

## KINETICS ASPECTS OF THE ELECTROOXIDATION OF VERATROLE IN WET ACETONITRILE

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### Abstract

The electrooxidation of veratrole (1,2-dimethoxybenzene) at a platinum surface, was evaluated in dry and wet acetonitrile in tetrabutylammonium tetrafluoroborate, using in situ UV-Visible spectroelectrochemistry. As the content of water was increased, a competition between growth of polyveratrole and formation of soluble species (mainly 2,3-dimethoxybenzoacetamide) was observed. It was found that the decay rate of the cation radical formed during the electrooxidation in dry acetonitrile obeys a second order kinetics ( $k_{f1} = 258 \text{ M}^{-1}\text{s}^{-1}$ ), involving a chemical step coupled to the first electron transference with growth of polyveratrole on the electrode surface. Under wet conditions, the decay rate constant of the cation radical follows a pseudo first order kinetics ( $k_{f2} = 2.40 \text{ s}^{-1}$  when measured by differential reflectance spectroscopy, DRS, and  $k_{f2} = 3.25 \text{ s}^{-1}$  when measured by absorbance determinations, AD), leading to formation of soluble species diffusing to the bulk.

**Keywords:** Polyveratrole, Oxidation of veratrole, Electrooxidation, Conducting polymers, Electropolymerization

### Resumen

Se evaluó la electrooxidación del veratrol (1,2-dimetoxibenceno) sobre una superficie de platino en acetonitrilo seco y húmedo en tetrafluoroborato de tetrabutilamonio, mediante espectroelectroquímica UV-Visible in situ. A medida que se aumenta el contenido de agua, se observa una competencia entre el crecimiento de poliveratrol y la formación de especies solubles (principalmente 2,3-dimetoxibenzoacetamida). Se encontró que la constante de velocidad de decaimiento del catión radical formado durante la electrooxidación en acetonitrilo seco, obedece a una cinética de segundo orden ( $k_{f1} = 258 \text{ M}^{-1} \text{ s}^{-1}$ ), involucrando una etapa química acoplada a la primera transferencia electrónica, con el crecimiento de poliveratrol sobre la superficie electródica. En medio húmedo, la constante de velocidad de decaimiento del catión radical sigue una cinética de pseudo primer orden ( $k_{f2} = 2.40 \text{ s}^{-1}$ , cuando se midió usando espectroscopía diferencial de reflectancia, DRS, y  $k_{f2} = 3.25 \text{ s}^{-1}$ , cuando se midió mediante absorbancia, AD), generándose especies solubles que difunden al seno de la solución.

**Palabras Claves:** Poliveratrol, Oxidación de veratrol, Electrooxidación, Polímeros conductores, Electropolimerización.

### 1. INTRODUCCION

In the electrochemical polymerization of pyrrole in acetonitrile it has been reported that water addition increases the nucleation rate of the oxidation process and exerts a favourable action in morphology and conductivity of polypyrrole [1-5]. On contrary, in the formation of polythiophene deposited from acetonitrile solution, the presence of water is catastrophic, since it inhibits completely the electrodeposition process [6-11]. Polyveratrole is obtained when a platinum surface is immersed in a solution containing veratrole and submitted to an oxidation potential ( $\sim 1.6 \text{ V}$  vs.  $\text{Ag}/\text{Ag}^+$ ) in  $\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$

[12-17]. It exhibits a stacking structure held by electrostatic or Van der Waals type forces that can capture supporting electrolyte counter ions. The influence of polymerization conditions (i.e. deposition potential, concentration of the monomer, nature of the supporting electrolyte) upon the mechanical and electrochemical properties of conducting polymers has been widely studied [18-27]. The effect of counter-ions, incorporated during the deposition process, has been discussed in terms of a rearrangement of the polymer, mobility of the ion during the redox reaction and conductivity of the deposits. Although some studies have been performed concerning the effect of the solvent upon

the electropolymerization process, little attention has been paid to its influence on the redox activity of the polymer itself.

Several authors have reported that films deposited from N-vinyl carbazole and other monomers [28-33] in acetonitrile, with water added, exhibit good adherence and smoothness; nevertheless, these films have lower conductivity than those grown in dry acetonitrile. The differences in conductivities have been attributed to structural transformations occurring during the polymerization process. Differences in conductive and mechanical properties of the polymeric materials can be also related to changes of the chain length. During the cycling process of the polymers, an interaction between ions and solvent occurs, and then, the presence of a nucleophilic solvents like water, could react with the cation radical or with the dication produced during the oxidation process, leading to a degradation of the material matrix.

The electrochemical formation of a trimer of veratrole (hexamethoxytriphenylene) was first reported by Beckgaard and Parker [34]. The use of a different medium (tetrabutylammonium tetrafluoroborate in anhydrous acetonitrile) and higher reaction potentials (over 1.6 V vs. Ag/Ag<sup>+</sup>) enabled us to observe a further reaction which is the electrodeposition of what we call polyveratrole (trimeric hexamethoxytriphenylene radical cation units that have laminar packing, as an ordered columnar phase system (similar to discotic liquid crystal). The radical cations would have parallel triphenylene rings and the  $BF_4^-$  counter ions packed compensating the positive charge of the cation radical [12].

Polyveratrole maintains its electronic/ionic conductivity in organic solution, which makes it an attractive material to be used as an electrode to follow some redox processes in these media, where metals could dissolve or react.

In this paper we are discussing, how low percentages of water (in acetonitrile, or in the supporting electrolyte) modifies both the mechanism and the kinetics of Polyveratrole formation, as well as the redox activity and stability of the material deposited under different conditions of humidity of the electrolytic medium, using electrochemical and in situ spectroelectrochemical methods.

## 2. EXPERIMENTAL

Solutions were prepared with acetonitrile HPLC

grade (from J. T. Baker) dried with molecular sieve (3Å). Highly pure Veratrole (Aldrich) was used without previous treatment and tetrabutylammonium tetrafluoroborate (TBATFB) was synthesised and purified as previously reported [13]. The concentration of veratrole was always 5 mM and the experiments were performed under inert atmosphere and at room temperature (20°C). Cyclic voltammetry experiments were performed in a one compartment, three electrodes cell. The working electrode was a platinum disk (0.28 cm<sup>2</sup> geometrical area) facing a platinum coil as a counter electrode, while the reference electrode was silver/(0.01M) silver nitrate in the same electrolytic medium. The in situ UV-Vis. experiments were performed in a typical optical cell of one compartment equipped with two optical, spectroil glass windows (45° reflectivity angle). The working electrode was a platinum disc polished to mirror with alumina (from 0.3μ to 0.05μ), the counter electrode was a platinum ring held parallel to the working electrode and the reference electrode, was silver/silver nitrate. Voltammetric measurements were performed using a μ-Autolab Potentiostat from ECO CHEMIE coupled to a PC microcomputer. UV-Visible spectroelectrochemical experiments were performed using an OMA III optical system coupled to a PAR 273 Potentiostat/Galvanostat. Optical measurements were obtained using an Oriel 66184 halogen-tungsten lamp (45° incident beam angle), a detector interphase EG&G1461, a computerised optical multichannel analyser (OMA) fitted with a cooled Si diode array EG&G 1234. The IR spectra were taken with a Perkin Elmer 1725X FTIR spectrometer and Gel Permeation chromatograms with a Perkin Elmer 2600 HPLC. Micrographs were taken with an S-2500 Hitachi scanning electronic microscope coupled to an EDX Kevex Model Delta III accessory and a metallographic microscope Nikon 90577. Ultra pure water (18MΩ) from Millipore was always used.

## 3. RESULTS AND DISCUSSION

### 3.1 Cyclic voltammetry

Cyclic voltammetry was performed to evaluate the oxidation of veratrole in dry acetonitrile (Figure 1a) and after adding water (Figures 1b to 1d).

The first voltammetric peak corresponds to formation of the cation radical of veratrole, and it is present in both dry and wet solvent, the second one is attributable to formation of polyveratrole fibrils

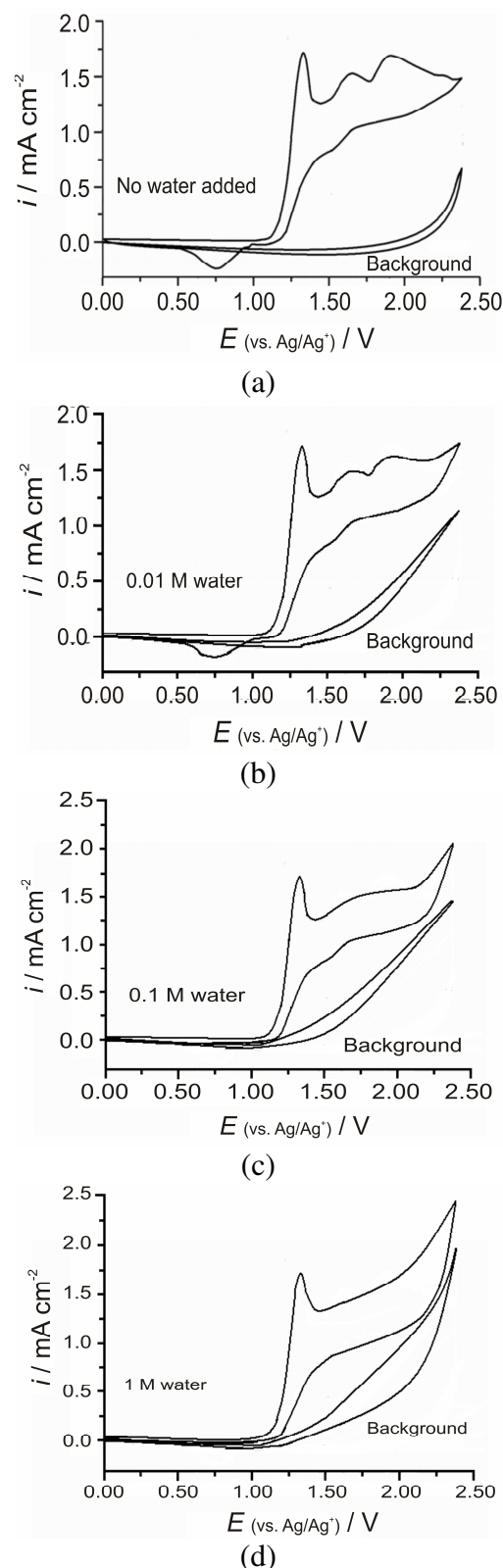
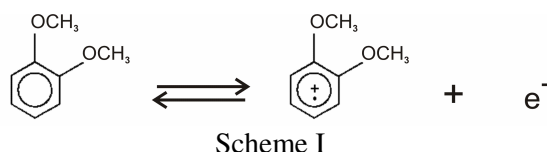
(is at this potential that fibrils formation is observed by SEM) as shown in Figure 2. The third peak corresponds to a further oxidation of the species.

When adding 0.01M water (Figure 1b), only small changes are observed and abundant deposit is still formed on the platinum electrode. As the amount of water is increased to 0.1M (Figure 1c) second and third peaks are not observed and no deposit is formed under these conditions. At even higher concentration of water (1 M), only the first voltammetric peak is observed (Figure 1d) and no polyveratrole is formed. Instead, the intermediate species undergoes a chemical reaction in the bulk solution inhibiting the formation of polyveratrole and generating only soluble products. The remarkable difference observed, indicates that there is a competition between the formation of polyveratrole (nucleation and growth) and the formation of soluble species in the presence of water.

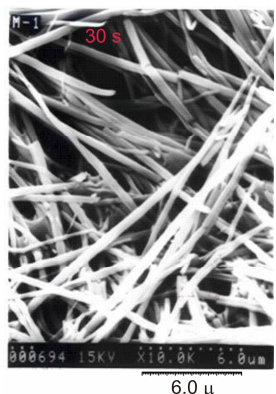
### 3.2 In situ UV-Visible Spectroelectrochemistry

In situ UV-Visible spectroelectrochemical measurements were performed to confirm that production of soluble species could occur simultaneously with the formation of the deposit on the electrode surface, as well as to define aspects of the reaction mechanism of veratrole in acetonitrile in the presence of water.

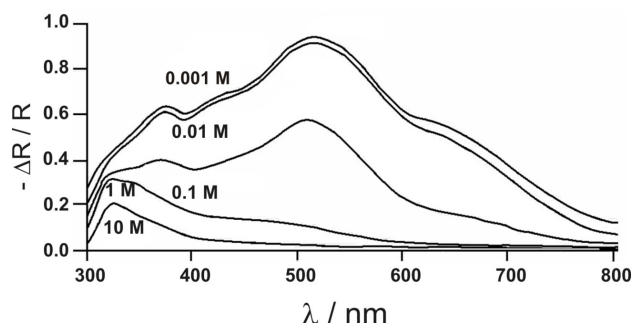
Figure 3 exhibits the UV-Visible spectra taken after 1.5 s of starting the experiment, showing all the absorbing species generated over each oxidation peak for several contents of water. At the first voltammetric peak, an intense signal at 520 nm is observed (scheme I), corresponding to formation of the cation radical of veratrole (reddish species). As the content of water is increased, the absorbing band at 520 nm is depressed and the signal at 640 nm, corresponding to the green material (indeed the hexamethoxytriphenylene cation radical) that grows on the electrode surface vanishes. For a content of water higher than 0.1M, the signal is not observed, suggesting that the cation radical veratrole is consumed to produce soluble species before the polyveratrole could be formed.



**Figure 1.** Cyclic voltammetry response for anodic oxidation of veratrole on Pt in acetonitrile/TBATFB at different concentrations of water: (a) No water, (b) 0.01M water, (c) 0.1M water and (d) 1M water.



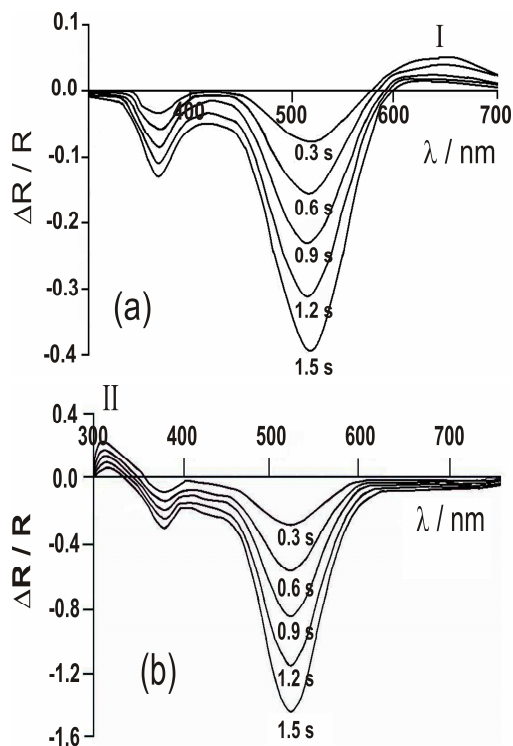
**Figure 2.** SEM micrograph of polyveratrole grown in dry acetonitrile/tetrabutyl-ammonium tetrafluoroborate on a platinum surface.



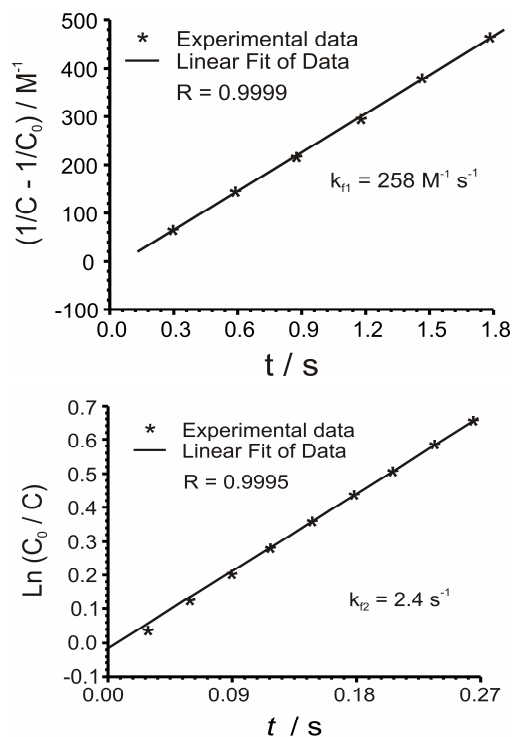
**Figure 3.** UV-Visible spectra taken after stepping the potential from 0.6 V to 1.28 V during 1.5 s, for different concentrations of water.

### 3.2.1 Differential Reflectance Spectro-electrochemistry

Differential spectra obtained at 1.52 V vs. Ag/Ag<sup>+</sup>, at different times after opening the circuit, for content of water lower than 0.01M is shown in Figure 4a and in Figure 4b for higher concentrations. When evaluating at open circuit the decay of the cation radical (520 nm), at low concentration of water (fig. 4a) the reaction followed a second order kinetics and  $1/C - 1/C_0 = k_{f1}t$ , a value of  $k_{f1} = 258 \text{ M}^{-1} \text{ s}^{-1}$  was estimated with a correlation factor of 0.9999 (Figure 5a). The spectroelectrochemical evaluation of the system at concentrations of water above 0.1M (Figure 4b) shows that the absorbing species at 640 nm (I), related to formation of the deposit vanishes as the concentration of water increases and a band at about 300 nm (II), associated to the formation of a soluble species starts to develop. A first order kinetic is then followed and  $\ln(C/C_0) = k_{f2}t$  gave a value of  $k_{f2} = 2.4 \text{ s}^{-1}$  with a correlation factor of 0.9995 (Figure 5b).



**Figure 4.** Differential spectra taken after opening the circuit, taking the reflectivity reference just before opening the circuit at (a) low and (b) high concentration of water.



**Figure 5.** Kinetics of (a) Second order rate constant estimated from the decay of the species observed at 520 nm. (b) First order rate constant estimated for the formation of soluble species at about 300 nm.

### 3.2.2 Evaluation of the homogeneous coupled rate constant at open circuit

This homogeneous rate constant was also estimated from the spectroelectrochemical experiments (optical transients,  $\Delta R/R$  vs.  $t$ ) to monitor the decay of the reaction intermediates produced during the oxidation of veratrole in wet acetonitrile. Since the absorbance ( $A$ ) is a parameter that is proportional to the concentration of the species under study and we have measured reflectance, we must relate it with absorbance [35].

Absorbance ( $A$ ) is related to reflectance ( $R$ ) by:

$$A(t) = -\ln\left(1 + \frac{\Delta R}{R}\right) \quad (1)$$

According to Beer-Lambert relationship, the absorbance can be expressed:

$$A(t) = \exp\left(-\frac{2\varepsilon}{\cos\theta}\right) \int_0^\infty C(x,t) dx \quad (2)$$

Where  $C$  is the concentration of the analyte,  $\varepsilon$  is the extinction coefficient and  $\theta$  is the reflectivity angle. Knowing that:

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \dots \quad (3)$$

Since  $C$  is very small, the exponential in equation 2 can be expanded and a simple expression can be written:

$$A(t) = 1 - \left(\frac{2\varepsilon}{\cos\theta} \int_0^\infty C(x,t) dx\right) \quad (4)$$

For a process governed by semi infinite linear diffusion, the current density ( $i$ ) is given by:

$$i = \frac{nFC\sqrt{D}}{\sqrt{\pi t}} \quad (5)$$

Where  $D$  is the diffusion coefficient. The concentration profile is then related with the current density by equation 6:

$$\int_0^\infty nFC(x,t) dx = \int_0^\infty i dt = 2nFC\sqrt{dt/\pi} \quad (6)$$

And the absorbance is:

$$A(t) = \frac{4\varepsilon nFC\sqrt{Dt}}{\sqrt{\pi} \cos\theta} \quad (7)$$

A plot of  $A(t)$  vs.  $t^{1/2}$  should be linear but, very often, a deviation of linearity is observed, probably due to the decay of the intermediate species.

Assuming that the decay follows a pseudo first order kinetics, the total amount of cation radical in the diffusion layer  $Q_{(k_f)}$  at a given time ( $t$ ) after switching the potential pulse, is given by:

$$Q_{(k_f)} = Q_0 - \int_0^t k_f Q_{(k_f)} dt \quad (8)$$

Where  $k_f$  is related to the total amount of cation radical in the diffusion layer at a time  $t$ , after the start of the anodic pulse;  $Q_0$  is the amount of species that would have been present if  $k_f$  was zero. Since  $A(t) = 2Q\varepsilon/\cos\theta$ , we can write:

$$Q_{k_f} = A(t)_{k_f} \frac{\cos\theta}{2\varepsilon} \quad (9)$$

$$Q_0 = A(t)_0 \frac{\cos\theta}{2\varepsilon} \quad (10)$$

By substituting 9 into 8:

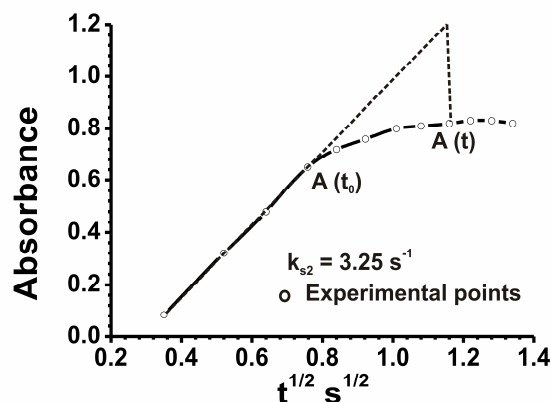
$$A(t)_{k_f} \frac{\cos\theta}{2\varepsilon} = \frac{\cos\theta}{2\varepsilon} [A(t)_0 - k_f] \int_0^t A(t)_{k_f} dt \quad (11)$$

and

$$A(t)_{k_f} - A(t)_0 = -k_f \int_0^t A(t)_{k_f} dt \quad (12)$$

$$k_f = -\frac{A(t)_{k_f} - A(t)_0}{\int_0^t A(t)_{k_f} dt}$$

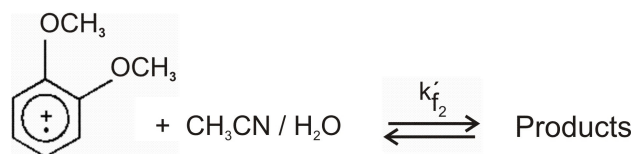
From the optical transient, a plot of Absorbance against  $t^{1/2}$  for a pseudo first order reaction (Figure 6), the homogeneous rate constant,  $k_{f2}$ , can be estimated by extrapolating the straight line within the non linear region and integrating from  $A(t_0)$  and  $A(t)$  the area under the line within the deviation area, using equation 13.



**Figure 6.** Plot Absorbance vs.  $t^{1/2}$  for a pseudo first order kinetics, taken from the optical transient.

By comparison with studies reported in literature [25,29,31] for the synthesis of different type of polymers (polypyrrole, polythiophene, etc.) performed in the same electrolytic medium as used in this work, it was found that the water and acetonitrile molecules are able to generate in situ complex species by means of hydrogen bonds.

It is a well-known feature that water in MeCN has nucleophilic properties and, of course, may act as a nucleophile towards suitable radical cations. In the case of veratrole, the reaction shown in scheme II could be taking place.



Scheme II

The reaction rate expression for this process is:

$$v = k_{f2} [\text{CR}^{+\bullet}] [\text{CH}_3\text{CN} / \text{H}_2\text{O}] \quad (12)$$

As the concentration of the complex is expected to be higher than the concentration of the cation radical of veratrole:

$$[\text{CH}_3\text{CN} / \text{H}_2\text{O}] \gg [\text{CR}^{+\bullet}]$$

a new pseudo first order rate constant ( $k_{f2}$ ) can be defined:

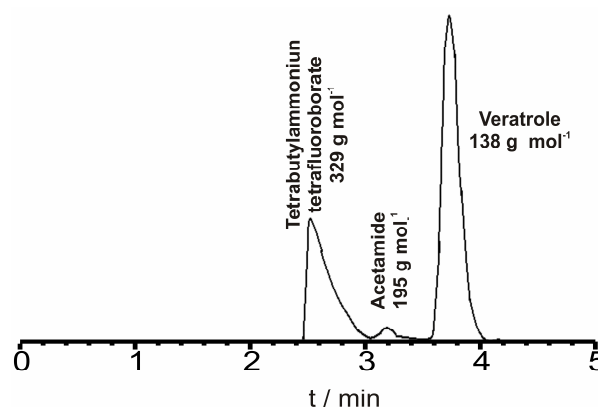
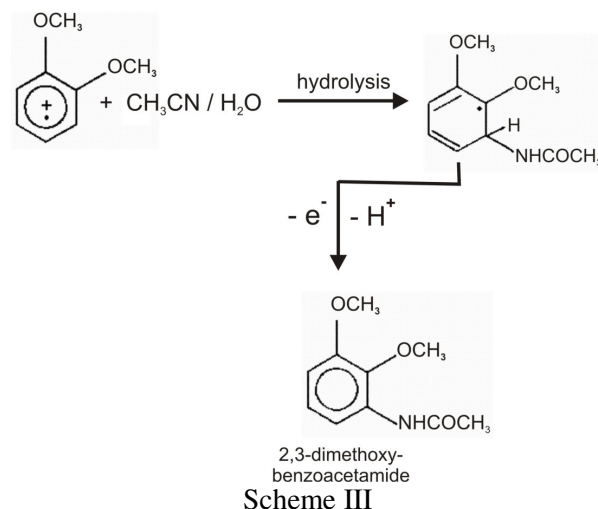
$$k_{f2} = k'_{f2} [\text{CH}_3\text{CN} / \text{H}_2\text{O}] \quad (13)$$

and equation 12 becomes:

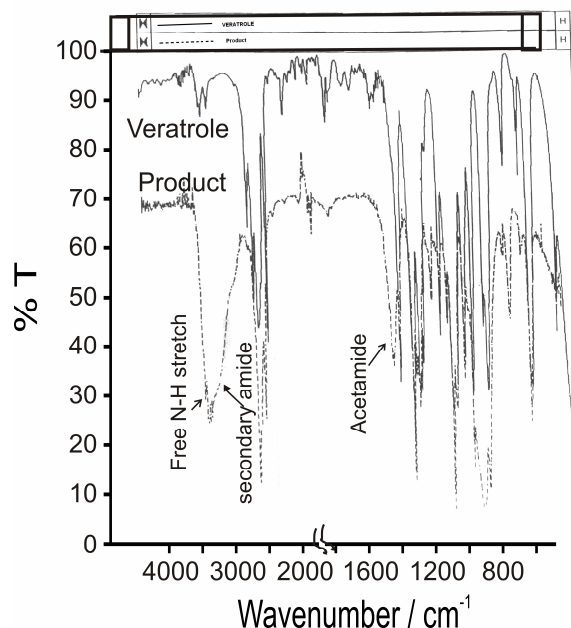
$$v = k_{f2} [\text{CR}^{+\bullet}]$$

### 3.3 Analysis of products

From Gel Permeation Chromatography (GPC) separations (Figure 7) and FTIR (Figure 8) of the electrolysis products for oxidation of veratrole, it was found that when the content of water was higher than 0.1M, the cation radical of veratrole reacts, chemically, with the acetonitrile, undergoing a further hydrolysis to produce 2,3-dimethoxybenzoacetamide, which is the soluble product that competes with the formation of polyveratrole deposit. These results allow us to suggest the reaction mechanism shown in scheme III for the electrooxidation of veratrole in wet acetonitrile.

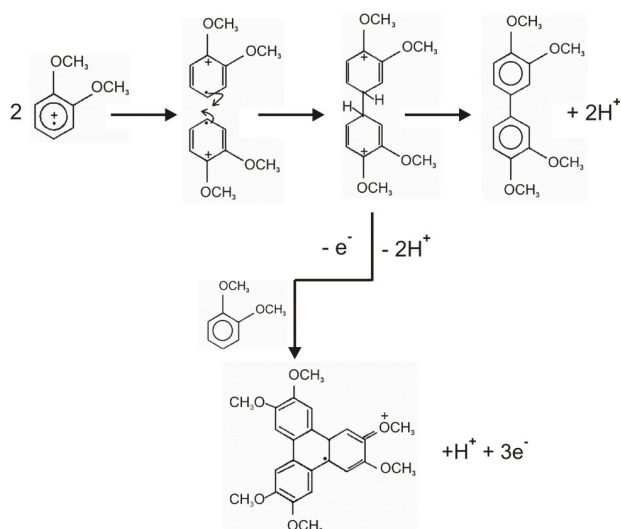


**Figure 7.** Gel Permeation chromatogram of the product after the electrolysis in wet solvent.



**Figure 8.** Infrared spectra of veratrole and the oxidation product after the electrolysis in wet solvent.

To confirm our arguments, a standard solution of benzoacetamide was prepared, in the same electrolytic solution used for the electrolyses, and ex situ UV-Visible spectra were taken for low concentration (Figure 9a) and high concentration (Figure 9b) of the acetamide. A signal at 246 nm (related to the electrolytic medium) that does not change when adding more acetamide and a band at 288 nm (obviously due to the benzoacetamide), since its intensity increases considerably when adding the acetamide where identified. These results allow us to suggest that the signal observed around 300 nm in Figure 6 when the circuit is open after the oxidation process, is due to formation of the 2,3-dimethoxybenzoacetamide during the chemical step coupled to the formation of the cation radical at high concentrations of water. From the electrochemical and spectroelectrochemical results it can be confirmed that variation of the amount of water in the electrolytic medium modifies the kinetics and the mechanism for the synthesis of polyveratrole an enable us to propose the mechanism shown in scheme IV.

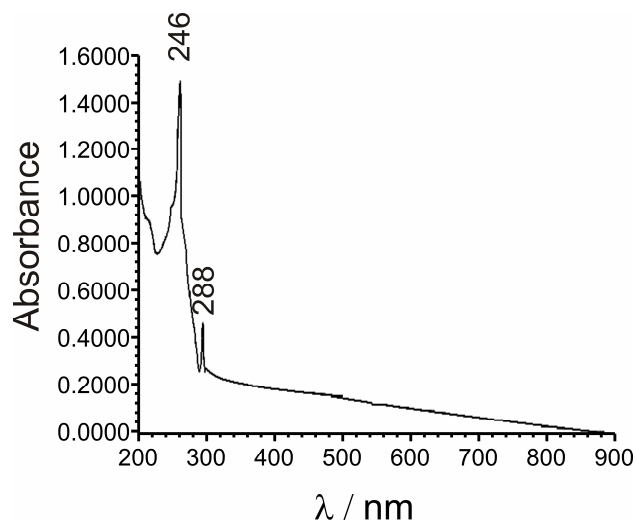


Scheme IV

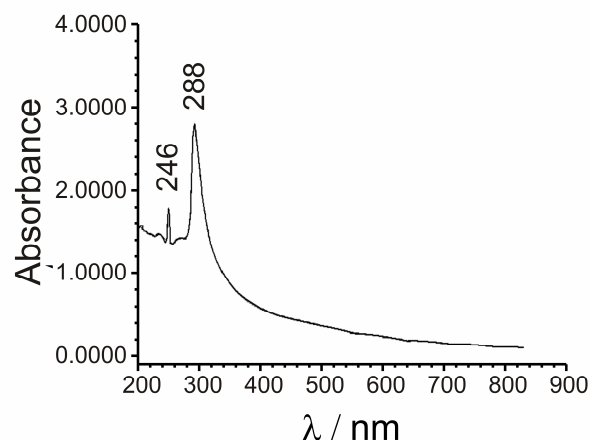
When the concentration of water is large enough ( $> 0.1$  M), the formation of the deposit on the electrode surface diminishes and the solution turns reddish since the cation radical reacts chemically with acetonitrile and water to produce the corresponding acetamide, following the steps shown in scheme III. At low concentrations of water, the decay rate of the cation radical is the coupled chemical step, to form the dimer, following a second order kinetics with a rate constant,  $k_f = 258 \text{ M}^{-1} \text{ s}^{-1}$ . At high concentrations of water, the decay rate of the cation radical follows a pseudo first order kinetics being

the rate constant

$$k_{f2} = k'_{f2} [H_2O] = 3.25 \text{ s}^{-1}$$



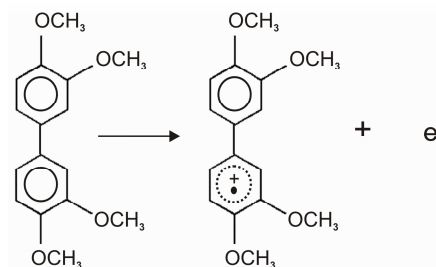
(a)

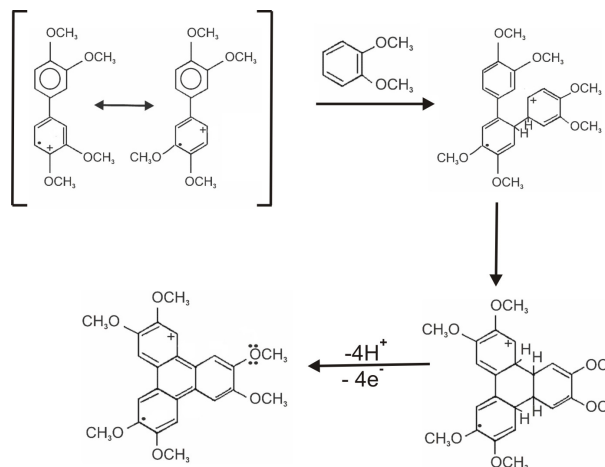


(b)

**Figure 9.** Ex situ UV-Visible taken for (a) low (b) high concentration of a standard solution of benzoacetamide

Scheme V shows the suggested pathways to produce the trimer Hexamethoxytriphenylene from the dimer of veratrole:





Scheme V

#### 4. CONCLUSIONES

The platinum electrode, modified with polyveratrole maintains the electronic/ionic conductivity of the polymer in organic solution and that makes it attractive as a new electrode for studying some redox processes. The results show that small amounts of water in the electrolytic medium modify both the kinetics and the mechanism of the electrodeposition by a change in the route followed toward products formation. High content of water, for instance over 1M, inhibits the formation of polyveratrole, the electrode surface varies, there is no deposit growing on the electrode surface, and the nature of final products changes. The electrochemical oxidation of alkoxyaromatics in dry acetonitrile is known to follow an ECE type of mechanism. The decay of the cation radical may occur by a side chain proton loss (scheme IV) or it may go through a nitrilium ion intermediate (scheme III). Which route is followed depends on the content of water in the electrolytic medium. The oxidation in dry acetonitrile follows a second order kinetics with  $k_{f1} = 258 \text{ M}^{-1}\text{s}^{-1}$ , a trimer cation radical is formed which associates with the counter ion of the supporting electrolyte to produce fibrils. In the presence of water, a route leading to formation of an intermediate nitrilium ion is followed (scheme III) to produce the acetamide obeying a pseudo first order kinetics with  $k_{p2} = 2.4 \text{ s}^{-1}$  (DRS),  $k_{p2} = 3.25 \text{ s}^{-1}$  (AD). With these results more information is added to the knowledge of the influence of polymerization conditions (deposition potential, concentration of the veratrole, the nature of the supporting electrolyte, etc.) upon the mechanical and electrochemical properties of this conducting material.

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