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Theoretical Description of Sotolone Electrochemical Determination in Wine in Basic Media over an Undoped Conducting Polymer

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Abstract: The electrochemical determination of sotolone in basic media over an undoped conducting polymer has been described for the first time. The alkaline hydrolysis, breaking the furanonic ring, leads to the appearance of an acid ion, entering the polymer matrix as a dopant. The stability analysis of the system, made by the development and investigation of the correspondent mathematical model, shows that the sotolon electrochemical determination is made efficiently. As for the oscillatory behavior, it may also be caused by the cyclic effect of chemical and electrochemical stages on the double electric layer capacitance and impedance.

Keywords: sotolone; conducting polymers; electrochemical sensors; oscillatory behavior; stable steady-state.

1. Introduction

Sotolone (Figure 1) is a natural aromatizer [1 – 4], present in Portuguese wine (Douro, Porto, and Madeira wine), fenugreek, curry, maple syrup, caramel, and burnt sugar. It 8is also present in rum, flor sherry, and roast tobacco. Moreover, it may be produced in humans with a specific genetic disorder called maple syrup urine disease, indicating the proper disease. Considering sotolone's influence on organoleptic properties of different food and drink items, like its importance for diagnostic purposes, the development of efficient and precise methods for its determination is really actual [5 – 8].

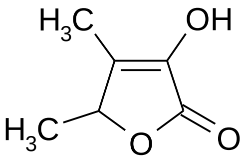

Figure 1. Sotolone.

Possessing electroactive groups, sotolone may be detected electrochemically by means of both anodic and cathodic electroanalytical processes. Nevertheless, in order to facilitate electrochemical determination, chemically modified electrodes may be used, and conducting polymers are the most used electrode modifiers [9 – 13].

Nevertheless, the use of novel electrode modifiers with novel analytes may be impeded by different factors of mechanistic nature, including direct and indirect action over the electroanalytical process. Such factors include the electrochemical oscillatory and monotonic instabilities, yet described for the similar electrooxidative, electrosynthetic and electroanalytical processes [14 - 18]. These factors may only be depicted by analyzing an adequately correspondent mathematical model. Moreover, such an investigation can also compare this system's behavior with that of similar ones without any experimental essay.

So, the goal of this work is the mechanistic theoretical analysis of the sotolone electrochemical determination over an undoped conducting polymer in alkaline media. To achieve it, we realize the specific goals: suggestion of the mechanism of the reaction consequence, leading to the appearance of analytical signal; development of the balance equation mathematical model, correspondent to the electroanalytical system; analysis and interpretation of the model in terms of the electroanalytical use of the system; the seek for the possibility of electrochemical instabilities and the factor, causing them; the comparison of the mentioned system's behavior with the similar ones [19 – 21].

2. System and its Modeling

Before we actually go to the mechanism, we should mention in detail the chemical composition of sotolone. It possesses a lactonic group, which acts as an ester, like an enolic group. For this reason, sotolon may be either reduced or oxidized, which provides an efficient cathodic or anodic electroanalytical process.

In basic media, sotolone undergoes alkaline hydrolysis. By this, the ester group is destroyed, yielding the 2,4-dihydroxypent-2-enoate ion. On anodic potential applied, it is intercalated towards the conducting polymer matrix, in which the 4-hydroxygroup is easily oxidized or grafted towards the polymer backbone. All stages influence the double electric layer (DEL) ionic force and, consequently, conductivity and resistance, which puts the base for the oscillatory behavior. Schematically, the electroanalytical process may be represented in Figure 2:

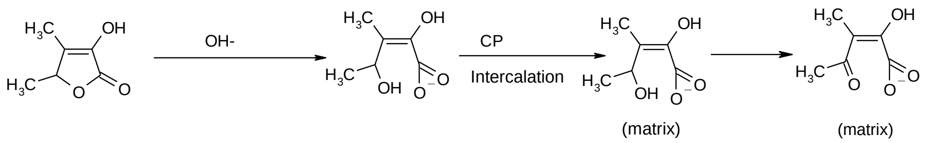

Figure 2. The scheme of the electroanalytical process.

Taking this into account, in order to describe the behavior of this system, we introduce three variables:

s – sotolone concentration in the pre-surface layer;

s* - the 2,4-dihydroxypent-2-enoate ion concentration in the pre-surface layer;

p – the 2,4-dihydroxypent-2-enoate ion-doped conducting polymer surface coverage degree.

Assuming some suppositions [18 – 21], we describe the system´s behavior by the trivariant balance equation-set (1):

$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(s_0 - s) - r_h\right) \\ \frac{ds*}{dt} = \frac{2}{\delta}(r_h - r_d) \\ \frac{dp}{dt} = \frac{1}{P}(r_d - r_O - r_g) \end{cases} \tag{1}$$

Herein, s_0 is sotolone bulk concentration, Δ is the diffusion coefficient, P is the undoped polymer surface coverage degree, and the parameters r are the correspondent reaction rates, calculated as:

$$r_h = k_h s \exp(-as) \tag{2}$$

$$r_d = k_d s * (1 - p) \exp\left(\frac{pF\varphi_0}{RT}\right) \tag{3}$$

$$r_O = k_O p \exp\left(\frac{qF\varphi_0}{RT}\right) \tag{4}$$

$$r_g = k_g p \exp\left(\frac{nF\varphi_0}{RT}\right) \tag{5}$$

The parameters k stand for the correspondent reaction rate constants; a is the parameter related to DEL changes during the dopant hydrolysis, n, p, and q are the numbers of the transferred electrons, F is the Faraday number, φ_0 is the potential slope, related to the zero-charge potential, R is the universal gas constant and T is the absolute temperature.

Taking into account the ion formation and transformation during the electroanalytical process, we conclude that the oscillatory behavior in this system will be more dynamic than in the simplest case. Nevertheless, in this electroanalytical process, the analytical signal interpretation is facilitated, as the steady-state stability becomes easy to obtain and maintain as furtherly exposed.

3. Results and Discussion

In order to investigate the behavior of the sotolone electrochemical determination over an undoped conducting polymer, we analyze the equation set (1) by means of the linear stability theory. The steady-state Jacobian matrix members for this system will be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \qquad (6)$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_h \exp(-as) + ak_h s \exp(-as)\right) \qquad (7)$$

$$a_{12} = 0 \qquad (8)$$

$$a_{13} = 0 \qquad (9)$$

$$a_{21} = \frac{2}{\delta}(k_h \exp(-as) - ak_h s \exp(-as)) \qquad (10)$$

$$a_{22} = \frac{2}{\delta}\left(-k_d(1-p)\exp\left(\frac{pF\varphi_0}{RT}\right) + jk_d s * (1-p)\exp\left(\frac{pF\varphi_0}{RT}\right)\right) \qquad (11)$$

$$a_{23} = \frac{2}{\delta}\left(lk_d s * (1-p)\exp\left(\frac{pF\varphi_0}{RT}\right)\right) \qquad (12)$$

$$a_{31} = 0 \qquad (13)$$

$$a_{32} = \frac{1}{P}\left(k_d(1-p)\exp\left(\frac{pF\varphi_0}{RT}\right) - jk_d s * (1-p)\exp\left(\frac{pF\varphi_0}{RT}\right) + jk_O p \exp\left(\frac{qF\varphi_0}{RT}\right) + jk_g p \exp\left(\frac{nF\varphi_0}{RT}\right)\right) \qquad (14)$$

$$a_{33} = \frac{1}{P}\left(-lk_d s * (1-p)\exp\left(\frac{pF\varphi_0}{RT}\right) - k_O \exp\left(\frac{qF\varphi_0}{RT}\right) + lk_O p \exp\left(\frac{qF\varphi_0}{RT}\right) - k_g \exp\left(\frac{nF\varphi_0}{RT}\right) + lk_g p \exp\left(\frac{nF\varphi_0}{RT}\right)\right) \qquad (15)$$

In order to simplify the determinant analysis necessary for the stability evaluation, we introduce three variables, rewriting the Jacobian determinant as (16):

$$\frac{4}{\delta^2 P}\begin{vmatrix} -\kappa - \Xi & 0 & 0 \\ \Xi & -\Sigma & -P \\ 0 & \Sigma - T & P - \Omega \end{vmatrix} \qquad (16)$$

Opening the straight brackets and applying the determinant negativity condition, salient from the Routh-Hurwitz criterion, we obtain the *steady-state stability* requirement, exposed as (17):

$$(\Xi - \kappa)(\Sigma\Omega - TP) < 0 \qquad (17)$$

which indicates that the topological zone, correspondent to the maximal sensitivity of the sensor, will be far narrower than for similar systems [18 – 21]. Nevertheless, it will remain relatively wide. Moreover, as no side processes may compromise the analyte and modifier stability, the steady-state stability will always correspond to the linear dependence between the electrochemical parameter and concentration. For those reasons, this system will remain electroanalytically efficient, and the electroanalytical process will be either diffusion or kinetically controlled.

As for the detection limit, it is defined by the *monotonic instability*, describing the margin between the stable and unstable states. Its condition is Det J = 0, or (18)

$$(\Xi - \kappa)(\Sigma\Omega - TP) < 0 \qquad (18)$$

The oscillatory behavior, generally realized beyond the detection limit, is also possible in this system. Moreover, it is far more probable than similar electroanalytical processes [19 – 21].

The electrochemical and chemical stages influence the double electric layer (DEL) and polymer backbone ionic force, resistance, and conductivity. Those influences are cyclical, providing oscillations in electrochemical parameters.

The oscillatory behavior is described by Hopf bifurcation conditions, defined by the positivity of the addendums in the main diagonal Jacobian elements. These elements are $jk_d s * (1-p)\exp\left(\frac{pF\varphi_0}{RT}\right)$, $lk_O p \exp\left(\frac{qF\varphi_0}{RT}\right)$, $lk_g p \exp\left(\frac{nF\varphi_0}{RT}\right)$ describing the cyclic influences of the electrochemical stages and $ak_h s \exp(-as)$ describing the analogous influences of the chemical stage. The oscillations are expected to be frequent and of small amplitude.

If the conducting polymer possesses an active amino group, sotolone will react with it, providing an alternative doping mechanism, permitting either anodic or cathodic analyte determination. This case will be described furtherly.

4. Conclusions

From the theoretical description of sotolone electrochemical determination over an undoped conducting polymer, it has been possible to conclude the polymer may serve as an excellent modifier for sucralose quantification. The stable, steady state is maintained easily. And the process may be diffusion-controlled or kinetically controlled. As for the oscillatory behavior in this system, it may be caused only by DEL influences of both electrochemical and chemical stages.

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Conflicts of Interest

The authors declare no conflict of interest.

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