative sweep none of these peaks show complementary peaks, indicating chemical follow-up reactions giving products detected as peaks c–c' and d–d' on the subsequent sweeps. It was observed that the system c–c' diminishes after continuous cycling in the same way as a, but the peak system d–d' increases, also showing the characteristic behavior of a deposited electroactive substance. This was verified by stirring the solution while cycling, because the system d–d' remained unchanged, as expected for an irreversible adsorbed electroactive substance. Analysis of the products employing IR

Fig. 1. Cyclic voltammogram of a Pt electrode contacting a 0.1 mol/L $\text{HClO}_4 + 0.4 \text{ mol/L NaClO}_4 + 1 \times 10^{-3} \text{ mol/L } o\text{-aminophenol (} o\text{-AP)}$ solution, pH 1. Scan rate, $\nu = 0.1 \text{ V s}^{-1}$; electrode area, $A = 0.126 \text{ cm}^2$.¹¹



and UV–vis spectroscopy (see the following) showed that the d–d' couple corresponds to a polymer of 3-aminophenoxazine (3APZ). A mechanism for the *o*-AP electro-oxidation was proposed in ref. 11 where the $o\text{-AP}^{+\bullet}$, formed in the first charge-transfer step, may follow different reaction paths (see the following). Thus, the formation of a composite of two different films, one of linear chain structure similar to polyaniline (PANI) and the other, with a phenoxazine-like chain structure, was proposed in ref. 11. The latter was considered to be the predominant product. To reinforce the conclusion about the proposed structure for the electroactive substance, the electrochemical properties of several compounds (*o*-anisidine, *p*- and *m*-aminophenol, *o*-phenylenediamine, etc.) with similar structures to *o*-AP were also analyzed in ref. 11. The presence of phenoxazine units in the structure of the polymer formed by the oxidation of *o*-AP was also confirmed by Barbero and co-workers in another work¹² by employing FT-IR spectroscopy. The electroactive substance formed by oxidation of *o*-AP was denominated POAP. An analysis of the voltammetric peak current (i_{pa}) as a function of the sweep rate (ν) and the initial concentration of *o*-AP was also carried out in ref. 11. It was observed that high concentrations of monomer favor higher rates of polymerization, with the consequent partial blocking of the electrode surface. This effect was more noticeable at high temperatures. However, the blocking effect was negligible at low monomer concentrations, and then the normal behavior for the cation radical dimerization reactions was observed. Barbero et al.¹¹ also prepared the electroactive polymer by chemical oxidation of *o*-AP, and its properties were compared with those of the electrochemically produced POAP. The chemical synthesis of POAP confirmed that the actual monomer in the formation of the polymer is the cyclic dimer of *o*-AP, 3APZ. A calculation of a global value of the rate constant for the dimerization reaction was carried out in ref. 11. With regard to the solution pH, a similar voltammetric response to the one shown in Fig. 1 was observed for pH values lower than 3. At pH values between 3 and 7, a diminished current of the peak system d–d', assigned to the film formation, was observed. Barbero et al.¹¹ remark that if extreme care is not taken in the preparation of a POAP film, not only in the concentration but also in the potential ranges, the possibility of side reactions and consequently “side” polymers, increases, and the real structures of the films obtained could be quite complex. Then, the best conditions proposed in ref. 11 for obtaining a reproducible POAP film are the repetitive cycling between -0.25 and 0.70 V (SCE) of an *o*-AP aqueous acid solution (pH 1) and an *o*-AP concentration less than 20 mmol/L . Figure 2 shows the voltammetric response of POAP in a monomer-free solution. The voltammogram is highly asymmetric, suggesting a complex redox behavior that does not follow the simple Nernstian model. The phenoxazine-like chain structure

Fig. 2. Cyclic voltammogram of poly-*o*-aminophenol (POAP) at pH 1. Scan rate, $\nu = 0.1 \text{ V s}^{-1}$; Pt electrode, electrode area $A = 0.126 \text{ cm}^2$; supporting electrolyte, $0.4 \text{ mol/L NaClO}_4 + 0.1 \text{ mol/L HClO}_4$.¹¹



proposed by Barbero et al.¹¹ is shown in Fig. 3, which demonstrates the redox switching of POAP in acidic media.

The electrochemical formation of POAP was also described by Ortega.¹³ Ortega¹³ focused his attention on the monomer purification before electropolymerization. *o*-AP (purum 90%) was purified by recrystallizing it three times in ethyl acetate. The very pale white plates were dried in a warm water bath under vacuum to eliminate residual solvent. The monomer was stored in a desiccator under vacuum until required. MNR, IR, and C¹³ spectra were recorded to ensure the absence of contaminant oxidation species in the monomer. A typical cyclic multisweep voltammogram of the Pt electrode in contact with 0.4 mol cm^{-3} of NaClO_4 and $10^{-2} \text{ mol dm}^{-3}$ of monomer solution is shown in Fig. 4.

The electrode potential was continuously swept at 100 mV s^{-1} between -0.25 and 0.75 V (SCE) .¹³ On the first positive sweep, only one irreversible peak is defined at 0.65 V (peak **a**, only visible at lower sensibility), which was attributed to the oxidation of the monomer to the monocation radical. No complementary peak to **a** was observed on the negative scan, whereas a large peak appeared at 0.23 V (peak **b**). This peak has a complementary one (peak **e**) at 0.29 V in the next positive scan and it was assigned to the redox reaction of a dimer formed prior to cyclization to produce 3APZ. It was also observed that, while peak **a** rapidly and continuously decreases up to a minimum, peaks **b** and **e** fall correspondingly. Also, after 8 or 10 min of cycling, the current response in the potential range from 0.0 to 0.2 V begins to increase continuously with successive potential scans, giving rise to peaks **c** and **d**, which were assigned to the build-up of an electroactive polymeric product on the electrode. Neither polymer nor couple **b** and **e** were formed if the potential scan did not reach 0.65 V . On the other hand, peaks from **b** to **d** were not observed when potential

cycling took place under continuous nitrogen bubbling. Thus, Ortega¹³ indicates that a slow chemical reaction is associated with the peaks **b** and **e** and, under stirred conditions, the intermediate corresponding to **b** and **e** peaks is moved away from the electrode, so that its further transformation into polymer is prevented. The comparison of voltammograms presented in Fig. 4 with those shown by Barbero et al.¹¹ for 3APZ, allowed Ortega¹³ to conclude that the coupling of 3APZ units to form the polymer is the process that occurs during the propagation of the polymeric chains, therefore, peaks **c** and **d** in Fig. 4 should be assigned to the redox reaction of 3APZ and POAP. Ortega¹³ remarked that the charge propagation proceeds slowly during the formation of POAP. The slow diffusion of *o*-AP species through the film to reach the electrode and produce more monocation radical was considered to be the cause by which peaks **a**, **b**, and **e** decrease with time, and then the produced film does not oxidize monomer because it is non-conducting at positive potentials. Also, that fact that the growth of the polymer starts after an induction time long after the peaks corresponding to *o*-AP radical cation and dimer become small was considered by Ortega¹³ as a confirmation that the propagation process involves further oxidation and coupling of 3APZ.

The electrochemical synthesis of POAP on the surface of a carbon paste electrode (CPE) in the presence of sodium dodecyl sulfate (SDS) is described by Ojani et al.¹⁴ These authors showed (as did Barbero et al.¹¹ and Ortega¹³) that, in the absence of SDS, *o*-AP is irreversibly oxidized at positive potential values ($0.7 \text{ V vs Ag/AgCl/KCl } 3 \text{ mol/L}$) without corresponding cathodic processes in the reverse scan. As in other works, after consecutive cycles one redox process was observed on the voltammetric response, which was assigned to 3APZ. The peaks corresponding to this process did not increase considerably with potential cycling. This effect was attributed by Ojani et al.¹⁴ to soluble products produced on the electrode surface that do not allow the monomer to reach the electrode surface and produce the monocation radical. Therefore, prolonged potential cycling was needed for transformation of the soluble 3APZ to POAP, which was observed within a potential range ($0.2 \text{ V} < E < 0.3 \text{ V}$) less positive than that of 3APZ. When SDS is added to the monomer solution, the monomer oxidation potential was shifted to less positive potentials (almost 0.075 V) and the oxidation current increased, as compared with the process in the absence of SDS. The rate of polymerization also increased considerably in the presence of SDS, and the peaks attributed to POAP grew simultaneously with that corresponding to 3APZ growth. Ojani et al.¹⁴ remarked that, in the presence of SDS, the monomer *o*-AP can easily reach the electrode surface and produce more monocation radical than in the absence of SDS. The rate of polymerization depends on the SDS concentration. Up to 0.1 mmol/L of SDS the rate of polymerization was not much larger than that observed without SDS. However, for SDS concentration values higher than 0.1 mmol/L , the rate of polymerization increased rapidly and, finally, it saturated at around 4 mmol/L . The redox behavior of the polymers synthesized in the absence and in the presence of SDS was also investigated in the supporting electrolyte solution. The comparison of the electrochemical response of the immediately prepared SDS/POAP/CPE electrode with that obtained after immersing the electrode for 1 h in 0.5 mol/L HClO_4 demonstrated that the immediately prepared electrode shows two redox couples at about 0.2 and 0.3 V , which were assigned to the phenoxazine units of POAP and 3APZ, respectively.

The electrochemical oxidation of *o*-AP from a $0.2 \text{ mol/L NaClO}_4 + 0.1 \text{ mol/L HClO}_4$ solution on platinum (Pt) and GC electrodes employing cyclic voltammetry (CV), was studied by Bulhões and co-workers.¹⁵ Cyclic voltammograms of Pt and GC electrodes in the electrolyte solution containing 5 mmol^{-1} of *o*-AP are compared in Fig. 5. *o*-AP oxidizes irreversibly on both electrodes, and two anodic peaks (I and II) are observed without corresponding cathodic processes in the reverse scan. Peaks I and II appear for the GC electrode as well separated waves and at more negative potentials

Fig. 3. Reaction scheme of poly-*o*-aminophenol (POAP) redox switching including oxidized and reduced forms.¹¹

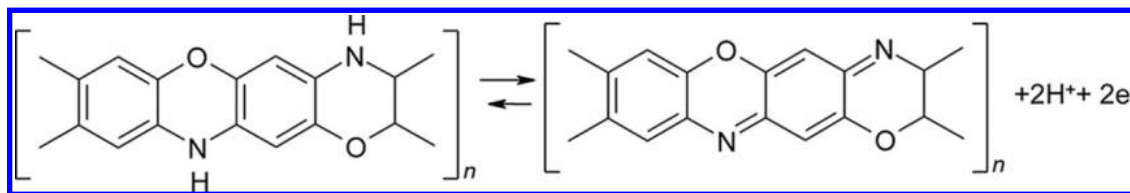
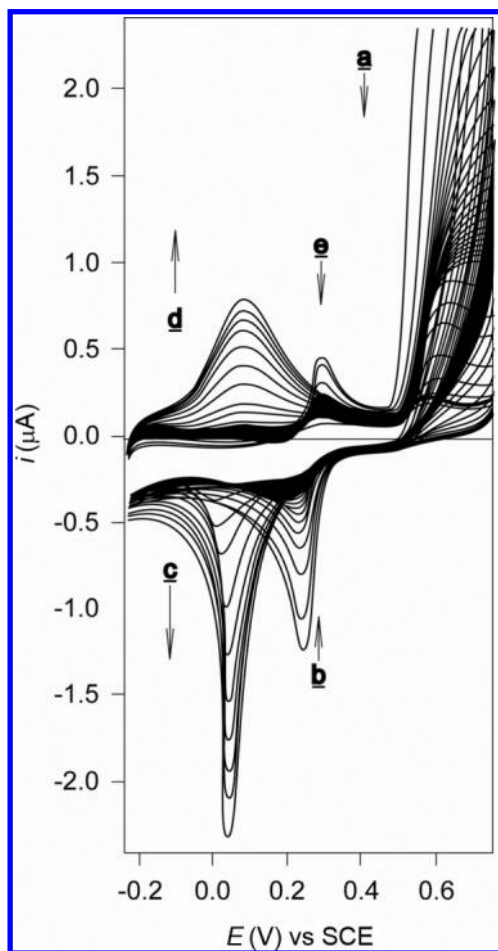


Fig. 4. Cyclic voltammograms of *o*-aminophenol (*o*-AP) at pH 0.9 in a solution containing $0.4 \text{ mol dm}^{-3} \text{ NaClO}_4$ ($v = 100 \text{ mV s}^{-1}$). Area of the working electrode, $1.9 \times 10^{-3} \text{ cm}^2$. Arrows indicate the change in the peak height as the electropolymerization is taking place.¹³



than for Pt, which was attributed to a more favorable process of oxidation on the former electrode material. Peak II was related to follow-up oxidation reactions after peak I. Besides the nature of the electrode surface, the characteristics of the films synthesized by Bulhões and co-workers¹⁵ depended on variables such as the final potential and the value of the potential scan rate. It was observed that the current of peak I increased linearly with the square root of the scan rate ($v^{0.5}$), indicating a process controlled by ion diffusion. The current function ($I_p v^{0.5} c$) vs $v^{0.5}$ plot showed the existence of successive electrochemical-chemical-electrochemical steps ($E(\text{CE})_n$) during the *o*-AP oxidation, and two electrons were estimated to be involved in the process. Bulhões and co-workers¹⁵ postulated that, besides a film with a ladder structure, the oxidation of *o*-AP can produce intermediate benzoquinone monoamine after successive cycling. They¹⁵ also remarked that, although APZ is formed in solution after successive cycling, it does not polymerize as proposed by Barbero et al.¹¹ and Ortega¹³. The electrode

material seems to affect the *o*-AP electropolymerization process. In this regard, the redox processes of the POAP films deposited on Pt and GC electrodes in the supporting electrolyte were found to be different. A less electroactive film was obtained on Pt electrodes and compared with GC electrodes.

The effect of the electrode surface on the electropolymerization process of *o*-AP was studied in detail by Yong and Zugeng.¹⁶ GC electrodes were chemically and electrochemically pretreated before electropolymerization of *o*-AP. The electrode surfaces were polished carefully to a mirror finish and then cleaned ultrasonically with triply distilled water for 3 min. This kind of electrode was denoted¹⁶ as an “untreated” electrode. In addition, electrochemical treatment of the electrodes was achieved by placing the polished electrodes in $0.1 \text{ mol/L H}_2\text{SO}_4$ at 1.85 V (SCE) for 5 min, and then they were cycled between -0.2 and 0.7 V for 15 min. Chemical pretreatment of the electrodes was achieved by immersing the electrodes in concentrated nitric acid (67% w/w) and sulfuric acid (98% w/w) for 10 min, respectively. In most of the experiments described in ref. 16 CV was employed to synthesize POAP films, using a potential sweep rate of 100 mV s^{-1} . Electropolymerizations were carried out on these different surfaces by cycling the electrode potential between -0.2 and 0.7 V and the net charge passed in each kind of electrode was assessed. As was proposed by Barbero et al.,¹¹ a composite of two different (ladder-like and linear chain) structures was considered to be formed on the electrode surfaces under the polymerization conditions employed in ref. 16. Figures 6a–6c compare three stable cyclic voltammograms of POAP films on untreated, chemically pretreated, and electrochemically pretreated GC electrode surfaces, respectively. The net charge during the electropolymerization process of each polymer film was 46 mC cm^{-2} . The oxidation current peak 1 and the reduction current peak 1' were attributed to the redox reaction of the polymer film. The highest peak current was obtained for the electrochemically treated GC electrode (Fig. 6c). The peak current value for the film formed on the electrochemically pretreated electrode was about four times that of the untreated electrode. The reversibility of the redox reaction was also improved and the ratio I_{pa}/I_{pc} was nearer to unity in the electrochemically pretreated electrode. These differences were attributed, in part at least, to the formation of thicker POAP films on the pretreated electrode owing to chemical oxidation of *o*-AP by some oxide species present on the surface electrode after pretreatment. The $\text{C}_n^+\text{HSO}_4^-$ species on the GC surface was considered as a possible oxidant and (or) newly formed oxide species after electrochemical pretreatment. On the other hand, Yong and Zugeng¹⁶ also verified that the electron-transfer rate from the polymer film to the electrode substrate on electrochemically pretreated GC electrodes was at least twice that of the electron-transfer rate for the untreated electrode. It was proposed that some functional group, such as quinone-like species, may serve as an “electron mediator” at the polymer-solution interface. The effect of the pretreatment potential on the electropolymerization rate of *o*-AP was also analyzed by Yong and Zugeng.¹⁶ The electropolymerization rate for the pretreated electrode was not very different from that for the untreated electrodes when the pretreatment potential was 1.55 V . However, it was observed that for pretreatment potentials of 1.85 and 2.05 V , the electropolymerization rate of the monomer increased with the increase of the pretreatment

Fig. 5. Cyclic voltammograms of (a) Pt and (b) glassy carbon (GC) electrodes in a 0.2 mol/L NaClO₄ + 0.1 mol/L HClO₄ + 5 mmol L⁻¹ *o*-aminophenol (*o*-AP) solution. Scan rate, $\nu = 100 \text{ mV s}^{-1}$.¹⁵

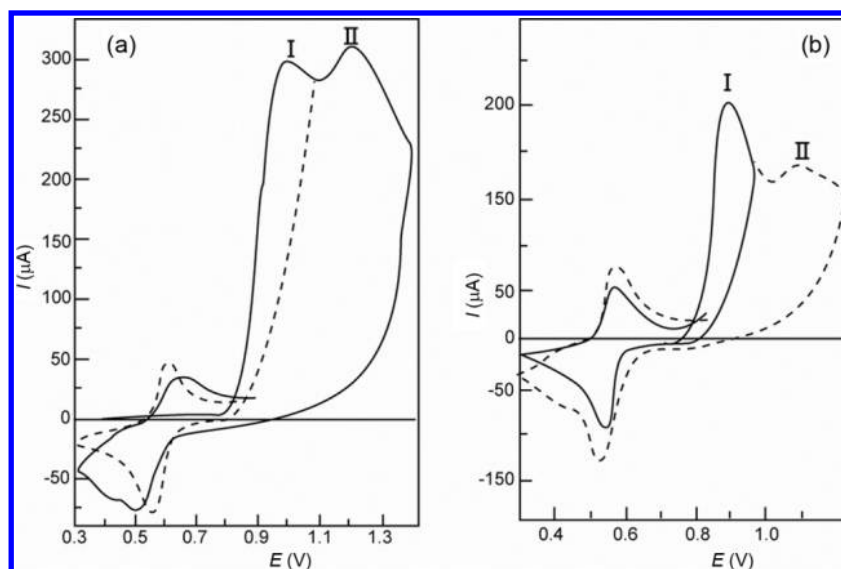
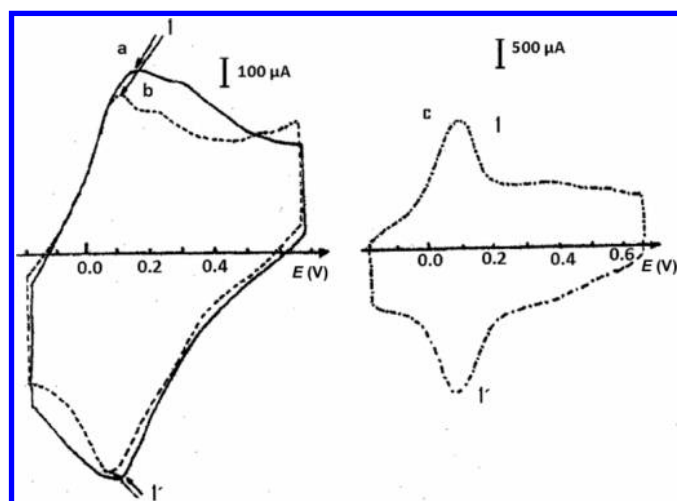


Fig. 6. Cyclic voltammograms of poly-*o*-aminophenol (POAP) films (46 mC cm⁻²) on different carbon electrode substrates in 0.1 mol/L H₂SO₄. (a) Original glassy carbon (GC) electrode. (b) Chemically pretreated electrode using 98% sulfuric acid for 10 min. (c) Electrochemically pretreated GC electrode at 1.85 V for 5 min, then cycled between -0.2 and 0.7 V for another 15 min in 0.1 mol/L H₂SO₄.¹⁶



potential. The faster polymerization rate at higher pretreatment potentials was attributed to the higher amounts of surface oxide species formed on the electrode surface. This study¹⁶ on different GC surfaces seems to indicate that oxide species formed on the electrode surface can play the role of oxidants within the electropolymerization process of *o*-AP and these species oxidize *o*-AP⁺ to the oligomer of *o*-AP. With regard to chemical pretreatment of the electrodes, Yong and Zugeng¹⁶ remarked that external reflection FT-IR spectra and attenuated total reflection (ATR) FT-IR spectra showed evidence that nitro groups are formed on carbon after chemical treatment with nitric acid. The effect of nitro and sulfate groups present at the surfaces of chemically pretreated GC electrodes on the electropolymerization of *o*-AP was also analyzed by Yong and Zugeng.¹⁶ It was observed that the electropolymerization rate for the electrodes that were treated with nitric acid was quite slow, even slower than the rate for untreated electrodes.

Fig. 7. Partially ring-opened structure of poly-*o*-aminophenol (POAP).¹⁷

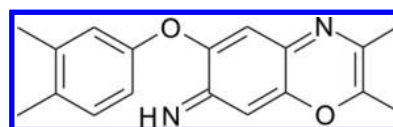
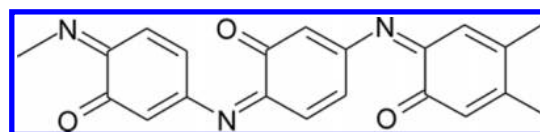


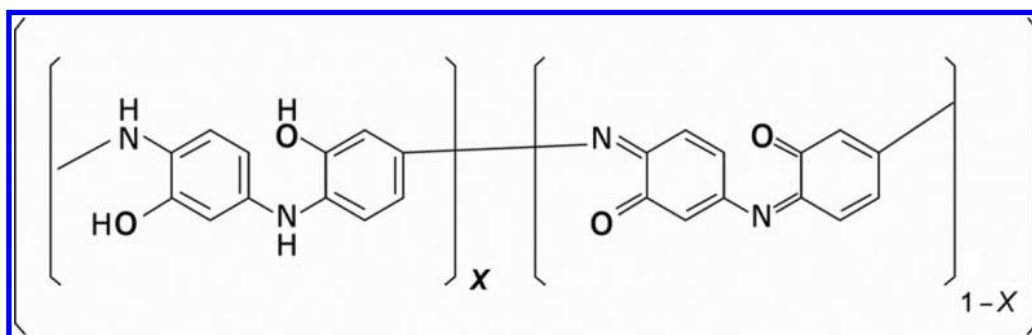
Fig. 8. Partially hydrolyzed structure of poly-*o*-aminophenol (POAP).¹⁷



In this regard, a polymer film whose charge was 46 mC cm⁻² was obtained in about 40 s on electrochemically pretreated GC electrodes. On both untreated and sulfuric acid-treated electrodes, the formation of a similar thickness of film took about 5 min. However, only a 23 mC cm⁻² thickness film was obtained on nitric acid-treated electrodes after 30 min of polymerization. All these findings allowed Yong and Zugeng¹⁶ to conclude that the different surface species present on different chemically pretreated GC electrodes may have different effects on the electropolymerization process of *o*-AP and different electropolymerization mechanisms may also be involved in the formation of POAP.

Oyama and co-workers¹⁷ prepared POAP on basal-plane pyrolytic graphite (BPG) and In-Sn oxide conducting glass (indium thin oxide, ITO) by electro-oxidative polymerization of *o*-AP. The electrode potential was cycled between -0.4 and 1.0 V (vs a sodium chloride saturated calomel electrode) at 50 mV s⁻¹ in a 0.5 mol/L Na₂SO₄ solution (pH 1) containing 50 mmol/L *o*-AP. As reported in other works,^{11-13,15} *o*-AP electro-oxidizes irreversibly at high positive potentials and, after the first reverse scans, anodic and cathodic currents are developed within the potential region between -0.2 and 0.2 V. The current response within this last potential region increased continuously with successive potential scans, indicating the build-up of the electroactive polymeric product POAP. As the potential scan was continued, both electrode (BPG and ITO) surfaces were covered with a brownish orange thin

Fig. 9. Structure of poly-*o*-aminophenol (POAP) as an alternating series of oxidized (quinonoid) and reduced (*N*-phenyl-*p*-phenylenediamine) repeating units.¹⁸



film. A reversible redox response of the POAP film was observed only in the presence of the supporting electrolyte solution (0.2 mol/L NaClO₄, pH 1). The amount of charge involved in both oxidation and reduction processes was found to be almost equal. POAP films obtained by Oyama and co-workers¹⁷ were characterized by IR spectroscopy, and the spectra of POAP were compared with those of *o*-AP and phenoxazine. From this comparison two structures of POAP were proposed: a partially ring-opened structure (Fig. 7) and another partially hydrolyzed structure (Fig. 8).

Zhang et al.¹⁸ studied the electrochemical synthesis of POAP on GC in a 1 mol/L SO₄H₂ + 0.5 mol/L Na₂SO₄ solution by CV and Raman spectroscopy. The evolution of the cyclic voltammograms during polymerization of *o*-AP within the potential range comprised between -0.2 and 1.0 V (SCE) was analyzed by Zhang et al.¹⁸ Three redox pairs were observed. The most negative redox pair was observed at around 0–0.15 V and it was the only noticeable feature in the cyclic voltammogram of POAP in an acid medium without the monomer. While this redox pair was attributed to the redox reactions of *o*-AP polymers and (or) oligomers, the other two more positive peak systems were associated with the oxidation of *o*-AP to the radical cation (OAP^{•+}) and its further oxidation to the dication, respectively. While the peaks of the redox pair at 0–0.15 V increased steadily with increasing the number of scans, showing the gradual but continual formation of electroactive POAP, the peaks of the other two redox pairs decreased. The flattening of the two more positive peak systems was attributed to a limitation on *o*-AP diffusion during the polymerization process. The scarce formation of the radical cation (polaron) and dication (bipolaron) during the polymerization was associated with restricted charge-transport processes and electron delocalization effects along a partly cross-linked polymer chain. Zhang et al.¹⁸ proposed that POAP is formed predominantly by the attack of oxidized monomers on the polymer growing chain. Their in situ Raman spectroscopy measurements suggest that the POAP matrix contains alternating oxidized (quinonoid) and reduced the (*N*-phenyl-*p*-phenylenediamine) repeating units (Fig. 9).¹⁸

Zhang and co-workers in another work¹⁹ synthesized POAP on GC and Pt electrodes from a solution containing 0.05 mol/L *o*-AP in a mixture of 1 mol/L H₂SO₄ and 0.5 mol/L Na₂SO₄ to study the oxidation process of POAP deposits of different thicknesses. Potential was scanned from -0.2 to 0.8 V (SCE) at 100 mV s⁻¹ for different numbers of cycles (*N*). The extent of the oxidation of the polymer films was investigated at the open-circuit potential of POAP. The synthesis conditions employed by Zhang and co-workers¹⁹ allowed them to propose the same POAP structure formulated in ref. 18 (Fig. 9). The relative proportions of alternating oxidized (quinonediimine) and reduced (phenylenediamine) repeating units were found to be dependent on the oxidation state of the polymer. Although the polymer synthesized in ref. 18 corresponds to the reduced state (*E* = -0.2 V) of POAP, it was observed in ref. 19 that it is readily oxidized by dissolved oxygen in the electrolyte and the extension of the oxidation depends on the film

thickness. Thick films were more difficult to oxidize and often resulted in a mixture of reduced and oxidized forms. With the diffusion of oxygen impeded by the increase of the film thickness, oxidation of thick POAP films was confined mostly to the polymer exterior. The structure of POAP proposed by Zhang and co-workers¹⁹ also allowed them to explain the interaction of the polymer with metal cations. In this regard, it was observed that when POAP films deposited from 150 voltammetric cycles are equilibrated in a 0.1 mol/L AgNO₃ solution for 30 min, the films capture silver cations. The cation capturing process was attributed to the simultaneous presence of hydroxyl and amino groups of the polymeric backbone of POAP, in which the lone pair electrons are available to coordinate with metal cations (Fig. 9). The interaction of POAP with silver ions ranged from redox reactions, in which cations were reduced to the metallic form, to a partial charge transfer between the metal and the polymer resulting in the formation of a metal-polymer complex. These two types of interactions predominate in thick films (*N* = 120) and thin films (*N* = 1). Films of moderate thickness (*N* = 20) exhibited intermediate behavior. The Ag⁺-POAP complex synthesized in ref. 19 was also compared with that of Ag-PANI.²⁰ It was indicated that the Ag⁺-POAP complex presents an improved stability over that of Ag⁺-PANI because of the cooperative action of the oxygen atom in the POAP chemical structure. Since the redox reaction of silver is within the range of the POAP redox reaction, changes of POAP conductivity were not significant during the redox reactions of the POAP-Ag⁺ complex. This was very different from the situation of the Ag⁺-PANI complex, where the redox switching of PANI between the insulating state of leucoemeraldine and the conducting state of emeraldine has substantial influence on the voltammetric response of silver redox behavior. Also, it was demonstrated by Zhang and co-workers¹⁹ that POAP is more resistant than PANI to electrochemical degradation and can capture four times more silver than PANI. The POAP-Ag(I) complex also exhibits electrocatalytic activity in dissolved oxygen reduction. However, it was observed that silver can be released from the complex upon acidification of the nitrogen and oxygen atoms or upon application of a sufficient positive potential.

The 1,4-substituted molecular structure of POAP proposed by Zhang and co-workers^{18,19} (Fig. 9) also seems to be consistent with the electrochemical response of POAP films to ferric cation in solution.^{21,22} It was reported by Yano et al.²¹ that POAP films obtained on ITO electrodes by electropolymerization of *o*-AP (0.1 mol/L) in a 0.1 mol/L H₂SO₄ aqueous solution, after being soaked in a ferric cation solution, can act as potentiometric Fe(III) ion sensors. In this regard, the POAP films immediately synthesized²¹ showed IR spectra that correspond to a 1,4-substituted structure. When these POAP films were soaked for 24 h in a 0.1 mol/L H₂SO₄ aqueous solution containing 50 mmol/L Fe₂(SO₄)₃, their XPS spectra showed iron ion capture. The ferric cation capturing process was attributed to the simultaneous presence of

hydroxyl and amino groups of the polymeric backbone of POAP. After this cation capture process, the electrode potential of the POAP film was measured in various aqueous solutions containing Zn(II), Ni(II), Cu(II), Fe(II), and Fe(III) ions at different concentrations. The relationship between the electrode potential (E) and the logarithm of the concentration (C) of the different cations in solutions was recorded. The electrode showed no potential response to ion concentration for Zn(II), Ni(II), Cu(II), and Fe(II) ions. However, it showed a Nernstian potential response to Fe(III) ions with a slope $-57 \text{ mV}/\log[\text{Fe(III)}]$. The response time was less than 10 s, and the response was observed until $[\text{Fe(III)}] = 10^{-4} \text{ mol/L}$. The response to Fe(III) ions in solution was considered indicative of the presence of Fe(II) in the POAP film. The presence of Fe(II) into the film was explained by considering that the captured Fe(III) are, at least in part, reduced to Fe(II) by the film. The potentiometric response was attributed to the electron transfer between Fe(II) ions into the film and Fe(III) ions in solution.

Despite the extensive electrochemical studies of potentiodynamically synthesized POAP, Holze and co-workers²³ investigated the potentiostatic electrochemical polymerization of *o*-AP at different electrode potentials ($E = 0.7, 0.8, \text{ and } 0.9 \text{ V vs SCE}$) with the aim of comparing the redox behaviors of the synthesized polymer by CV and potentiostatically. POAP films potentiostatically synthesized at 0.7 V showed two redox processes. The first redox process was centered at $E = 0.16/0.15 \text{ V (SCE)}$ and the second one was observed at $E = 0.35/0.29 \text{ V}$. The contribution of the second redox process decreases as the potential applied during the electrosynthesis is increased. Voltammograms of POAP obtained at the higher potential (i.e., 0.90 V) showed a sharp cathodic peak with two distinct anodic peaks on the forward scan. Furthermore, the voltammogram of POAP obtained at $E = 0.90 \text{ V}$ presented a somewhat intermediate behavior between that of films obtained potentiostatically at $E = 0.7 \text{ V}$ and that of film potentiodynamically synthesized. To interpret the second redox process at potentiostatically synthesized POAP films, the dependence of the cyclic voltammogram upon potential scan rate and solution pH was analyzed by Holze and co-workers.²³ With regard to potential scan rate, both the anodic and cathodic peak currents of the first redox process were found to scale linearly with the potential sweep rate in the range $10 \text{ mV s}^{-1} < \nu < 100 \text{ mV s}^{-1}$, indicating that the electrochemical process of POAP is a surface process and kinetically controlled. The second redox process was not well-defined enough to apply the same analysis. With regard to the pH effect, by increasing the solution pH from 0 to 1.0, the first redox couple remained almost unaffected, whereas the peak currents of the second redox pair were decreased. Whereas the first redox pair showed a little change up to pH 2.0, the second redox pair was affected to a great extent as the anodic peak was replaced by a shoulder and the cathodic peak by a current plateau. By increasing the solution pH to 3.0, the first redox pair was further shifted towards negative potentials, but the second pair was almost completely replaced by anodic and cathodic current plateaus. Beyond pH 3, the first redox couple was also affected very much. Raman and UV-vis spectra were also recorded by Holze and co-workers²³ to differentiate potentiostatically and potentiodynamically synthesized POAP films. Although Raman and UV-vis spectra of potentiostatically and potentiodynamically synthesized POAP films were found to be similar, some differences were observed in the dependence of the band intensities on the applied potential. These differences were assigned to the ladder-type polymer structure. Raman and UV-vis spectroscopic measurements reveal that the redox transition of potentiostatically synthesized POAP from the completely reduced state to the completely oxidized one proceeds through two consecutive reactions in which a charged intermediate species takes part. Then, in the light of these electrochemical and spectroscopic analyses,²³ a mechanism for the redox transformation of potentiostatically prepared POAP films was proposed, in which phenoxazine units take part.

The development of a NO sensor based on hybrid films of POAP and the metal complex sulfonated nickel phthalocyanine (NiSuPh) was reported by Barbero and co-workers.²⁴ POAP films were produced by cycling the base electrode (Pt or GC) between -0.25 and 0.7 V (SCE) at 50 mV s^{-1} in a 0.05 mol/L o-AP solution in 0.5 mol/L HClO_4 . To incorporate the metal complex, NiSuPh was added to the solution at a 10 mmol/L concentration. The polymerization in the presence of the metal complex was faster than with *o*-AP alone. This fact was attributed to a template effect of the sulfonic groups. After several cycles (>50) a film of POAP/NiSuPh was deposited on the electrode. The incorporation of the metal complex into the polymer film was tested by ex situ reflection-absorption FT-IR spectroscopy. The hybrid film, produced with the metal complex, revealed new bands at 1063 and 1030 cm^{-1} , with respect to those corresponding to POAP. These bands were assigned to stretching of the sulfonate group. The bands were retained in a solution after cycling without the complex, even at pH 7. The modified electrodes were tested for NO electrochemical oxidation. A peak at 0.95 V was observed on the cyclic voltammogram that corresponds to NO oxidation, and it increases with NO concentration. It was observed that both POAP and POAP/NiSuPh films present higher electrocatalytic activity for NO oxidation than the base substrate (GC). The oxidation current, in the electrode modified with the complex, is higher and the oxidation overpotential is lower, indicating that the Ni complex incorporated into the hybrid film could electrocatalyze NO oxidation. The peak current was measured to determine the concentration of NO in the solution. The peak current was linear up to a concentration of $200 \mu\text{mol/L}$.

The electro-oxidation of methanol in aqueous acid solutions using GC electrodes modified by a thin film of POAP containing dispersed Pt and Pt alloy microparticles was studied by Golabi and Nozad.²⁵ Pt, Pt-Ru, and Pt-Sn particles were incorporated into the polymer film by electrochemical deposition, and the following electrodes were synthesized: GC/POAP/Pt, GC/POAP/Pt-Ru, and GC/POAP/Pt-Sn. A mean value of $0.52 \pm 0.02 \mu\text{m}$ was employed for the polymer film thicknesses in the different electrodes. Electropolymerization of *o*-AP was performed either by potentiodynamic or potentiostatic methods. In the potentiodynamic procedure the electrode potential was swept between -0.10 and 1.00 V (SCE) at a scan rate of 20 mV s^{-1} . In the potentiostatic method, the electrode potential was fixed at 1.0 V for a given time. In both cases, an aqueous solution containing $0.10 \text{ mol/L HClO}_4$ and 0.10 mol/L o-AP was used as electrolyte. In all experiments the working electrode was submerged in open-circuit position into the methanol solutions. Voltammograms were recorded by sweeping the potential from 0.0 to 1.00 V (vs SCE) . Although the Pt loading for both electrodes (GC/Pt and GC/POAP/Pt) was similar, it was observed that the peak current for the oxidation of methanol (0.63 V vs. SCE) increased from $0.48 \text{ mA (GC/Pt electrode)}$ to $1.73 \text{ mA (GC/POAP/Pt)}$ (area of the GC electrodes, 0.07 cm^2). This result was explained in terms of an enhancement of Pt microparticle efficiency towards the catalytic oxidation of methanol in the presence of POAP. Similar results were also obtained when Pt was replaced by Pt-Sn or Pt-Ru alloys. Chronoamperometric experiments indicated the existence of an increase in the real surface area of a GC/POAP/Pt electrode with respect to that of a GC/Pt electrode (the area of the GC/POAP/Pt electrode was 2.85 times larger than that of the GC/Pt electrode). An augmentation of the real surface was invoked then²⁵ to explain the increase in reactivity of the electrocatalyst deposited in the presence of POAP. Thus, the role of the polymeric matrix is not directly connected with an increase of the intrinsic specific activity of the electrocatalyst, but the polymer film only acts as a good and proper bed for deposition of electrocatalyst particles and increases the catalytic activity of active sites.

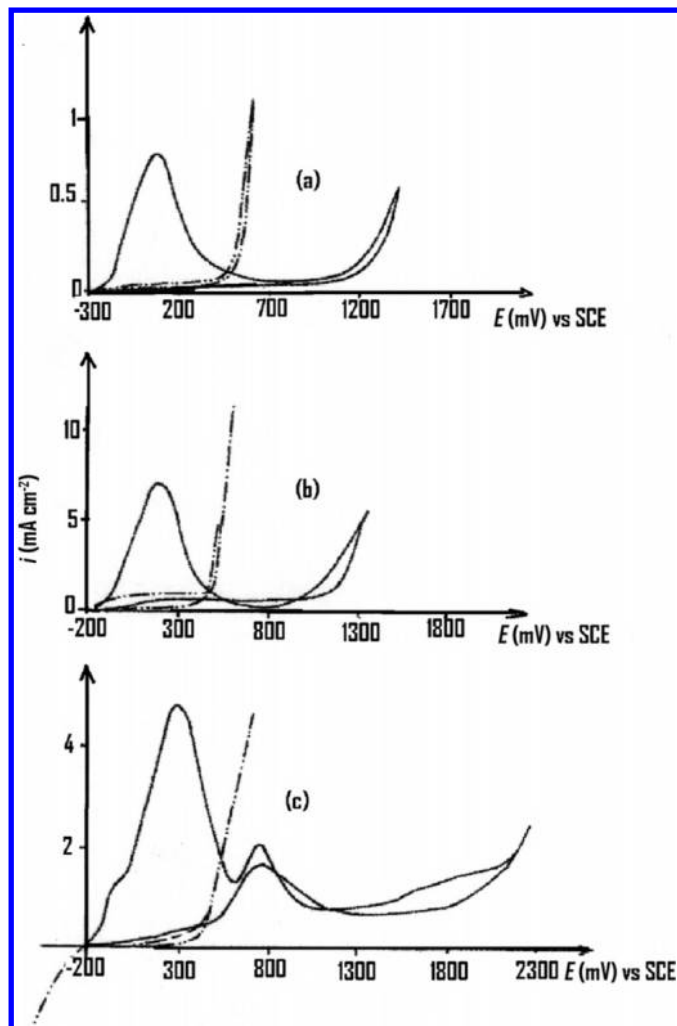
Electropolymerization of *o*-aminophenol in alkaline and neutral media – The use of POAP as a component of biosensors and electrocatalysts

The electropolymerization of *o*-AP from a 0.3 mol/L NaOH hydroalcoholic solution (70 vol % H₂O, 30 vol % CH₃OH) containing 0.1 mol/L *o*-AP to produce a protective polymer layer on different substrates (vitreous carbon, platinum, and copper) was described by Guenbour et al.²⁶

Figures 10a–10c show the CV curves obtained, respectively, for vitreous carbon (VC), Pt, and copper in the 0.3 mol/L NaOH hydroalcoholic solution free of monomer (broken line). The oxidation leads to an increase of the current near 0.3 V (SCE). The addition of 0.1 mol/L of *o*-AP to the hydroalcoholic solution (continuous line) induced a current peak with a maximum at 0.09 V (VC), 0.16 V (Pt), and 0.2 V (copper). This peak was attributed to the oxidation of *o*-AP that began at –0.2 V and pH 12. In the case of VC and Pt substrates (Figs. 10a and Fig. 10b, respectively) the peak of current was followed by a wide passivity domain, characterized by a very weak current, showing the formation of a very protective film. After the forward part, the reverse curve with negligible current confirmed the insulating character of the film and showed the irreversibility of the system. Figure 10c illustrates the behavior of the copper substrate. The forward part of the curve for copper presents a second peak at a high potential (0.765 V vs SCE), attributed to the substrate oxidation through the holes of the growing film. To confirm this assertion, the polarization curve was stopped before the apparition of the second peak; the reverse curve shows the presence of the protective film. However, as the voltammetric scan was extended towards the second peak domain, the voltammetric response did not show the formation of a protective layer. Then the films synthesized²⁶ by using the cyclic potential sweep method in the first potential domain, between –0.2 and 0.65 V, were washed with ethanol and water and then heated in an oven at 120 °C for 30 min. The films obtained were yellowish and very adherent. The films in acidic solution became brownish orange. However, films obtained on copper in the second potential domain were not adherent, which was attributed to the oxidation products of the substrate mixed with the organic film. To avoid strong corrosion of the copper substrate the potential was kept below 0.65 V.²⁶ Chronoamperometric studies were also carried out.²⁶ For constant potential values within the first peak domain, below 0.65 V, a progressive decrease of current densities for the three substrates was observed. Stationary currents were achieved after 20 min. This behavior confirmed the insulating character of the film. For copper polarized at 0.51 V (near the maximum potential peak or slightly higher), very uniform yellowish layers were obtained. After washing and heating at 120 °C for 30 min, the resultant films were very adherent. For the copper substrate, the electrochemical treatment at high potentials corresponding to the second peak of the polarization curve led to a very different behavior. It was observed that, during a treatment at 0.76 V, current densities have high values, which were attributed to the corrosion phenomenon. The analysis of the electrolyte by atomic absorption revealed the presence of copper ions in the solution, which confirmed the dissolution of the substrate. The physical characteristics of the film deposited on copper were dependent on the concentration ratio $R = [\text{NaOH}/\text{o-AP}]$. Results reported by Guenbour et al.²⁶ refer to hydroalcoholic solutions containing 0.3 mol/L NaOH and 0.1 mol/L *o*-AP ($R = 3$), and the films obtained were homogeneous and very adherent. However, the authors remark that with $R = 1$ the films were not adherent and presented cracks and large pores. POAP layers deposited on the copper substrate (four cycles between –0.23 and 1.2 V) were also analyzed by Guenbour et al.²⁶ by employing IR and XPS spectrometry techniques.

Thin nonconducting POAP films synthesized in neutral media were also employed as protective layers for biosensor applications. In general, POAP films are simultaneously synthesized with

Fig. 10. Voltammograms obtained in 0.3 mol/L NaOH hydroalcoholic solutions (pH 12.7) for (a) vitreous carbon, (b) platinum, and (c) copper. (—) with 0.1 mol/L *o*-aminophenol (*o*-AP) and (---) without *o*-AP. Scan rate, 30 mV s^{–1}.²⁶



different electroactive materials such as hemoglobin, quinhydrone, carbon nanotubes, Prussian Blue (PB), and other polymers such as poly(*o*-phenylenediamine) and polypyrrole (PPy), which act as electron mediators^{19,27–37} for the building of different biosensors. POAP is also widely used as an enzyme matrix in the construction of hydrogen peroxide biosensors because of its catalytic properties towards hydrogen peroxide reduction and limited permeability to small organic molecules.^{28–31,36,37} An interesting review about synthesis and applications of nonconducting POAP films in bioelectrochemistry and electrocatalysis is found in ref. 38.

In the next paragraphs the construction and characteristics of some biosensors based on POAP are described.

A series of iron–cobalt (Fe–Co) films were electrodeposited on gold electrodes from solutions containing 6 mmol/L Fe(CN)₆^{3–} with different concentrations of Co(II) to obtain the hydrogen peroxide biosensor reported by Tao et al.²⁸ The Fe–Co film deposited from a solution with an iron molar ratio of 0.4 showed the largest response current to H₂O₂. Therefore, the optimized Fe–Co film was combined with a nonconducting POAP film that entraps hemoglobin (Hb) to construct the biosensor Hb/POAP/Fe–Co/Au electrode with a detection limit of 1.2 × 10^{–5} mol/L. The electrochemical copolymerization of *o*-AP and Hb on the Fe–Co/Au electrode was performed in a 5 mmol/L *o*-AP and 0.04 mmol/L Hb acetate buffer solution (pH 5.0) where the electrode was cycled

between -0.2 and 0.8 V (vs SCE) at a scan rate of 50 mV s^{-1} . All films used in ref. 28 were grown for 15 cycles. Hemoglobin was also immobilized simultaneously with quinhydrone (QH₂) on POAP films to construct the Hb/QH₂/POAP biosensor.²⁹ The response current of the Hb/QH₂/POAP film to H₂O₂ was almost twice that of the Hb/POAP film. The higher catalytic activity of the former biosensor to H₂O₂ was attributed to the redox mediation of QH₂. The Hb/QH₂/POAP modified electrode was prepared by continuous cyclic scanning from -0.2 to 0.8 V (SCE) (15 cycles) at a scan rate of 50 mV/s in 0.2 mol/L freshly prepared acetate buffer solution (pH 5.0) containing 0.01 mol/L *o*-AP, 4×10^{-5} mol/L Hb, and 1×10^{-3} mol/L QH₂.

Experimental conditions related to the preparation and characteristics of an amperometric glucose biosensor based on the immobilization of glucose oxidase (GOx) in an electrochemically polymerized nonconducting POAP film at PB-modified Pt micro-electrode are described by Pan et al.³⁰ With regard to this micro-electrode (Pt/PB/POAP/GOx), the PB acts as a typical electroactive film that exhibits catalytic properties for H₂O₂ oxidation and the POAP film is a typical nonconducting film that acts as an effective barrier to protect the electrode from fouling. The effect of the interferents (ascorbic acid (AA), uric acid (UA), and acetaminophen (AMP)) decreased significantly owing to the selective permeability of POAP. The effect of the pH value of the detection solution on the response behavior of the PB/POAP/GOx electrode operated at 0.6 V was also investigated by Pan et al.³⁰ The Pt/PB/POAP/GOx electrode can be used over a wide pH range (pH 4.5–8), and the maximum response current was observed at pH 7. The dependence of the response current on pH was attributed to the entrapment of GOx in a POAP film at a PB-modified electrode, making GOx more active at neutral media. Additionally, at pH 5.6 there was a higher response current.

A reagentless lactate amperometric biosensor, constructed by immobilizing pyruvic transaminase (GPT) and L-lactate dehydrogenase (LDH) together with its cofactor, nicotinamide adenine dinucleotide (NAD⁺), in carbon paste using a poly(*o*-phenylenediamine) (PPD) film (CP/LDH–GPT–NAD⁺/PPD) has been described previously.³² Interference by direct electrochemical oxidation of easily oxidizable substances, such as uric acid, L-ascorbic acid, L-cysteine, glutathione, and paracetamol was drastically reduced by covering the PPD-modified electrode with a second electrochemically synthesized nonconducting POAP film (CP/LDH–GPT–NAD⁺/POAP–PPD). POAP was potentiostatically grown at $+0.7$ V (Ag/AgCl) over 15 min from a 0.1 mol/L phosphate and 0.01 mol/L glutamate supporting electrolyte at pH 9.5 containing *o*-AP at the 2.5×10^{-3} mol/L level.

Laccase immobilized in a POAP matrix catalyses oxygen reduction without any additional mediators.³⁴ In this regard, POAP is able to mediate the electron transfer between the enzyme active site and the electrode surface. The role of laccase in the electrodeposition of POAP was studied by Palys et al.³⁴ The entrapment procedure was carried out by electrodeposition of the monomer on a GC electrode (GCE) or on a glass plate covered with semiconducting ITO electrode from a 0.1 mol/L phosphate buffer solution (pH 5.55) containing 25 μ g/mL of laccase and 10 mmol/L of the monomer. The electrodeposition was carried out by cycling the electrode potential between -0.1 and 0.9 V (Ag/AgCl) applying a scan rate of 20 mV s^{-1} . Cyclic voltammograms of POAP obtained in the monomer solution with and without laccase were compared by Palys et al.³⁴ Although both voltammograms exhibited a single redox process, the peak currents differed significantly. The layer obtained in the presence of laccase reveals current values that are larger by one order of magnitude. It was concluded that laccase largely facilitates POAP formation. The optimal enzyme activity was reached for POAP layers prepared for 10–20 electrodeposition cycles. A shift of the oxygen reduction potential towards more negative values was observed with an increase of the number of electrodeposition cycles. The diminished enzyme activity observed for larger numbers of electrodeposition cycles was attrib-

uted to the lower conductivity of the thick POAP films as compared with that of the thin ones. Palys et al.³⁴ also demonstrated that laccase can be utilized as a polymerization initiator with no need for electrochemical monomer oxidation.

An amperometric glucose biosensor that is based on the immobilization of GOx in a composite film of POAP and carbon nanotubes (CNT), which are electrochemically copolymerized at a gold electrode, was described by Pan et al.³⁵ They observed that the response current increases with an increase in the polymerization cycle number, until a maximum value of 15 cycles. In this regard, they suggested that when the number of cycles is less than 15, the amount of enzyme entrapped in the POAP film increases with an increase of polymerization cycle number. However, after the number of cycles is higher than 15, GOx may be covered by the POAP film, causing a decrease in the available amount of GOx.

The fabrication and characterization of a glucose sensor based on a PPy–Pt composite – modified GCE, which was covered by a layer of POAP–GOx film, were reported by Scolari and Tucceri.³⁷ The prepared electrode was denoted as POAP–GOx/PPy–Pt/GCE. The glucose response of the enzyme electrode was measured on the basis of the electro-oxidation current of H₂O₂, which is produced during enzymatic reaction. A mechanism was proposed for the POAP–GOx/PPy–Pt/GCE electrode polarized at 0.6 V (SCE) in which the added glucose is transferred quickly into the POAP film so as to be oxidized by the entrapped GOx in the presence of O₂. The generated H₂O₂ can penetrate through the POAP film and be electrocatalytically oxidized at the PPy–Pt conducting nanocomposite. With regard to the POAP film thickness, the maximum current response at the POAP–GOx/PPy–Pt/GCE was obtained when the polymerization cycle number for POAP–GOx was 15.

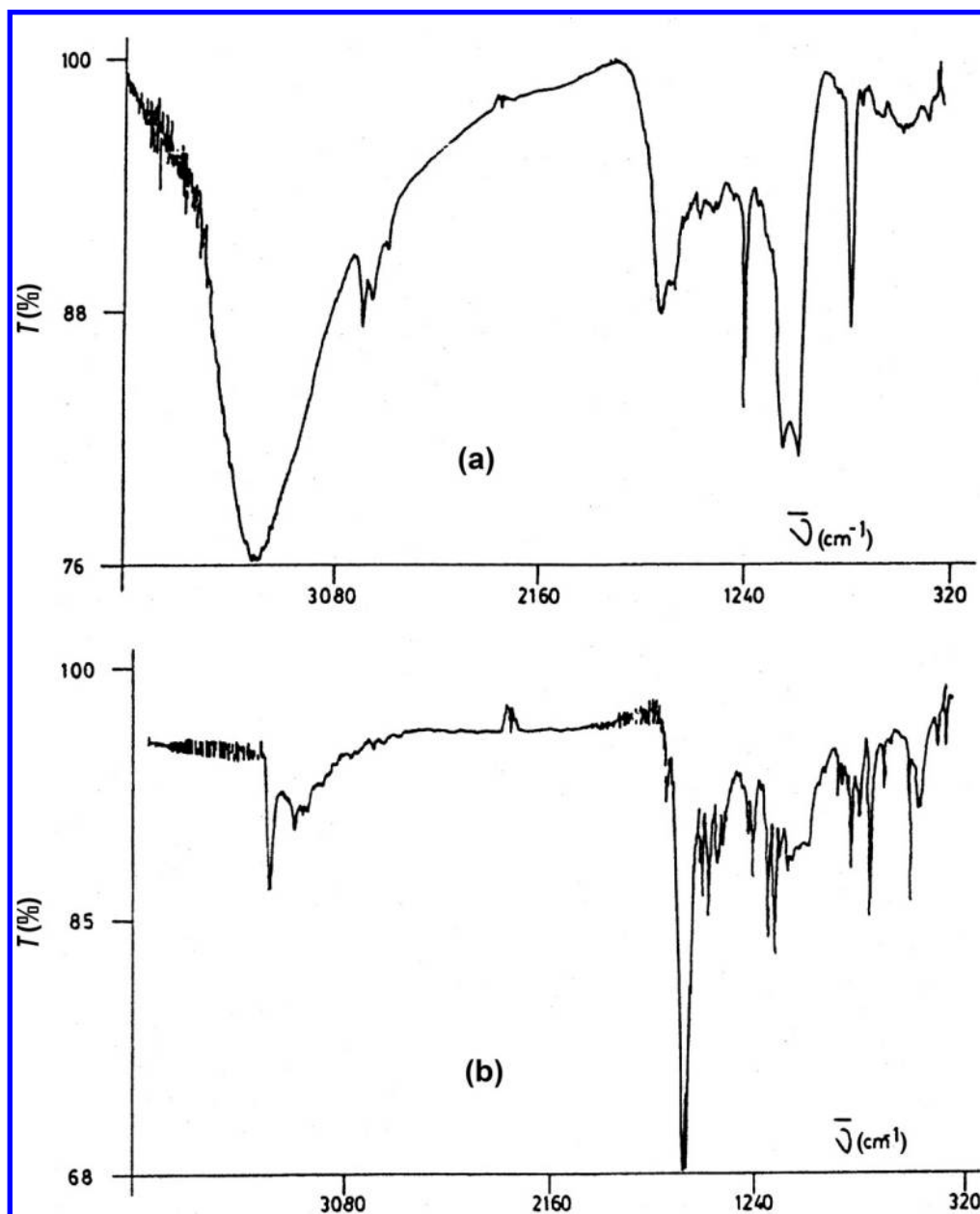
The structure of electrochemically synthesized poly(*o*-aminophenol) films studied by spectroscopic methods – The oxidation products of *o*-aminophenol and the redox process of poly(*o*-aminophenol)

As well as electrochemical methods, knowledge about the structure of POAP in both acidic and basic media was obtained by the application of different spectroscopic techniques. The study of the redox conversion of POAP employing spectroscopic analysis has also greatly contributed to the elucidation of the structure of the polymer.

Spectroscopic characterization of poly(*o*-aminophenol) films synthesized in an acid medium

Characterization of electrochemically synthesized POAP films in an acid medium employing IR and UV–vis spectroscopy was carried out by Barbero et al.¹¹ These authors compared the IR spectrum of an electrochemically prepared POAP film with that of 3-aminophenoxazone (Fig. 11). The broad band centred at 3400 cm^{-1} was assigned to the stretching of the N–H bonds and the bands at 1350 and 1240 cm^{-1} were ascribed to the –C–N–C– stretching of the secondary amines (Fig. 11a). Although stretching of the C=N bond was observed at 1633 , 1462 , and 1384 cm^{-1} , some of these bands were also assigned to the C–C bond. The characteristic =C–C=O stretching in 3APZ at 1573 cm^{-1} (Fig. 11b) only appears as a weak absorption in the POAP. This band in POAP was assigned to a terminal group. The C–O (1201 cm^{-1}) and the –C–O–C– symmetric stretching are very well defined in POAP. The peak at 800 cm^{-1} was assigned to the –C–H– bending vibration of aromatic ortho-substituted aromatic rings. The peak at 1092 cm^{-1} was ascribed to the ClO₄[–] band. However, this last peak was associated with an impurity because it disappeared after exhaustive washing of the film. Barbero et al.¹¹ noted the absence of the characteristic strong absorption of the carbonyl group (1680 cm^{-1}) and the phenol group (2600 cm^{-1}) in the POAP spectrum. The absence of the carbonyl band was considered to be an indication of an insignificant quantity of *o*-quinone in the film. In the same way, the absence of

Fig. 11. IR spectra of (a) electrochemically prepared poly-*o*-aminophenol (POAP) and (b) 3-aminophenoxazine.¹¹

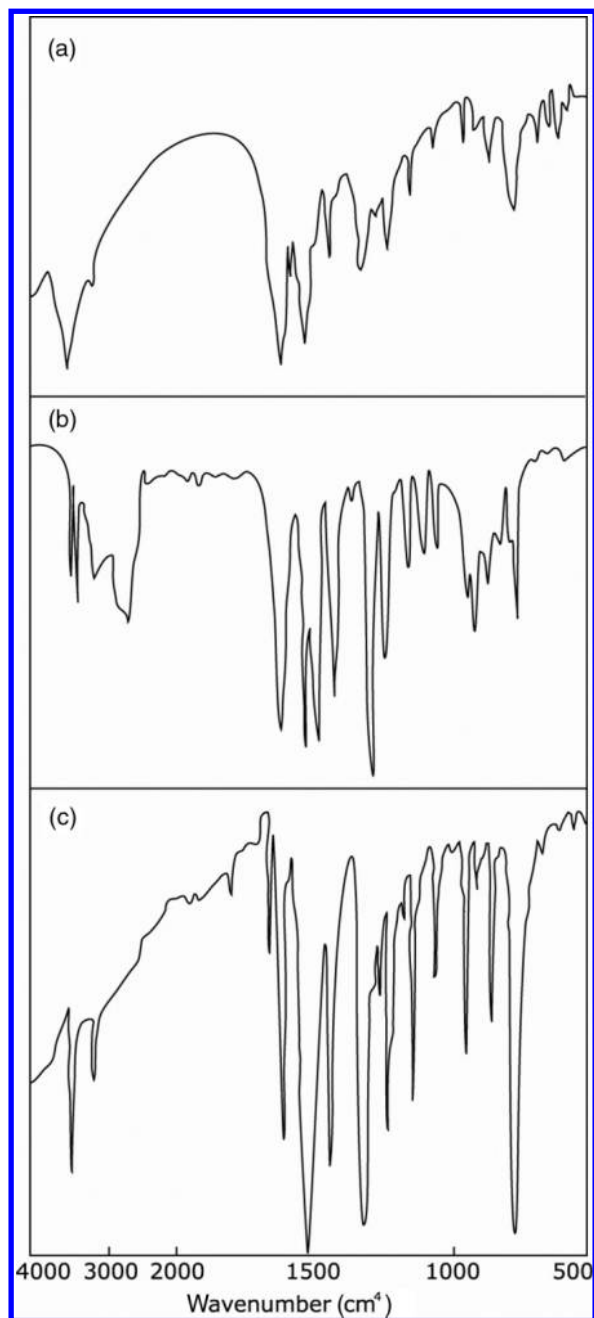


an important hydroxyl group absorption band was attributed to a low proportion of a linear chain polymer structure. The POAP structure was also studied by in situ UV-vis spectroscopy by Barbero et al.¹¹ A broad maximum around 480 nm was observed in the oxidized state of POAP. As the UV-vis spectrum has the same characteristics of that reported for 3APZ, it was considered as a confirmation that the film consists of phenoxazine-like units. Then, on the basis of the IR and UV-vis spectroscopic analysis, the structures shown in Fig. 3 were proposed for POAP in the reduced state and in the oxidized one, respectively.

The IR absorption spectrum of the oxidized form of POAP was compared with those of *o*-AP and phenoxazine by Kunimura et al.¹⁷ (Figs. 12a–12c). Some common absorption peaks were observed for the three compounds, but other peaks were not common. The absorption peaks due to the N–H stretching vibrations of the imino group of the POAP film and phenoxazine were observed at 3420 cm⁻¹, whereas two absorption peaks corresponding to the N–H stretching vibrations of the amino groups of *o*-AP were,

as expected, observed at 3340 and 3420 cm⁻¹. The presence of a relatively strong absorption peak around 3420 cm⁻¹ was considered as an indication that POAP does not possess a completely ring-closed structure (Fig. 3), as proposed by Barbero et al.¹¹ In this regard, a partially ring-opened structure as the one shown in Fig. 7 and (or) a relatively low degree of polymerization of *o*-AP was proposed by Kunimura et al.¹⁷ The absorption peaks ascribable to the stretching vibrations of C–N bonds were observed for POAP at 1250 and 1310 cm⁻¹. Similar peaks were observed for *o*-AP and phenoxazine. The peak at 1645 cm⁻¹ in the POAP spectrum was assigned to the stretching of the C=N bonds present in a ladder polymer with phenoxazine rings. The absorption peaks at 1050 and 1235 cm⁻¹, which are characteristic of the C–O–C stretching vibration, were observed for POAP and phenoxazine, but not for *o*-AP. Peaks at 760, 850, and 935 cm⁻¹ for POAP were assigned to 1,2-disubstituted, 1,2,4-trisubstituted, and (or) 1,2,4,5-tetrasubstituted benzene structures, respectively. All of these structures were considered to be possible for POAP. Furthermore, from the fact that

Fig. 12. IR absorption spectra of (a) a poly-*o*-aminophenol (POAP) film (oxidized form), (b) *o*-aminophenol (*o*-AP), and (c) phenoxazine. The POAP film was prepared on pyrolytic graphite (BPG).¹⁷



the absorption peak assigned to the stretching vibration of the C=O bonds of the aromatic keto groups was observed at 1670 cm^{-1} , the partially hydrolyzed structure shown in Fig. 7 was proposed for POAP by Kunimura et al.¹⁷ and the structure shown in Fig. 8, which was assumed to proceed from a polymerization via C–N=C bonds, was also proposed as a possible structure of POAP.

The role of laccase on the electrochemical synthesis of POAP from 0.1 mol/L phosphate buffer (pH 5.5) solutions was described by Palys et al.³⁴ They demonstrated that laccase can be utilized as a polymerization initiator with no need of electrochemical monomer oxidation.³⁴ Raman spectra of POAP electrodeposited at pH 5.5 with and without the presence of laccase in the polymerization bath and the spectrum of the POAP obtained by the enzyme polymerization of *o*-AP were compared in ref. 34. Raman bands of

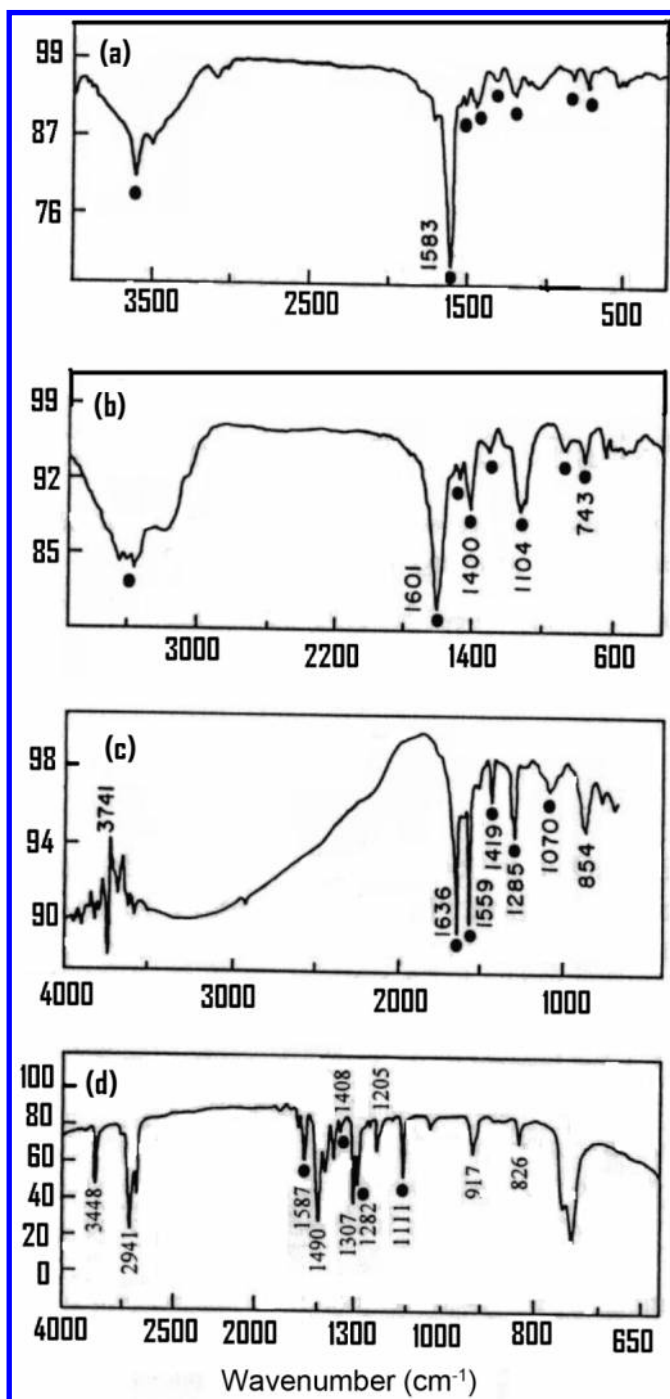
2,2'-dihydroxyazobenzene (DHAB) and 3APZ were observed in the spectra obtained at pH 5.5. Raman spectra of DHAB are characterized by the strong band at 1390–1400 cm^{-1} owing to the N=N stretching mode. The electrochemically synthesized POAP film shows a strong band at 1397 cm^{-1} , which was attributed to the N=N stretching mode of DHBA. This band is weaker in the spectrum of the POAP film electrodeposited in the presence of laccase and it disappears completely in the spectrum of POAP obtained by enzymatic polymerization of *o*-AP. This effect was attributed to the fact that N–N coupling only occurs during the electrochemical oxidation of *o*-AP. Several 3APZ modes were also observed in the spectra of the three POAP samples (578, 1150, 1278, 1475, 1505, 1605, and 1660 cm^{-1}). Slight shifts in band positions were attributed to further oxidative polymerization of 3APZ to POAP. Since the POAP structure contains conjugated double bonds, shifts of aromatic ring modes were considered probable. Despite the presence of laccase in the electrodeposited POAP films being confirmed by a test using syringaldazine, its contribution to the Raman spectra seems to be very weak. Only weak features at 468 and 1264 cm^{-1} were assigned to the enzyme. The enzymatically synthesized spectrum of POAP shows a very strong band at 1504 cm^{-1} , with a frequency that is identical to the aromatic ring mode of 3APZ. As this frequency also coincides with the primary amine deformation mode of *o*-AP, it was suggested that it is related to either the monomer that did not react, to 3APZ, or to short oligomers. Typical UV–vis spectra of POAP electrodeposited in the presence and in the absence of laccase were also noted by Palys et al.³⁴ Both spectra are characterized by a broad absorption band with a maximum at 445 and 430 nm for the film obtained in the presence and absence of laccase, respectively. As a similar band was observed for potentiostatic (410 nm)²³ and potentiodynamically (440 nm)^{39,40} electrodeposited POAP films, the bands at 445 and 430 nm in ref. 34 were attributed to the conjugated π bonds of POAP. The small difference in the position of the bands was related to possible differences in the chain lengths of POAP prepared in the presence and the absence of laccase.

With the aim of discerning between the possibility that 2-aminophenoxazin-3-one (APZ) is the repetitive unit of POAP films and the possibility that it is incorporated onto the film structure during its synthesis, a spectroscopic characterization of soluble products in an electrolyzed *o*-AP solution was carried out by Bulhões and co-workers.¹⁵ Drastic optical changes were noted after applying a constant potential of 0.85 V (vs reversible hydrogen electrode (RHE)) on a Pt wire immersed into a spectrophotometer cell containing an *o*-AP solution. Each deconvoluted UV–vis spectrum of this solution led to two or three main absorption bands, depending on the time at which the measurement was taken. For the purpose of comparison, the spectra of the electrolyzed solution were compared with that of APZ. Whereas the electrolyzed solution presented an absorption band at 400 nm, a well-defined band at 460–470 nm characterized APZ. The absorption band at 400 nm was assigned to quinone intermediates continuously formed during electrolysis (benzoquinone, benzoquinone–monoimine, and benzoquinone–diimine). Although the isolation of intermediates failed,¹⁵ APZ was identified as the final product after extraction from the electrolyzed *o*-AP solution. This assignment was supported by not only UV–vis spectroscopy but also IR and ¹H NMR spectroscopy and elemental analysis. To establish if APZ undergoes any polymerization processes, Pt and GC electrodes were cycled in a medium containing chemically synthesized APZ. While no process of charge transfer was obtained for Pt electrodes cycled in the APZ medium, GC electrodes present one well-resolved redox process. However, the electroactive response of GC was only associated with an activation process of the electrode surface after prolonged cycling. Therefore, the voltammetric results obtained by Bulhões and co-workers¹⁵ seem to indicate that APZ does not undergo any polymerization processes. In another experiment carried out by Bulhões and co-workers,¹⁵ chemically prepared APZ was dissolved in acetone and

dropped on Pt and GC electrodes to prepare APZ films. In this case, a single well-defined redox process was observed on the voltammograms on both Pt and GC electrodes. Owing to the similarities between redox responses of POAP-modified Pt and GC electrodes and APZ-modified Pt and GC electrodes, an IR study was also performed¹⁵ to establish whether APZ is the repetitive unit of POAP films, if it is incorporated into the film structure, or if POAP films and modified electrodes cycled in an APZ medium may present similar redox responses. The IR spectra of the chemically synthesized APZ, the soluble product extracted after electrolysis of *o*-AP solution, a POAP film and phenoxazine were then compared by Bulhões and co-workers¹⁵ (Figs. 13a, 13b, 13c, and 13d, respectively). Similar IR signals for the extracted product and APZ indicated that they are the same materials. In this regard, Figs. 13a and 13b present similar signals (the main coincident peaks are indicated with points) at 3300–3500 cm⁻¹ owing to the presence of NH₂ groups and at about 1600 cm⁻¹ owing to the axial stretching of the C=O groups in the APZ structure. However, POAP presents a different spectrum (Fig. 13c) and, therefore, different structures were proposed by Bulhões and co-workers¹⁵ for POAP films and APZ. Common peaks are observed in Figs. 13c and 13d at 1070 and 1111 cm⁻¹, respectively, which were assigned to the stretching of the C–O–C linkages. Also, the peaks in the 1400–1600 cm⁻¹ region were attributed to the stretching of C–H and C–C groups. Similarities were found between the POAP film spectrum and that of phenoxazine. It was concluded by Bulhões and co-workers¹⁵ that, although POAP films may be present as phenoxazine units and similar redox responses can be expected for POAP films and APZ-modified electrodes, APZ does not polymerize.

Salvagione et al.¹² studied the oxidation of *o*-AP, and the polymer formed, by *in situ* FT-IR spectroscopy. The aim of this work was to prove that the most probable structure of the polymer formed in the oxidation of *o*-AP contains the phenoxazine unit. Figure 14 shows the spectra of a 1 mol/L HClO₄ + 5 × 10⁻³ mol/L *o*-AP solution with a polycrystalline Pt electrode immersed in it being polarized at different potential values. The electrode was immersed at 0.1 V (RHE) into the spectroelectrochemical cell and then the potential was stepped up to 0.4 V and the reference spectrum was collected. The potential was then stepped up to 0.4 V and the reference spectrum was collected. The potential was then polarized to higher values to oxidize the *o*-AP, and the sample spectra were acquired at 0.8 and 1.0 V. In the spectrum at 0.8 V (RHE) (Fig. 14a) two positive bands at 1510 and 1471 cm⁻¹ were observed. These two bands were assigned to the aromatic C=C stretching vibration and the ring C=C vibration of meta-disubstituted benzenes. The positive character of these bands was attributed to consumption of the species related to these features at the sample potential. At 1.0 V (Fig. 14b), these two bands were observed together with a strong band at 2345 cm⁻¹ corresponding to the formation of CO₂ in the solution. No clear bands were observed at lower sample potentials. When the same spectrum is collected in deuterated water (Fig. 14c), two negative bands at 1683 and 1645 cm⁻¹ were observed. These bands were associated with the C=O and C=N stretching vibrations, respectively. Figures 15a and 15b show the spectra of POAP in 1 mol/L HClO₄ solution in the absence of *o*-AP in water and in deuterated water, respectively. The reference spectrum was obtained at 0.1 V, so it contains the vibrational information corresponding to the reduced form of the film. The electrode was then polarized to 0.7 V (RHE), and the sample spectrum was collected. Similar bands were observed in both spectra. Figure 15a displays two clear positive bands at 1513 and 1278 cm⁻¹ and a broad negative band at 1580 cm⁻¹. The band at 1513 cm⁻¹ is also present in the spectra in D₂O (Fig. 15b), but, in this case it was observed at 1517 cm⁻¹ and was assigned to the C=C stretching of the aromatic ring. This band was not observed after polymer oxidation. The broad negative band at 1580 cm⁻¹ was also present in deuterated water, but, in this case, the band has contributions from several bands at 1564, 1606, and 1648 cm⁻¹, and it was assigned to either a quinoid ring or a C=N stretching vibration in the phenoxazine

Fig. 13. IR spectra of (a) the extracted product from electrolyzed *o*-aminophenol (*o*-AP) solution, (b) chemically synthesized 2-aminophenoxazin-3-one (APZ), (c) poly-*o*-aminophenol (POAP) film (prepared on Pt by cyclic voltammetry, 400 cycles), and (d) model compound (phenoxazine).¹⁵



units produced upon complete polymer oxidation (Fig. 3). The 1648 cm⁻¹ band was attributed to C=N stretching where conjugation with a phenyl group shifts its frequency to higher values, and it was more clearly observed in deuterated water owing to the reduced interference of water absorptions. Another negative band was observed at 1330 cm⁻¹ in both spectra, which was also clearly seen at low potentials. This band was assigned to the C=N stretching of quinoid rings containing C=N and C–N groups. To check these assignments the spectra for phenoxazine in the same

Fig. 14. FT-IR spectra for a Pt electrode in a 1 mol/L HClO₄ + 5 × 10⁻³ mol/L *o*-aminophenol (*o*-AP) solution. (a) Sample potential, 0.8 V; (b) sample potential, 1.0 V; and (c) spectrum obtained at 0.9 V in deuterated water. P-polarized light, 100 interferograms. Reference potential, 0.4 V.¹²

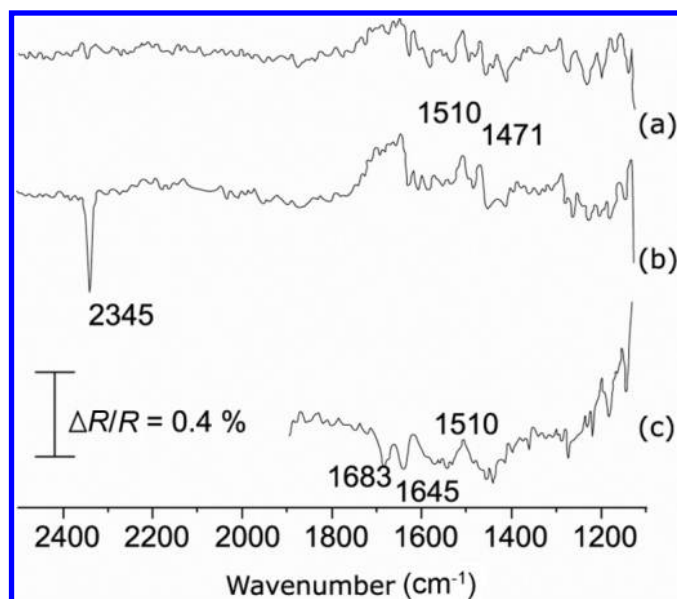
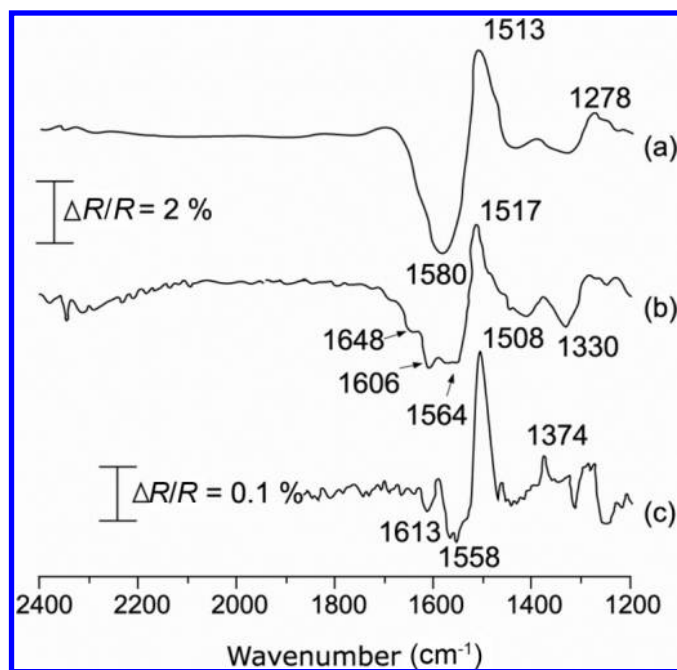


Fig. 15. FT-IR spectra for a Pt electrode covered with poly-*o*-aminophenol (POAP) in 1 mol/L HClO₄ solution in (a) water and (b) deuterated water. Sample potential, 0.7 V; and reference potential, 0.1 V. P-polarized light, 100 interferograms. (c) FT-IR spectrum obtained for a Pt electrode in 1 mol/L HClO₄ + 5 × 10⁻⁴ mol/L phenoxazine solution in deuterated water. Sample potential, 0.7 V; and reference potential, 0.4 V. P-polarized light, 100 interferograms.¹²



range of potentials was also obtained by Salvagione et al.¹² Figure 15c shows the spectrum obtained from a 1 mol/L HClO₄ + 5 × 10⁻⁴ mol/L phenoxazine solution in deuterated water, where the polycrystalline platinum electrode immersed in it was polarized at different potential values. A series of reference and sample spectra were collected at 0.2 and 0.7 V and then co-added. The

Table 1. Vibration modes observed by Raman spectroscopy in poly(*o*-aminophenol) (POAP)-modified Au electrodes at 0.1 V in 1 mol/L HClO₄.⁴¹

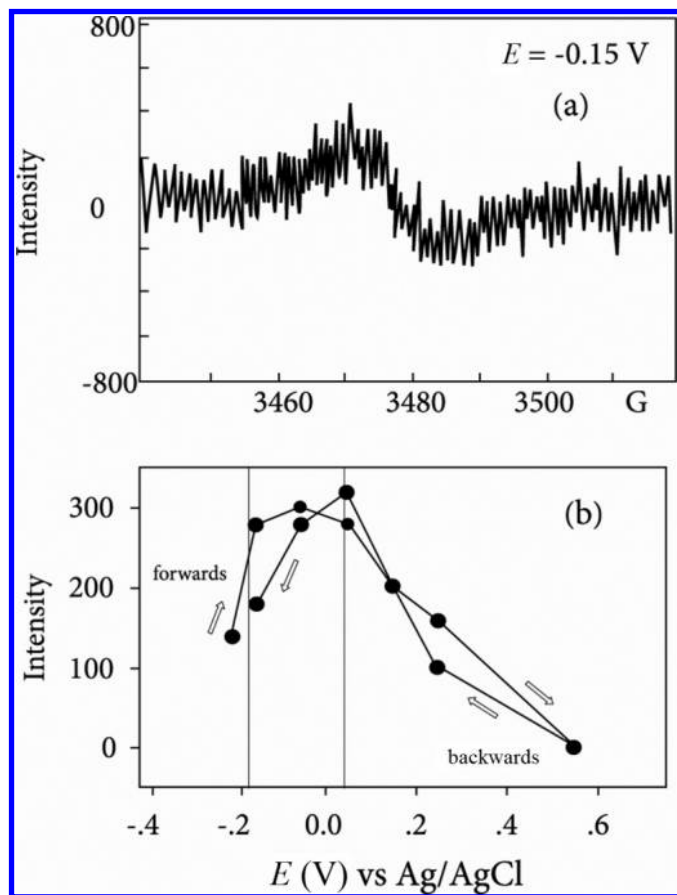
Wavenumber (cm ⁻¹)	Vibration modes
1638	-C=N- stretching of quinonimine units
1593	>C=C< stretching of quinoid units or N-H ⁺ deformation vibration on secondary amines
1520	-C=C- stretching in the aromatic ring
1474	-C=N- stretching of quinoid units
1390	C-C stretching of quinoid units
1328	>C-N ⁺ - stretching
1160	C-H bending in plane
925	Perchlorate vibration band
576	Ring deformation of benzenoid units

spectrum obtained showed a sharp and negative band at 1508 cm⁻¹ corresponding to the disappearance of the aromatic ring at the sample potential. A positive band at 1374 cm⁻¹ was also observed that was assigned to the C-N stretching of the secondary aromatic amine that also disappeared at 0.7 V. Two negative bands were observed at 1558 cm⁻¹ that were associated with the C=N stretching vibration of the imine group that is produced at higher potentials in the oxidation of phenoxazine. Salvagione et al.¹² concluded that the most probable structure of the polymer formed in the oxidation of *o*-AP contains the phenoxazine unit as the main constituent of its structure. Theoretical calculations carried out by Salvagione et al.¹² seemed to confirm that the polymer obtained by electro-oxidation of *o*-AP has a ladder structure built by phenoxazine units. In this regard, they¹² calculated the electronic density of *o*-AP by employing the semiempirical self-consistent field method (AM1). They determined that *o*-AP has a high electron density in the para position with respect to the -NH₂ group. Therefore, dimers could be formed through the attack of the cation radical at that position. The dimer of *o*-AP has a higher electron density in the para position with respect to the -OH group, allowing the closing of the phenoxazine ring.

The redox process of POAP in acid medium studied by spectroscopic methods – Intermediate species during the redox switching of POAP

Raman spectroscopy and voltammetry were coupled to identify structural changes during the redox process of POAP.⁴¹ Voltammetric measurements at different perchloric acid concentrations carried out by Salvagione et al.⁴¹ revealed the existence of two redox processes for POAP films. Raman spectra of a POAP film deposited on an Au electrode at different electrode potentials were obtained. The different bands of POAP extracted from an in situ Raman spectrum acquired at 0.1 V are listed in Table 1. Bands at 1593, 1474, 1390, and 1160 cm⁻¹ were associated with quinoid groups and bands at 1520 and 576 cm⁻¹ were assigned to aromatic rings. The band at 1638 cm⁻¹ was attributed to the -C=N- in quinonimine units. The intensity of some of these bands was found to be dependent on the applied potential. The behaviour of the bands with the applied potential shows that when the potential increases, the band at 1474 cm⁻¹ increases and the band at 1638 cm⁻¹ also increases until a potential of about 0.2 V and, thereafter, it diminishes. The fitting of both bands by Lorentz curves allowed for the quantification of the evolution with the potential of the corresponding species associated to these bands. The integrated intensity was related to the concentrations of species responsible for these bands. The behaviour of the band at 1638 cm⁻¹ was attributed to a typical intermediate species. Since POAP has a conductivity maximum at about 0.04 V (SCE), the intermediate species was related to the polymer conductivity and, therefore, it was assigned to a charged species. The existence of intermediate species was associated to an oxidation process that

Fig. 16. (a) Typical electron spin resonance (ESR) spectrum of an 80 nm thick poly-*o*-aminophenol (POAP) film on a Pt electrode at pH 0.9. Plot (b) illustrates the change in the ESR intensities as a function of potential. The maximum intensities are shown between the dotted straight lines.¹³



occurs by two consecutive reactions from the totally reduced phenoxazine form to the completely oxidized one, through a charged species, which was considered to be a cation radical. The behaviour of the integrated Raman intensity of the band at 1638 cm^{-1} was considered to be similar to that of the band at 750 nm observed in the absorbance vs potential dependence in the UV-vis region reported by Tucceri et al.⁴² As the maximum absorbances of both bands (750 nm⁴² and 1638 cm^{-1}) appear approximately at the same potential, this was considered to be indicative of the existence of two redox processes in the oxidation of POAP. Thus, Raman⁴¹ and UV-vis⁴² measurements seem to suggest that the third species could be a cation radical. A redox mechanism of POAP was proposed by Salvagione et al.⁴¹ where the first step involves mainly the anion exchange and the second step involves the insertion/expulsion of protons.

Evidence about the existence of cation radical species during the redox conversion of POAP was also reported by Ortega.¹³ Ortega¹³ studied the conducting potential range of POAP by employing CV and electron spin resonance (ESR) measurements. POAP films deposited on a Pt electrode were introduced into a solution at pH 0.9, which was free of monomer and then ESR spectra were recorded at different potentials, scanning forwards and backwards from -0.250 to 0.55 V (Ag/AgCl). Figure 16 shows a typical signal at negative potentials, which starts decreasing until it reaches a very small value at 0.55 V. The maximum in the ESR spectra occurs in the potential ranging from -0.24 to approximately 0.0 V (SCE). The decrease and further absence of a detectable ESR signal at higher potentials than 0.55 V was attributed to

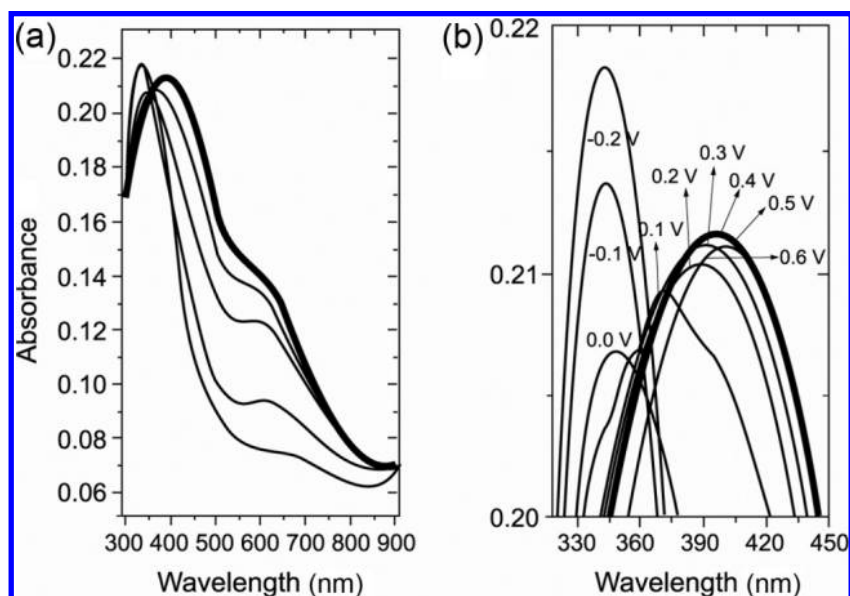
Table 2. Vibrational bands in Raman spectra ($\lambda_0 = 647.1$ nm) for a poly(*o*-aminophenol) (POAP) film in a 0.5 mol/L H_2SO_4 solution.²³

Wavenumber (cm^{-1})	Description
1645	C=N stretching of quinonimine units
1598	C=C stretching of quinoid units
1522	C=C stretching in the aromatic ring
1472	C=N stretching of quinoid units
1402	C-N ⁺ stretching of radical semiquinone
1330	C-N ⁺ stretching
1170	C-H bending in plane
982 and 1050	Sulfate modes
578	Ring deformation of benzenoid units

a combination of radicals to give rise to dication species, which are not ESR active because of their paired spin. Ortega¹³ concludes that, at high positive potential values, the creation of bipolarons by a combination of polarons is possible at POAP films.

The existence of charged intermediate species together with structural changes during the redox process of POAP was also reported by Holze and co-workers.²³ They investigated the potentiostatic electrochemical polymerization of *o*-AP at different electrode potentials by employing in situ Raman spectroscopy. In situ Raman spectra in the potential range between the reduced state ($E = -0.2$ V vs SCE) and the oxidized state ($E = 0.5$ V vs SCE) of POAP in 0.5 mol/L H_2SO_4 solution were compared by Holze and co-workers²³ for both potentiostatically and potentiodynamically synthesized POAP films. The various bands together with their possible assignments are shown in Table 2. The bands at 1598, 1472, and 1170 cm^{-1} were associated to quinoid groups, whereas the bands at 1522 and 578 cm^{-1} were attributed to benzoid rings. The band at 1330 cm^{-1} was assigned to a semiquinone species with an intermediate structure between amines $-\text{C}-\text{NH}-$ and imines $-\text{C}=\text{N}-$ resulting in polarons. However, Holze and co-workers²³ also observed an additional band at 1402 cm^{-1} that was completely missing in the spectra reported by Salvagione et al.⁴¹ It was assigned to the radical semiquinone C-N⁺ formed during the partial oxidation of *N,N'*-diphenyl-1,4-phenylenediamine. The bands located at 982 and 1050 cm^{-1} were assigned to the internal modes of the sulfate anion of the electrolyte solution. Holze and co-workers²³ observed that the intensity of some of the bands depends on the applied potential. For instance, the band located at 1170 cm^{-1} grew in intensity when the potential was shifted up to $E = 0.2$ V, beyond this value it diminished with a further increase of the potential. The dependence of the intensity of this band on electrode potential was considered to be a characteristic feature of the oxidized form of POAP and was attributed to the CH-bending vibrational mode of the quinoid-like rings formed during electro-oxidation. The bands in the frequency range 1300–1400 cm^{-1} were associated mainly with the stretching vibrations of charged C~N⁺ segments (~ denotes the bond intermediate between the single and double bonds). Although the Raman features of the POAP films potentiostatically and potentiodynamically synthesized by Holze and co-workers²³ were similar, some marked differences with respect to the potential dependence of some bands were observed. A difference was observed in particular with respect to the potential dependence of the band around 1645 cm^{-1} . The intensity of this band sharply increased at 0.3 V and slowly decreased at more positive potentials for the POAP film synthesized potentiostatically. However, in the case of the potentiodynamically prepared POAP this band attained the intensity maximum at about $E = 0.2$ V. The band located at 1645 cm^{-1} was assigned²³ to $-\text{C}=\text{N}-$ in quinonimine units, and was considered to correspond to the C-N-C bond of a heterocyclic six-membered ring structure arising from ortho-coupling rather than para-coupling during the electropolymerization, resulting in a ladder polymer. As this band did not disappear even at the highest applied potential, the oxi-

Fig. 17. (a) In situ UV-vis spectra of poly-*o*-aminophenol (POAP) at different applied electrode potentials. The POAP film was prepared on indium thin oxide (ITO)-coated glass at 0.8 V (1 h electrolysis) from a solution containing 0.05 mol/L *o*-AP in 0.5 mol/L H₂SO₄ solution. (b) Enlarged spectra of (a) between 320 and 450 nm.²³



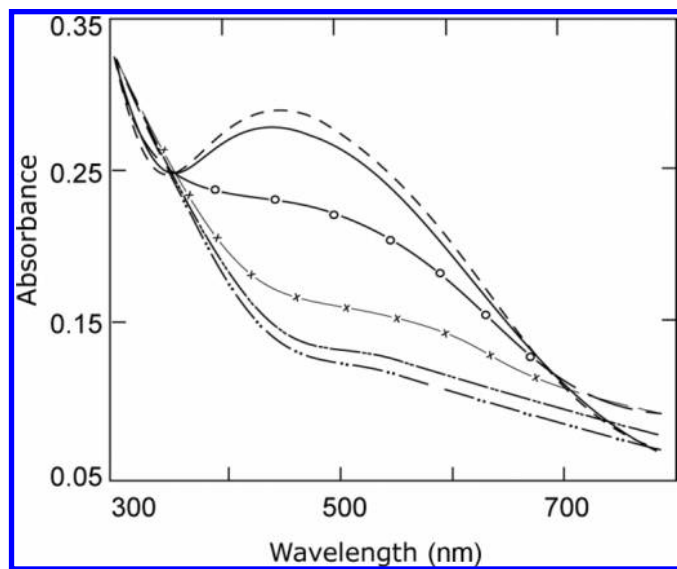
duction of fully reduced POAP synthesized potentiostatically to fully oxidized POAP was assumed to proceed via an intermediate half-oxidized state. This assumption is supported by the fact that the maximum intensity of the band at 1645 cm⁻¹ was observed at a roughly middle potential between the two redox processes observed on the cyclic voltammograms of POAP shown in ref. 23. The effect was associated with the maximum polaron concentration in the polymer. The increase of potential beyond the maximum intensity, which leads to the fully oxidized state of the polymer, was attributed to a lowering in the polaron concentration, probably by the coupling into bipolarons. The band observed around 1598 cm⁻¹ was assigned to the quinoid units and grew in intensity with increasing electrode potential. The band at 1472 cm⁻¹ was only observed at electrode potentials within the range 0.3 V < E < 0.4 V.

Structural changes during the redox process for chemically synthesized POAP were also analyzed by employing ex situ and in situ UV-vis measurements. POAP was chemically synthesized by treatment of an acid solution of *o*-AP with CuCl₂, and the oxidative polymerization was followed by UV-vis spectroscopy.¹⁸ Prior to the addition of CuCl₂, two absorption peaks were found on the monomer solution spectra at 258 and 460 nm that were assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic structure (benzene structure) and the oxidized form of *o*-AP, respectively. A new absorption peak at 410 nm was developed after the addition of Cu(II) and its intensity increased with time at the expense of the peak at 460 nm. The peak at 410 nm was assigned to the radical cation (oxidized form) of POAP. The solid polymer synthesized by Zhang et al.¹⁸ was also examined by X-ray photoelectron spectroscopy (XPS).¹⁸ The authors remarked that the C1s, N1s, and O1s spectral features were similar to those reported for POAP electrochemically prepared in other works.⁴³ The carbon spectrum was deconvoluted to estimate the extent of carbon involved in the C-C, C-N, and C=O bonds. A ratio of 3:2:1, indicating a good degree of polymerization, was obtained by Zhang et al.¹⁸ They¹⁸ concluded that polymer growth proceeds mainly through the reactions between the growing polymer (POAP) and the oxidized monomer units, and subsequent cyclization of the functional units in the polymer leads to a ladder structure. The relative reflectance change ($\Delta R/R$) as a function of the wavelength within the visible spectrum region was also employed by Zhang et al.¹⁸ to study the structure of

electrochemically synthesized POAP films. The wavelength dependence of $\Delta R/R$ for a POAP film electrochemically deposited on Pt when it is polarized at various potentials is shown in ref. 18. A broad absorption band extending from 410 to 532 nm was observed for polarization within the range 0.1–1.1 V (SCE). The band intensity increased with increasing potential, turning the film dark brown. In addition, a slight blue shift simultaneous with the intensity increase was noted. The absorption band was assigned to the formation of radical cations at POAP as the polymer matrix became oxidized. The blue shift with the increase in potential was attributed to a larger fraction of radical cation species contained in the polymer as it becomes more oxidized. According to Zhang et al.,¹⁸ the oxidation of POAP is not complete even at 0.5–0.6 V (SCE); therefore, the broad band at 410 nm was considered to be composed of $\pi \rightarrow \pi^*$ transitions proceeding from both the oxidized (quinonoid) and reduced (*N*-phenyl-*p*-phenylenediamine) units (Fig. 9).

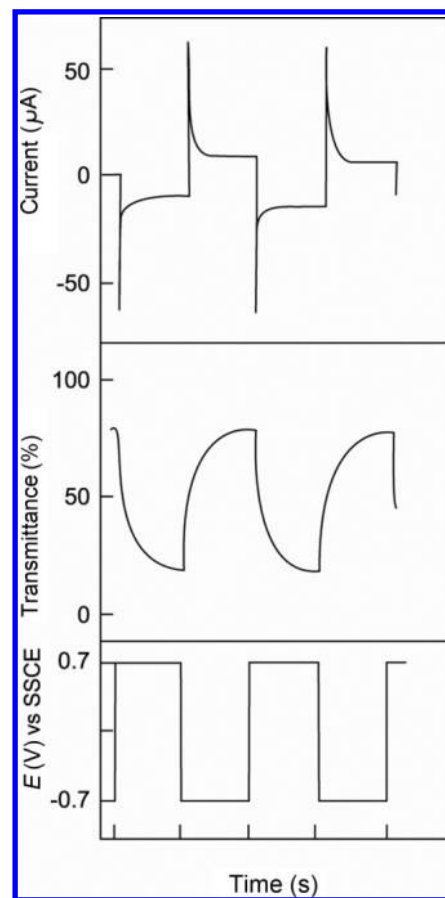
UV-vis spectra of POAP films synthesized potentiostatically at different electrode potentials were analyzed by Holtze and co-workers.²³ Figures 17a and 17b show UV-vis spectra of a POAP film at different electrode potentials within the range -0.2 V < E < 0.6 V (SCE). Three absorption peaks located at $\lambda = 350$, 410, and 610 nm were observed. At E = -0.2 V the polymer is in its reduced state, and the corresponding spectra show an absorption band located at approximately at $\lambda = 350$ nm. This band was attributed to the phenoxazine structure. With increasing potential, the oxidation of POAP takes place, leading to the formation of radical cations. Holtze and co-workers²³ observed that, as the potential is increased from -0.2 to 0.1 V, the intensity of the band at $\lambda = 350$ nm decreases and, at 0.1 V, it split into at least two bands. With a further increase of the potential the intensity of one of these bands was diminished, while the other one started to shift to lower energies and changed into a broad maximum around $\lambda = 410$ nm. The absorption band at $\lambda = 610$ nm increased in intensity up to 0.2 V and then it became nearly constant with a further increase of potential. The behaviour of the in situ UV-vis spectra of the potentiostatically synthesized POAP films presented in ref. 23 was considered as a verification of previous results reported by Ortega,¹³ indicating that the redox transition of POAP from its completely reduced state to its completely oxidized state proceeds through two consecutive reactions in which a charged intermediate species takes part.

Fig. 18. Absorbance as a function of wavelength at fixed electrode potentials (E) in 0.4 mol/L NaClO₄ + 0.1 mol/L HClO₄. -0.2 V, (— · —); 0.0 V, (— · — · —); 0.1 V, (-x-); 0.2 V, (-o-); 0.5 V, (-); 0.7 V, (- · -).



A spectroelectrochemical study of the redox process of POAP was reported by Tucceri et al.⁴² Absorbance changes in the wavelength region between 300 and 800 nm, at different pH values and in the presence of different supporting electrolytes, were recorded and analyzed at different degrees of oxidation of POAP. Two types of experiments were carried out by Tucceri et al.:⁴² (i) at a fixed wavelength, the electrode potential was swept at scan rates between 0.005 and 0.03 V s⁻¹ and (ii) at a fixed electrode potential the wavelength was scanned. Figure 18 shows the spectra of POAP films at different electrode potentials in the region where the film is electrochemically active (-0.2 V < E < 0.7 V vs SCE). The absorbance of the film at the negative potential limit (-0.2 V) was attributed to the tail of the UV band related to the $\pi \rightarrow \pi^*$ transition of the basic aromatic structure of the phenoxazine units. A reaction scheme for the POAP redox switching, which also includes protonation reactions, is shown in ref. 42. The redox switching of POAP was interpreted in terms of the oxidation of amine groups to imine groups. As POAP is progressively oxidized, several changes in the spectral response were observed by Tucceri et al.:⁴² (i) a decrease of the absorbance in the wavelength region at about 340 nm; (ii) a broad maximum was developed at 450 nm; and (iii) in the region of $\lambda > 750$ nm, the absorbance first increased with a potential up to $E = 0.1$ V and then, for $E > 0.1$ V, the absorbance decreased. The broad band growing at 450 nm as the potential increases in the positive direction was assigned to the partially oxidized phenoxazine structure. While the decreases of the absorbance at $\lambda = 340$ nm, as the potential increases in the positive direction, was attributed to the disappearance of the reduced form of POAP, the increase of the absorbance at $\lambda = 450$ nm was associated with the increase of the oxidized form with the potential scan. For $\lambda = 750$ nm, the absorbance presents a maximum at $E = 0.15$ V, which was considered to be indicative of the existence of a transient species. The spectra of reduced ($E = -0.2$ V) and oxidized ($E = 0.7$ V) states of POAP were also found to be dependent on pH. The absorbance difference ($\Delta A = A_{\text{ox}} - A_{\text{red}}$; A_{ox} , absorbance of the oxidized state; A_{red} , absorbance of the reduced state) was analyzed⁴² and represented, at different pH, as a function of the wavelength while the polymer goes from the reduced state to the oxidized one. A slight increase of the UV tail was observed under these conditions and it was attributed to poor protonation of the polymer as it becomes oxidized. This effect was associated with the conversion of one protonated amino group to a nonpro-

Fig. 19. The responses of current and transmittance at 440 nm of the poly-*o*-aminophenol (POAP) film ($\phi = 0.2 \mu\text{m}$) coated indium thin oxide (ITO) electrode to a potential pulse between -0.7 and 0.7 V in 0.2 mol/L NaClO₄ aqueous solution (pH 1). Electrode area, 0.20 cm².¹⁷



nated imino group. Tucceri et al.⁴² concluded that, as the pH increases, the reduction of the oxidized species becomes progressively hindered and, consequently, the amount of oxidable species available in the film decreases. Experiments carried out by Tucceri et al.⁴² in the presence of different anions (perchlorate, sulfate, and benzenesulfonate) at pH 1, showed that the absorbance with potential at 440 nm decreases in the sequence ClO₄⁻ > HSO₄⁻ > benzenesulfonate. That is, the absorbance decreases with increasing the anion size, because the anion size follows the sequence ClO₄⁻ ≤ HSO₄⁻ < benzenesulfonate. The transient response at 750 nm was also dependent on the nature of the anion of the supporting electrolyte; thus, for benzenesulfonate the change was smaller, but the decay was slower than for perchlorate and bisulfate.

The UV-vis absorption spectra of the oxidized and reduced forms of a POAP-film-coated ITO electrode were analyzed by Oyama and co-workers.¹⁷ The maximum absorption peak of the oxidized form was observed at 400 nm and that of the reduced one at 600 nm. A reversible colour change of the film between brown and pale green was observed when the electrode potential was cycled between -0.7 and 0.7 V vs SCE. Figure 19 shows the response of the current and transmittance at 440 nm of the electrode during the potential step within the electrochromic region. The colour accumulated in the anodic step was bleached in the cathodic one. No substantial change in the transmittance response of the electrode was observed, even after a potential stepping of 100 cycles. The brown colour of the oxidized form remained substantially unchanged even after standing in air at open circuit for a period of 6 months. On the other hand, the reduced form was

gradually oxidized by oxygen in air and consequently became coloured. The colourlessness of the reduced form was held under an atmosphere of nitrogen gas.

Barbero et al.⁴⁴ reported a spectrophotometric and ellipsometric study of POAP formed by electropolymerization of *o*-AP on Au and Pt surfaces. POAP films of different thickness (d) were synthesized by CV in ref. 44. The films were subjected to different polarization conditions (reduced and oxidized states), and the ellipsometric readings of the polarizer and analyzer (Δ and Ψ values, respectively) at $\lambda = 541.6$ nm were obtained. It was observed that up to one particular film thickness (50 nm), reversing the potential from the oxidized to the reduced state and vice versa, resulted in the same ellipsometric readings for each state (i.e., oxidized and reduced), thus showing that the film behaves reversibly from the optical viewpoint. Experimental values of ψ and Δ for both states, for the different thicknesses at one wavelength, were fitted by a single film model in which it was assumed that the complex refractive index of the film (\tilde{n}) for each state (oxidized (\tilde{n}_{ox}) or reduced (\tilde{n}_{red})) was independent of the film thickness. The best fit allowed for the determination of \tilde{n} and k (real part of the complex refractive index) common to all thicknesses for each state. The corresponding \tilde{n} values were $\tilde{n}_{\text{red}} = 1.704 - i0.02$ and $\tilde{n}_{\text{ox}} = 1.699 - i0.175$, where i is the imaginary unit for the complex numbers, at $\lambda = 546.1$ nm. These values indicate that the film is transparent in the reduced state and opaque in the oxidized one. As the value of the real part of \tilde{n} was common to both states and it was slightly higher than that reported for PANI, Barbero et al.⁴⁴ inferred that the structure of POAP is similar to that proposed for PANI. Also, from the determination of ψ vs Δ dependence, it was concluded that POAP in the oxidized state should have a higher thickness (d_{ox}) than in the reduced (d_{r}) one. From the poor fitting at $d > 50$ nm it was suggested that thick POAP films exhibit a less densely packed structure or an increasing surface roughness or both, as compared with thin POAP films. Similar experiments as those described were carried out by Barbero et al.⁴⁴ at different wavelengths within the range $350 \text{ nm} < \lambda < 650 \text{ nm}$. In this regard, by repeating the same fitting procedure, the n and k values together with the thickness were determined for both film conditions (oxidized and reduced states). It was observed that, for low thicknesses, d_{ox} was bigger than d_{r} . However, this difference tended to disappear for high film thicknesses. A voltammetric cathodic charge vs ellipsometric thickness relationship for POAP was also reported by Barbero et al.⁴⁴ They observed that the charge (Q) increased linearly with the film thickness obtained by ellipsometry during the negative potential scan. However, as d increased beyond 40 nm, the slope of the Q vs d dependence became smaller. This fact was considered to be indicative of a decrease in the film density, i.e., the ellipsometric thickness would be bigger than the electrochemically active portion of the film.

Spectroscopic studies of POAP films synthesized in basic and neutral media

Kudelski and co-workers⁴⁵ studied the chemical and electrochemical oxidation of *o*-AP over a wide pH range. A mixture of at least eight different compounds obtained from the chemical oxidation of *o*-AP were separated chromatographically⁴⁵ and then their surface-enhanced Raman scattering (SERS) spectra were compared. 3APZ was identified as the main product by recording an IR spectrum, and the second product of the chemical oxidation of *o*-AP was identified as DHAB. 3APZ is formed by the simultaneous N–C and O–C coupling of *o*-AP monomer units. The N–N coupling yields DHAB. With regard to the solution pH, DHAB was formed mainly in neutral and basic solutions of *o*-AP, whereas at low pH values, 3APZ was considered to be the main oxidation product. Also, the two main products identified by Kudelski and co-workers⁴⁵ after electrochemical oxidation of *o*-AP were 3APZ and

DHAB. 3APZ could be oxidized at the electrode forming a ladder structure polymer.

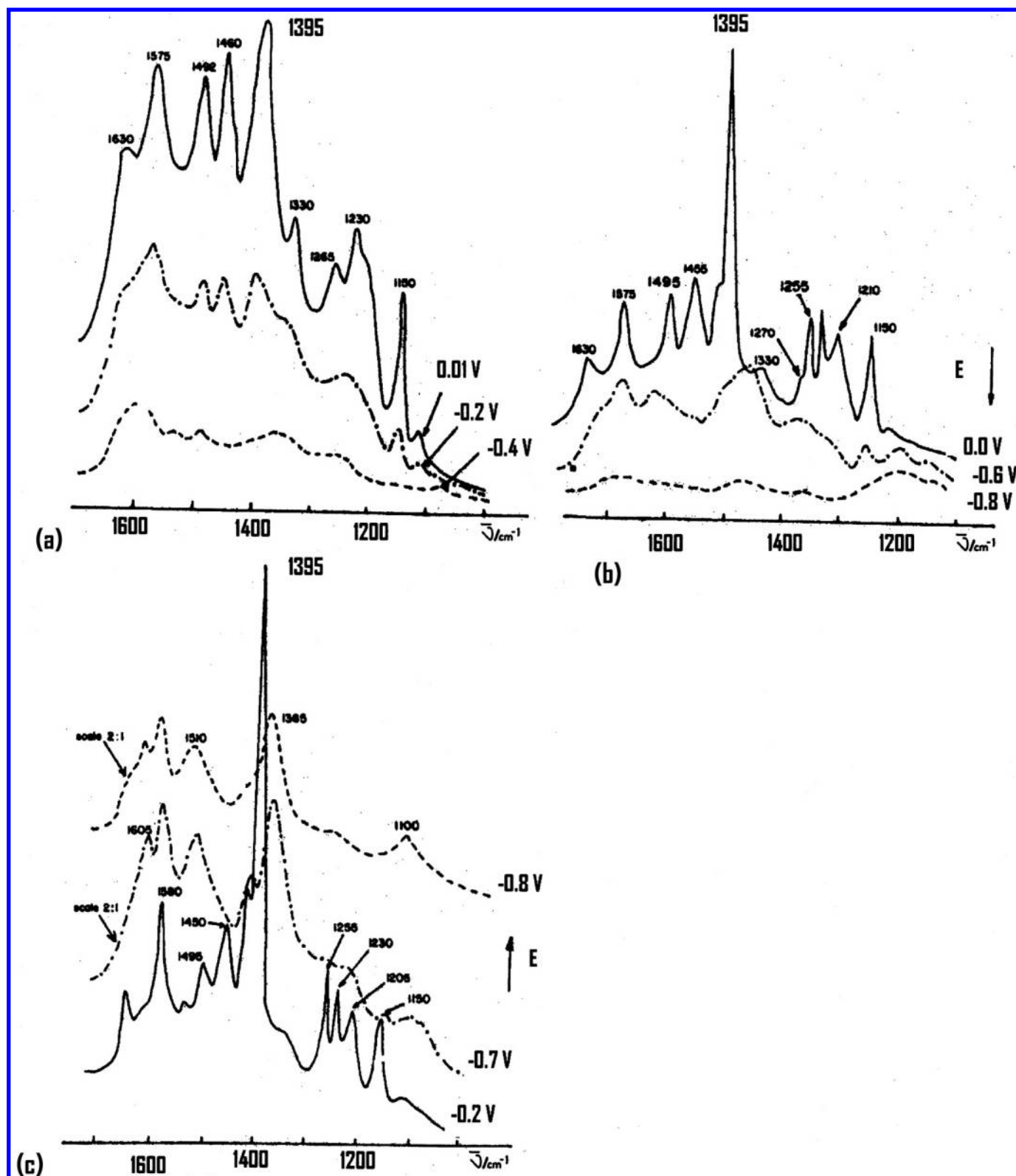
Figure 20 shows SERS spectra of a silver electrode immersed in *o*-AP at different pH and electrode potential values. A band at 1395 cm^{-1} is clearly observed in all spectra. This band was assigned to nitrosophenol. As demonstrated in Fig. 20, this band exhibits a strong intensity in alkaline solutions, but is weaker in the acidic medium. By comparing the behaviour of this band with the band at 1390 cm^{-1} observed in the SERS spectra of nitrosobenzene, it was concluded that at open-circuit potential, the *o*-AP on the silver electrode was already oxidized into two major products, 3APZ and DHAB. The SERS spectrum of the *o*-AP solution also depends on the applied electrode potential. At pH 3.0 (Fig. 20a), the spectrum is most intense at the stationary potential electrode $E = 0.01 \text{ V}$, weak at -0.2 V , and almost absent at -0.4 V after the reduction of 3APZ. At pH 7.5 (Fig. 20b), the overall intensity of the spectrum significantly diminishes at more negative potential values (about -0.6 V). In alkaline solutions (Fig. 20c), the main band ascribed to 3APZ and DHAB disappear at -0.7 V after a reduction of azo compounds to hydrazo compounds. The spectrum observed at more negative potential values in neutral and alkaline pH was attributed to the hydrazo species, which are products of the reduction of DHAB.

The electropolymerization of *o*-AP in alkaline media (pH 12) on copper electrodes was studied by Guenbour et al.²⁶ IR spectrometry was employed to characterize the polymer films. The IR spectrum of the POAP film and that of the 2-aminophenol compound were compared.²⁶ The film spectrum did not present the O–H band (3375 cm^{-1} for the stretching vibration and 1268 cm^{-1} for the bonding vibration), characteristics of the 2-aminophenol. Instead of these bands, that of C–O–C at 1297.7 cm^{-1} , was observed. This spectral difference was considered to be consistent with an electropolymerization process of *o*-AP, which proceeds through the anodic oxidation of the monomer. The absence of the band at 1700 cm^{-1} , assigned to C=O groups, confirmed the only formation of a polyether compound. The presence of the characteristic strong absorptions corresponding to the bands of the $-\text{NH}_2$ group in the ranges $300\text{--}3500 \text{ cm}^{-1}$ and $1590\text{--}1610 \text{ cm}^{-1}$ were observed in the IR spectra of the films. Electron spectroscopy for chemical analysis (ESCA) analysis of the POAP films was also carried out by Guenbour et al.²⁶ The spectrum of the oxygen 1s was interpreted as being composed of different peaks, 531.5, 532.9, and 533.9 eV, attributed, respectively, to the oxygen bonding to a metal in an oxide, to the oxygen of water adsorbed molecules, or to hydroxide group (OH) and to C–O–C bonds. The third component at high energy (286.5 eV) of the C_{1s} spectrum was assigned to C–O–C bonds and the low-energy components were considered to be characteristics of C–C bonds (284.6 eV) and C–N bonds (285.5 eV). The N_{1s} spectrum was assigned to the three types of bonds of the 2-aminophenol: O–N, N–H, and C–N (389.9, 400.3, and 401.2 eV). Copper in its oxidized forms was also observed in the film: Cu_2O (932.6 eV) and CuO (933.7 eV). The higher energy component (934.5 eV) was attributed to a complex formed with the organic compounds. IR studies were also carried out by Guenbour et al.²⁶ and they seemed to indicate that the POAP film growing process in alkaline media involves the deprotonation of the aminophenol molecule, which is probably chemisorbed at the metal surface, followed by oxidation and electropolymerization reactions. In this whole process, the polymerization affects the $-\text{OH}$ group by the formation of C–O–C bonds while the $-\text{NH}_2$ groups are preserved.

Formation mechanism of poly(*o*-aminophenol) films

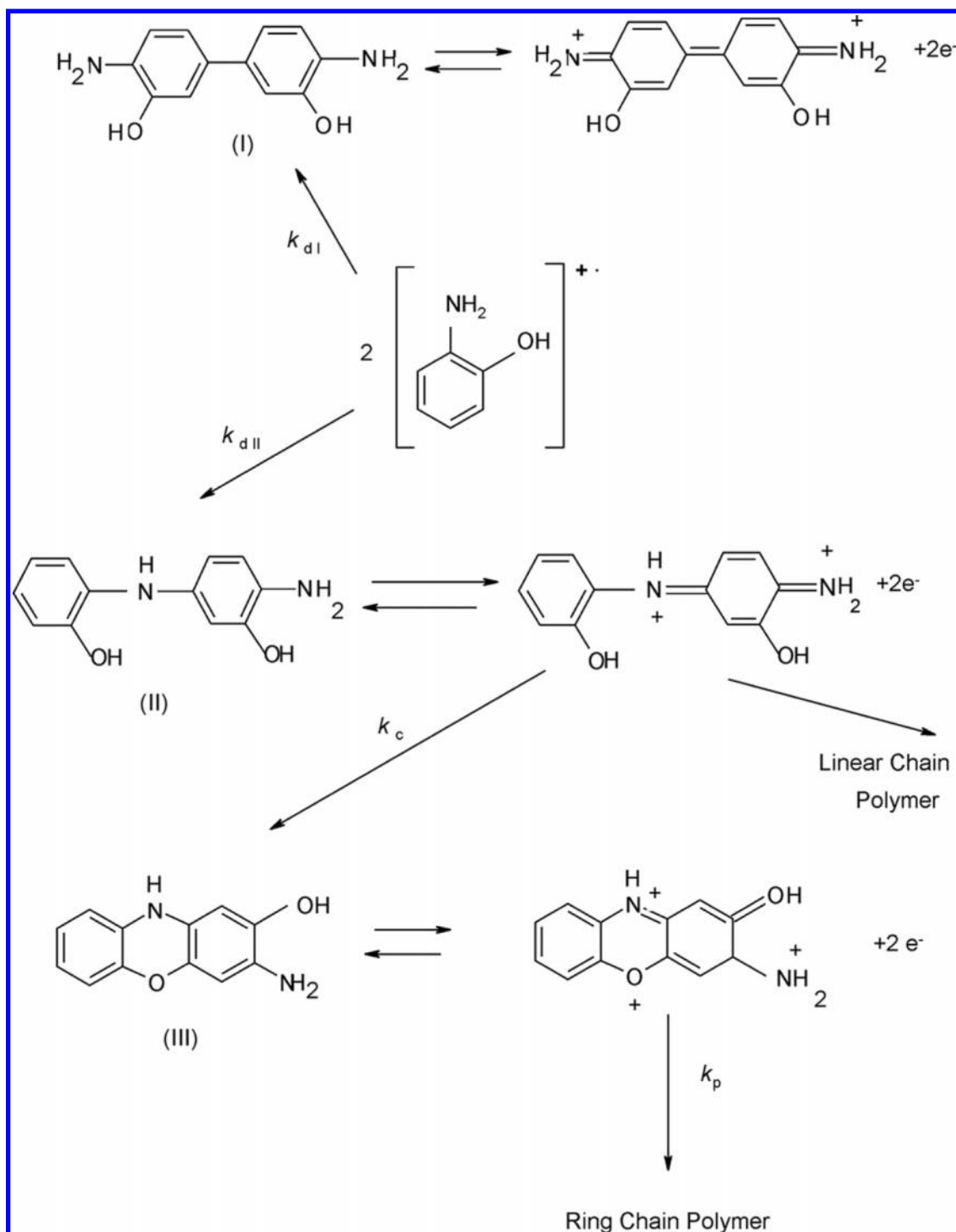
On the basis of the electrochemical and spectroscopic studies reported in ref. 11, Barbero et al. explained the formation of POAP films in acid medium employing the generalized mechanism of anodic oxidation of anilines in aqueous media solutions. These authors proposed that a radical cation $\text{o-AP}^{+\cdot}$ is

Fig. 20. Surface-enhanced Raman scattering (SERS) spectra of *o*-aminophenol (*o*-AP) solutions at (a) pH 3.0, (b) pH 7.5, and (c) pH 9.7 for different electrode potentials.⁴⁵



formed in a first charge transfer step and then it may follow the reaction paths shown in Fig. 21. The *o*-AP^{•+} radical may dimerize by either C-C coupling or C-N coupling to give species (I) and (II), respectively (Fig. 21). The dimers oxidize to the correspond-

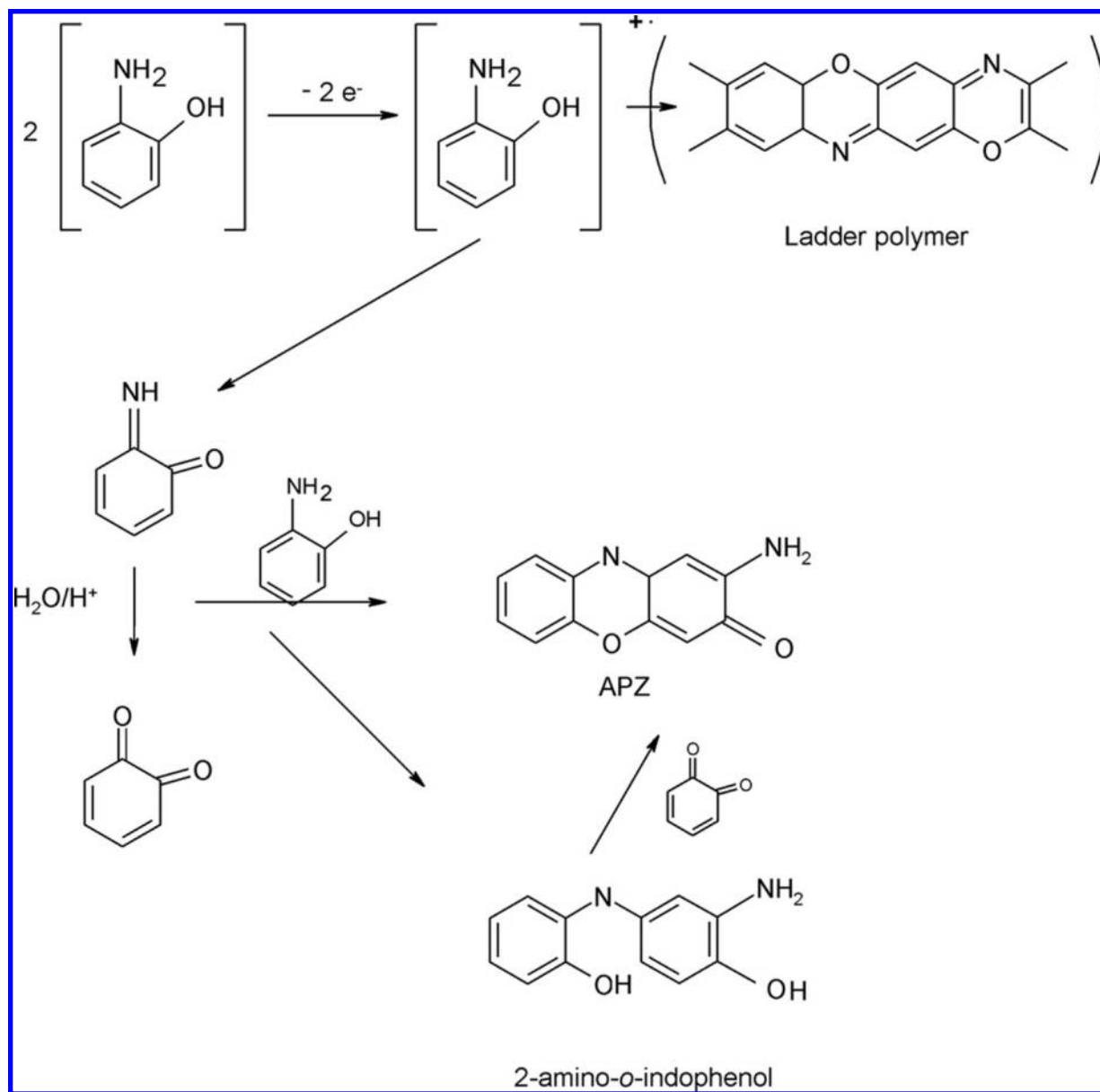
ing dications. The oxidized dimer II can suffer a cyclization reaction to give species III, which is oxidized further to 3APZ. The product distributions analyzed by Barbero et al.¹¹ allowed the authors to establish that the rate constants for the dimer

Fig. 21. Mechanism of anodic oxidation of *o*-aminophenol (*o*-AP).¹¹

formation follow the order $k_{dI} < k_{dII}$ and both rate constants are higher than the cyclization rate (k_c), to give species III. However, the rate of polymerization (k_p), to obtain the immobilized couple on the electrode surface, was lower than k_c . The possibility that the dication of compound II can polymerize was not disregarded. Therefore, the formation of a composite of two different films, one of linear chain structure similar to PANI and the other with a phenoxazine-like chain structure, was assumed to be possible. The latter product was considered to be the predominant one by Barbero et al.¹¹

Bulhões and co-workers¹⁵ postulated that electrochemical oxidation of *o*-AP consists of a first oxidation step involving a two-electron transfer to form radical cations followed by chemical couplings of radical cation – radical cation or radical–monomer species (E(CE)) mechanisms to form a ladder polymer with phenoxazine units. However, radical cations can also react quickly near the electrode surface, and after the first step involving two electrons, soluble products are easily formed by hydrolysis (Fig. 22). Thus, besides a film with a ladder structure, Bulhões and co-workers¹⁵ proposed that oxidation of *o*-AP can produce inter-

Fig. 22. Mechanism of *o*-aminophenol (*o*-AP) electro-oxidation in aqueous acidic medium.¹⁵

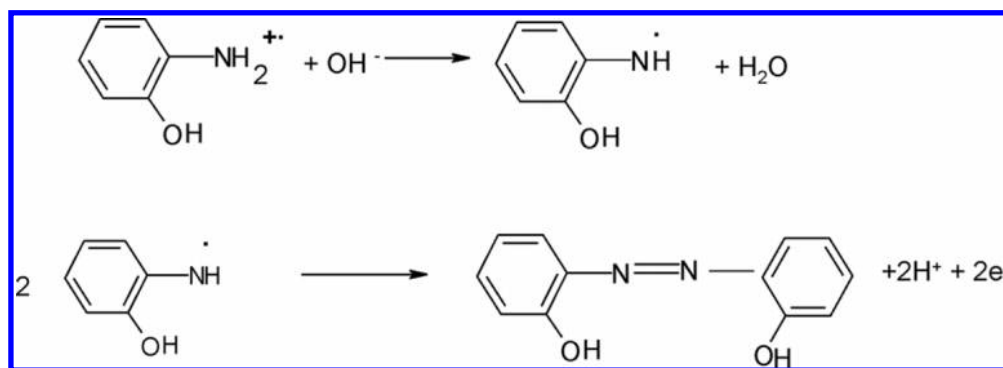


mediate benzoquinone monoamine after successive cycling. Particularly at less controlled conditions such as at higher final potentials and lower scan rates, monoamines can react with neutral *o*-AP giving an intermediate (2-amino-*o*-indophenol) prior to cyclization to APZ. The low solubility of POAP films was attributed to the stiffness of the ladder phenoxazine backbone, which also seems to justify the low conductivity of POAP (10^{-7} S cm^{-1}) as compared with that of PANI (1 S cm^{-1}).

Kudelski and co-workers^{45,46} combined CV and SERS measurements to study the formation mechanism of POAP at different pH. The SERS results⁴⁶ from a roughened silver electrode in contact with an *o*-AP solution had suggested the presence of at least two oxidation products (nitrophenol and nitrosophenol) on the electrode surface at open-circuit potential. Typical cyclic voltammetric curves obtained for a silver electrode in 0.1 mol/L LiClO₄ solutions of *o*-AP at different pH values are shown in ref. 46. In all cases one pair of redox peaks was observed. However, two pH ranges with different curve features could be distinguished. Within the range of moderate pH (9.1 and 7.2), potentials of anodic (E_{pa}) and cathodic (E_{pc}) peaks changed slightly with pH. However,

within the second pH range (pH 3.6 and below) E_{pa} and E_{pc} were strongly pH-dependent. These different features of the CV curves within these two pH ranges were attributed to the presence of two different electroactive oxidation products on the surface of the silver electrode. To identify products formed during the potential cycling, cyclic voltammograms were recorded in different solutions of 0.1 mol/L LiClO₄: (i) saturated with nitrosobenzene (pH 10, 6.7, 3.6, and 1.3), (ii) saturated with azoxybenzene (pH 10, 7.0, 3.7, and 2.0), and (iii) on a roughened silver electrode modified with 3APZ. In the first two cases no redox peaks were found in the potential range from 0.15 to -0.5 V (SCE) for nitrosobenzene (pH 1.3) and azoxybenzene (pH 2.0) solutions. However, for nitrosobenzene solutions with pH values in the range 10 to 3.6, two pairs of slightly pH-dependent redox peaks were recorded. The first pair of redox peaks was assigned to the well-known reduction reaction of nitrosobenzene ($\text{C}_6\text{H}_5\text{NO}$) to phenylhydroxylamine ($\text{C}_6\text{H}_5\text{NHOH}$) and the re-oxidation of $\text{C}_6\text{H}_5\text{NO}$ to $\text{C}_6\text{H}_5\text{NHOH}$. The second pair of redox peaks was attributed to the reduction of azoxy species, which are formed by the chemical reaction of $\text{C}_6\text{H}_5\text{NO}$ and $\text{C}_6\text{H}_5\text{NHOH}$ to hydrazobenzene and re-oxidation

Fig. 23. Formation of azo species from *o*-aminophenol (*o*-AP) on the silver electrode in an alkaline medium.⁴⁵



of hydrazobenzene to azobenzene. In solutions containing azoxybenzene only one pair of redox peaks was recorded. As it is well known that azoxybenzene can undergo irreversible reduction to azobenzene followed by a two-electron reversible reduction to hydrazobenzene, the observed pair of redox peaks was ascribed to an azo-hydrazo redox reaction. CV curves for nitrosobenzene, azoxybenzene, and *o*-AP solutions at moderate pH (about 7) were also compared by Kudelski and co-workers.⁴⁵ As a pair of redox peaks was obtained for *o*-AP solutions in neutral and alkaline media and they were attributed to the azo-hydrazo couple. Thus, Kudelski and co-workers⁴⁵ assumed that, after oxidation of *o*-AP to *o*-AP^{•+} in neutral and alkaline media, dimerization of *o*-AP^{•+} by N-N coupling takes place. Then, the formation of azo species from *o*-AP on the silver electrode in an alkaline medium was postulated, and the reaction path was considered to be similar to that proposed for the formation of azobenzene from the aniline molecule (Fig. 23). To interpret the CV curves for *o*-AP solutions at pH < 4, cyclic voltammograms for a roughened silver electrode modified with 3APZ (Ag/3APZ) were analyzed in the potential range from -0.2 to -0.4 V (SCE). Only one pair of reversible redox peaks was observed on the curves. The dependence of the peak potentials on pH indicated that protons are essential for the electrode reaction. It was not possible to determine E_{pa} and E_{pc} precisely for the Ag/3APZ electrode at pH < 2, since E_p is in the potential range of silver oxidation, but data obtained for Pt/3APZ electrode at pH < 3 suggested that E_p changes at a rate about 60 mV/pH. This relationship indicated that protons and electrons take part in the electrode reaction of 3APZ in a 1:1 ratio. Therefore, it was postulated that in more acidic solutions the favoured path after oxidation of *o*-AP to *o*-AP^{•+} is dimerization of *o*-AP^{•+} with N-C coupling resulting in the cyclic dimer 3APZ.

Concluding remarks

POAP films have been synthesized by electrochemical oxidation of acid and basic *o*-AP solutions. Whereas DHAB is formed mainly in neutral and basic solutions, at low pH values, 3APZ was considered to be the main electro-oxidation product. 3APZ is formed by the simultaneous N-C and O-C coupling of *o*-AP monomer units, and it can be oxidized at the electrode forming a ladder polymer with a phenoxazine-like chain structure. The N-N coupling yields DHAB in basic media.^{45,46}

On the basis of spectroscopic measurements, different structures have been proposed for POAP. Besides a completely ring-closed structure with phenoxazine units^{11,13,15,23}, two other structures, a partially ring-opened and another partially hydrolyzed, have been formulated for POAP. In situ Raman spectroscopy measurements suggest that the POAP matrix contains alternating oxidized (quinonoid) and reduced (*N*-phenyl-*p*-phenylenediamine) repeating units.^{18,19} The 1,4-substituted molecular structure of POAP proposed by Zhang et al.^{18,19} provides an explanation for the interaction of the polymer with metal cations.

The cation-capturing process by POAP was attributed to the simultaneous presence of the hydroxyl and amino groups of the polymeric backbone, in which the lone pair electrons are available to coordinate with metal cations.

With regard to the mechanisms of POAP formation, most authors^{11,13-15,23} postulated that, in acidic solutions, the favoured path after oxidation of *o*-AP to *o*-AP^{•+} is dimerization of *o*-AP^{•+} with N-C coupling resulting in the cyclic dimer 3APZ. Oxidation of 3APZ leads to a ladder structure polymer with phenoxazine units. However, the *o*-AP^{•+} radical may also dimerize by C-C coupling. Thus, the formation of a composite of two different films, one of a linear chain structure similar to polyaniline (PANI) and the other with a phenoxazine-like chain structure, was assumed to be possible for POAP. Bulhões and co-workers¹⁵ postulated that electrochemical oxidation of *o*-AP consists of a first oxidation step involving a two-electron transfer to form radical cations, followed by chemical couplings of radical cation-radical cation or radical-monomer species to yield a ladder polymer with phenoxazine units. However, the radical cations can also react quickly near the electrode surface to produce soluble products by hydrolysis. Therefore, besides a film with a ladder structure, Bulhões and co-workers¹⁵ proposed that oxidation of *o*-AP can produce intermediate benzoquinone monoamine after successive cycling. Spectroscopic measurements demonstrate the formation of azo species from alkaline solutions of *o*-AP.^{34,45} Kudelski and co-workers⁴⁵ postulated that, after oxidation of *o*-AP to *o*-AP^{•+}, dimerization of *o*-AP^{•+} by N-N coupling takes place, and the reaction path in basic media was assumed to be similar to that proposed for the formation of azobenzene from the aniline molecule.

It has been demonstrated that some substances, such as sodium dodecyl sulfate,¹⁴ increased the rate of polymerization of *o*-AP in acid media because, in its presence, the monomer can more easily reach the electrode surface and produce more monocation radical than in its absence. Also, some electrode surface pretreatments affect the electropolymerization rate of *o*-AP. It has been proven that the electron-transfer rate from a POAP film to a GCE is twice the amount when the GC surface was electrochemically pretreated beforehand (electrode subjected to 1.85 V (SCE) for 5 min in a 0.1 mol/L H₂SO₄ solution), when compared with the results for an untreated surface.

The redox switching of POAP from the totally reduced form to the completely oxidized one in acid medium was also studied by employing UV-vis and Raman spectroscopies and ERS measurements.^{13,23,41,42} The existence of transient species during the redox process of POAP was demonstrated by analyzing the potential dependence of some spectral bands. In this regard, the redox process of POAP was interpreted in ref. 42 in terms of the oxidation of amine groups to imine groups. To this end, absorbance changes in the wavelength region between 300 and 800 nm at different pH values were recorded and analysed at different degrees of oxidation of POAP. Three bands were studied: 340, 450,

and 750 nm. The band at 340 nm was attributed to the phenoxazine structure of the polymer. The band at 450 nm was assigned to the partially oxidized phenoxazine structure. At $\lambda = 750$ nm, the absorbance presented a maximum at $E = 0.15$ V (SCE), which was considered to be indicative of the existence of a transient species. The same conclusion was reached by studying the potential dependence of some bands of the Raman spectra of POAP.⁴¹ For instance, the intensities of the band at 1638 cm^{-1} attributed to $-\text{C}=\text{N}-$ in quinonimine units and the band at 1474 cm^{-1} assigned to the $-\text{C}=\text{N}-$ stretching were analyzed by Slavagione et al.⁴¹ as functions of the applied electrode potential. They determined that when the potential increases, the band at 1474 cm^{-1} increases, and the band at 1638 cm^{-1} also increases until a potential of about 0.2 V and, thereafter, it diminishes. This behaviour was considered indicative of the existence of an intermediate species. The existence of intermediate species was associated with an oxidation process that occurs through two consecutive reactions through a charged species, which was considered to be a cation radical. From another point of view, the effect was also associated with the maximum of polaron concentration in the polymer. The increase of potential beyond the maximum intensity was attributed to a lowering in the polaron concentration, probably by coupling into bipolarons. In the same sense, although the Raman features of the POAP films synthesized potentiostatically and potentiodynamically were similar²³ and marked differences with respect to the potential dependence of some bands were observed. A difference was observed particularly with respect to the potential dependence of the band around 1645 cm^{-1} assigned to the $\text{C}=\text{N}$ stretching of quinonimine units. The intensity of this band sharply increased at 0.3 V and slowly decreased at more positive potentials for POAP films synthesized potentiostatically. However, in the case of POAP films potentiodynamically prepared, this band attained the intensity maximum at about $E = 0.2$ V. Thus, the oxidation of POAP synthesized potentiostatically was assumed to proceed via an intermediate half-oxidized state. The behaviour of the in situ UV-vis spectra of POAP films potentiostatically synthesized²³ also demonstrated that the redox transition of POAP proceeds through two consecutive reactions in which a charged intermediate species takes part. Evidence about the existence of cation radical species during the redox conversion of POAP was also obtained by ERS measurements.¹³

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