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Theoretical Description for Diclophenac Electrochemical Determination over an Undoped Conducting Polymer

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Abstract: The theoretical description for diclofenac electrochemical determination over an undoped conducting polymer in doping conditions. In the basic solution, diclofenac ion enters the polymer matrix as a dopant. The doping is followed by hydrolysis and electrooxidation of the resulting phenolic ion, accompanied by the grafting to the proper polymer backbone. Analyzing the correspondent mathematical model by linear stability theory and bifurcation analysis, we confirm that the electroanalytical process remains efficient despite the high probability of the oscillatory behavior.

Keywords: diclofenac; electrochemical doping; conducting polymer; electrochemical sensors; stable steady-state.

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1. Introduction

Diclofenac (Fig. 1) is one of the anti-inflammatory drugs and pain killers, mostly used worldwide [1–4]. Its mechanism of action is based on the alkaline hydrolysis of chlorine atoms (Fig. 1), yielding a polyphenolic compound, scavenging the ROS, yielding in the inflamed tissue during the inflammation process.

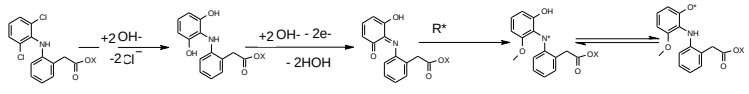

Figure 1. Diclofenac mechanism of action.

$X = Na^+, K^+, NH_4^+$

New radicals will be more difficult to recombine, thereby detaining the inflammation process and providing pain relief. Diclofenac is applied topically, orally, rectally, intravenously, and intramuscularly.

On the other hand, acidic media provokes gastritis and gastric ulcers due to the acidic hydrolysis, yielding a weak acid (Fig. 2).

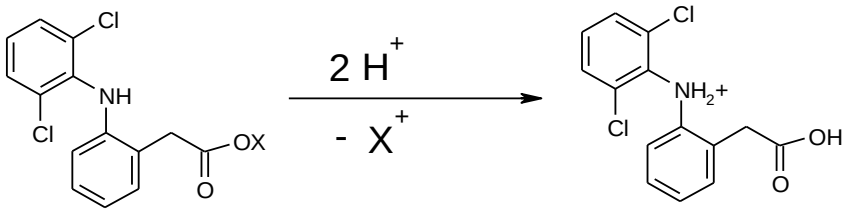

Figure 2. Acidic hydrolysis of diclofenac.

Also, its excessive concentrations, like long-time use, may lead to the side effects like tiredness, slumber, nausea, and vomiting [5–8]. Therefore, developing an efficient method for diclofenac quantification is actual [9–14].

Diclofenac is one of the most popular objects for electroanalytical processes nowadays [15–20]. Either direct electrooxidation or selective membrane development is admitted. In the first case, chemically modified electrodes are widely used [15–18].

Conducting polymers, combining the metal conductivity with plastics flexibility, corrosion resistance, and modification facility, is why they are widely used in electroanalytical processes [19–25]. Many monomers, including small and large conjugated molecules, may be used. Both doped and undoped conducting polymers may be employed in the electroanalytical detection of diclofenac. Nevertheless, considering the ionic nature of the analyte, the undoped polymer is recommended to provide the immobilization of diclofenac ions towards the polymer matrix.

Also, the mechanism of the electrochemical and chemical reactions providing the analytical signal may be unclear. This leads to the necessity of investigating the most probable mechanism of the electroanalytical process, including detecting the parameter region corresponding to the most efficient sensing. Also, the electrochemical instabilities described for the analogous systems [31-33] may impact the electroanalytical behavior.

The resolution of mentioned problems requires the mechanistic theoretical investigation of the electroanalytical process, also capable of comparing the behavior of this system with that of the similar ones without any experimental essay. Therefore, this work gives the theoretical analysis of the system with diclofenac determination over an undoped conducting polymer, including stability and instability analysis and the behavior comparison with similar systems [34 – 35].

2. Materials and Methods

With the anodic potential applied on the first electrochemical stage, diclofenac ion enters the polymer matrix, which becomes doped. After this, diclofenac in the matrix will be hydrolyzed, yielding the hydroquinonic form, which is oxidized to its quinonic form, mimicking the alkaline hydrolysis exposed above in Fig. 1.

The parallel oxidation mechanism involves the polymer backbone, which becomes covalently bound to the dopant, reason why, to describe the system´s behavior, we introduce three variables:

f – diclofenac concentration in the pre-surface layer;
p – diclofenac-doped polymer surface coverage degree;
p* - diclofenac hydrolysate-doped polymer surface coverage degree.

Assuming some suppositions, described in [34 – 35], we may describe this process by the BDES (1):

$$\begin{cases} \frac{df}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(f_0 - f) - r_d\right) \\ \frac{dp}{dt} = \frac{1}{P}\left(r_d - r_h - r_{g1}\right) \\ \frac{dp*}{dt} = \frac{1}{P*}\left(r_h - r_q - r_{g2}\right) \end{cases} \quad (1)$$

Herein, f_0 is diclofenac bulk concentration, Δ is the diffusion coefficient, P and P* are two doped polymer forms maximal surface concentrations, and the parameters r are the correspondent reaction rates, calculated as:

$$r_d = k_d f(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right) \quad (2)$$

$$r_h = k_h p \exp(-ap) \quad (3)$$

$$r_{g1} = k_{g1} p \exp\left(\frac{mF\varphi_0}{RT}\right) \quad (4)$$

$$r_q = k_q p * exp\left(\frac{pF\varphi_0}{RT}\right) \quad (5)$$

$$r_{g2} = k_{g2} p * \exp\left(\frac{qF\varphi_0}{RT}\right) \quad (6)$$

Herein, the parameters k are the correspondent reaction rate constants, and a is the parameter related to DEL changes during the dopant hydrolysis, n, m, 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.

Considering the presence of multiple electrochemical processes, the oscillatory behavior in this system will be more frequent. Nevertheless, the electroanalytical process is expected to be efficient, as shown below.

3. Results and Discussion

To describe the system with the electroanalytical determination of diclofenac in basic media over an undoped conducting polymer, we analyze the equation-set (1) using linear stability theory. The steady-state Jacobian matrix members will be described as (7):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (7)$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_d(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right)\right) \quad (8)$$

$$a_{12} = \frac{2}{\delta}\left(k_d f \exp\left(\frac{nF\varphi_0}{RT}\right) - jk_d f(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right)\right) \quad (9)$$

$$a_{13} = \frac{2}{\delta}\left(k_d f \exp\left(\frac{nF\varphi_0}{RT}\right) - lk_d f(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right)\right) \quad (10)$$

$$a_{21} = \frac{1}{P}\left(k_d(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right)\right) \quad (11)$$

$$a_{22} = \frac{1}{P}\left(-k_d f \exp\left(\frac{nF\varphi_0}{RT}\right) + jk_d f(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right) - k_h \exp(-ap) + ak_h p \exp(-ap) - k_{g1} \exp\left(\frac{mF\varphi_0}{RT}\right) - jk_{g1} p \exp\left(\frac{mF\varphi_0}{RT}\right)\right) \quad (12)$$

$$a_{23} = \frac{1}{P}\left(-k_d f \exp\left(\frac{nF\varphi_0}{RT}\right) + lk_d f(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right) - lk_{g1} p \exp\left(\frac{mF\varphi_0}{RT}\right)\right) \quad (13)$$

$$a_{31} = 0 \qquad (14)$$

$$a_{32} = \frac{1}{P_*}(k_h \exp(-ap) - ak_h p \exp(-ap)) \qquad (15)$$

$$a_{33} = \frac{1}{P_*}\left(-k_q exp\left(\frac{pF\varphi_0}{RT}\right) + lk_q p * exp\left(\frac{pF\varphi_0}{RT}\right) - k_{g2} \exp\left(\frac{qF\varphi_0}{RT}\right) + lk_{g2} p * \exp\left(\frac{qF\varphi_0}{RT}\right)\right) \qquad (16)$$

To simplify the determinant analysis necessary for the stability evaluation, we introduce three variables, rewriting the Jacobian determinant as (17):

$$\frac{2}{\delta PP_*}\begin{vmatrix} -\kappa - \Xi & \Lambda - \Sigma & \Lambda - T \\ \Xi & \Sigma - H - \Gamma_1 & T - N \\ 0 & H & -\Omega - \Gamma_2 \end{vmatrix} \qquad (17)$$

The Routh-Hurwitz criterion application to this system with the subsequent determinant analysis yields the steady-state stability requirement, exposed as (18):

$$-\kappa(H\Omega + H\Gamma_2 + HN + \Gamma_1\Omega + \Gamma_1\Gamma_2 - \Sigma\Omega - \Sigma\Gamma_2 - HT) - \Xi(H\Omega + H\Gamma_2 + HN + \Gamma_1\Omega + \Gamma_1\Gamma_2 - H\Lambda - \lambda\Omega - \Lambda\Gamma_2) < 0 \qquad (18)$$

This indicates that the parameters of the most efficient sensing [32–35] form a narrower topological zone due to the higher probability of the destabilization factors realization. Nevertheless, it will remain relatively wide. Moreover, as no side processes 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 electroanalytical efficient, and the electroanalytical process will be either diffusion or kinetically controlled.

The detection limit is defined by the *monotonic instability*, describing the margin between the stable and unstable states. Its condition is Det J = 0, or (19)

$$-\kappa(H\Omega + H\Gamma_2 + HN + \Gamma_1\Omega + \Gamma_1\Gamma_2 - \Sigma\Omega - \Sigma\Gamma_2 - HT) - \Xi(H\Omega + H\Gamma_2 + HN + \Gamma_1\Omega + \Gamma_1\Gamma_2 - H\Lambda - \lambda\Omega - \Lambda\Gamma_2) = 0 \qquad (19)$$

The oscillatory behavior generally realized beyond the detection limit is also possible in this system. Moreover, it is far more probable than in similar electroanalytical processes [32–35].

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

The oscillatory behavior via Hopf bifurcation is described by the positive positivity of the addendums in the main diagonal Jacobian elements. These elements are $jk_d f(1 - p - p*) \exp\left(\frac{nF\varphi_0}{RT}\right)$, $lk_q p * exp\left(\frac{pF\varphi_0}{RT}\right)$, $lk_{g2} p * \exp\left(\frac{qF\varphi_0}{RT}\right)$ describing the cyclic influences of the electrochemical stages and $ak_h p \exp(-ap)$ describing the DEL ionic force, conductivity, and impedance cyclic changes during the chemical reactions. The oscillations frequency is expected to be high, and the amplitude is expected to be small. The oscillatory scenario becomes even more realistic if the diclofenac and hydrolysate molecules enter horizontal electropolymerization in the doped state. By this, a bilayer conducting polymer may be yielded. This system will be described in our next works.

4. Conclusions

From the theoretical description of diclofenac 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. The oscillatory behavior in this system 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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