

**In situ Monitoring of the Effect of the Presence of Water Upon the Electropolymerization of Veratrole in Acetonitrile, using UV-Visible Spectroelectrochemistry**

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The impact of electropolymerization parameters (deposition potential, monomer concentration, nature and concentration of the supporting electrolyte, etc.) upon the degree of polymerization as well as mechanical and electrochemical properties has been widely discussed (1-5). It has been found (6-9) that the presence of water affects the polymerization process, changing the properties of the polymers and even inhibiting the polymerization itself.

We are reporting the effect of the presence of water on the kinetics parameters of the electrodeposition of Polyveratrole using both electrochemical and in situ Spectroelectrochemical techniques.

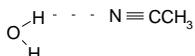
Cyclic Voltammetry of 1,2-dimethoxybenzene (Veratrole) in dry acetonitrile shows three oxidation peaks. As the content of water in the anolyte increases, the second peak (1.50 V) corresponding to deposition of Polyveratrole decreases. When  $[H_2O] > 0.1 M$ , the peak disappears, no deposit is observed on the electrode surface and soluble species are detected in the anolyte.

From the first voltammetric peak (1.20 V), the reaction order respect to water was zero, which allowed us discard the possibility of a direct chemical reaction between water and the cation radical of Veratrole formed at the first voltammetric wave. The electrochemical experiments showed a remarkable competition between electrodeposition (nucleation and growth) and formation of soluble species.

Figure 1 shows how the signal at 520 nm is depressed as the content of water increases, indicating a fast reaction of the cation radical. The signal observed at 640 nm, corresponding to the green deposit of Polyveratrole, disappears.

Differential spectra (figure 2) taken at open circuit, after application of a step potential (1.50 V) at low concentration of water, still shows the signal at 640 nm and we were able to observe a second order reaction for the decay of the cation radical of Polyveratrole (figure 4). In figure 3, however, for a higher content of water, the signal at 640 nm is not observed and formation a new species is observed at 310 nm. In this case, a pseudo-first order decay of the cation radical is observed.

Analyses of products confirmed that, in the presence of water, a complex species :



is formed, favoring the formation of a nitrilium ion on the ring as an intermediate species and, as a consequence of further hydrolysis, the acetamide is formed in detriment of the nucleation and growth of Polyveratrole (scheme I).

**References**

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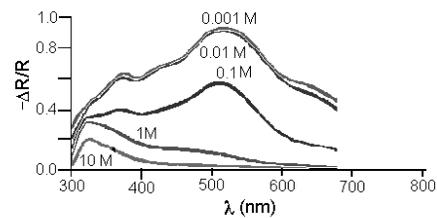


Fig.1.- Spectra taken during application of a pulse of 1.20 V during 1.5 s

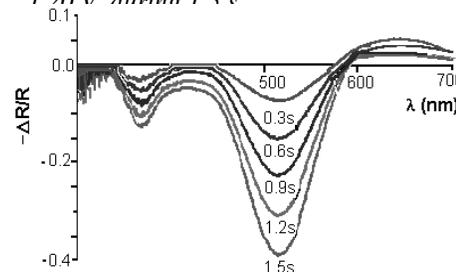


Fig. 2.- Differential Spectra taken at open circuit. The reference was taken just before opening the circuit, at low concentration of water

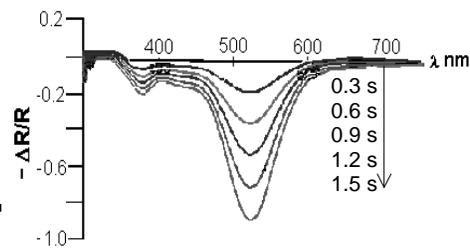


Fig. 3.- Differential Spectra taken at open circuit. The reference was taken just before opening the circuit, at high concentration of water

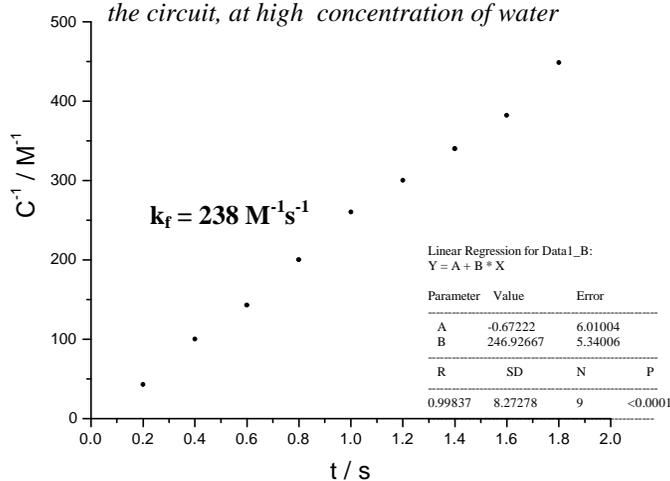


Fig. 4.- Second order homogeneous rate constant for the decay of Veratrole cation radical at low concentration of water.

