

Full Paper

The Mathematical Description for Sucralose Electrochemical Detection on the Overoxidized Polypyrrole

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Received: 10 April 2017 / Accepted: 13 May 2018 / Published online: 31 May 2018

Abstract- The system with the sucralose electrochemical detection on the overoxidized polypyrrole has been described mathematically. The correspondent mathematical model has been developed and analyzed by means of linear stability theory and bifurcation analysis. It was shown that the overoxidized polypyrrole may serve as a modifier for sucralose electrochemical detection in neutral solutions, participating in the electroanalytical process as a substrate. The electroanalytical process is diffusion-controlled. The possibility of oscillatory and monotonic instabilities has also been verified.

Keywords- Sucralose, Electrochemical sensors, Conducting polymers, Overoxidized polypyrrole, Stable steady-state

1. INTRODUCTION

Sucralose [1–3] is one of the most used sugar substitutes in the world. It is three times as sweeter as aspartame, twice as sweeter as saccharin and 800 to 1000 times sweeter than the sucrose [4–5].

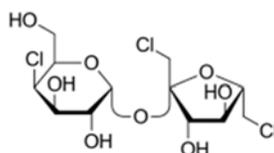


Fig. 1. Sucralose Chemical Composition

It has been considered idoneous for use in the USA, in Canada, in Australia and in the European Union [4]. Its chemical composition is related to that of the carbohydrates. But, containing three chlorine atoms, it may present toxic effects like mutagenesis, carcinogenesis, provoke obesity and growth of glycosis levels [3–4,6–8]. Moreover, while kept in unappropriate way, it may form dioxines, even more toxic compounds [9]. The sucralose decomposition during baking may lead to the chloropropanoles formation [10]. So, the development of an efficient method for sucralose electrochemical detection is really actual [11–14], and the use of electrochemical methods for it would be very interesting.

For now, no direct electrochemical methods for sucralose have been developed, except, HPLC with amperometric pulse [15–16]. In order to immobilize sucralose selectively, it would be suitable to modify the electrode with overoxidized polypyrrole [17], which, despite of being less conducting than the neutral and doped polypyrrole, may have electroanalytical applications [18–19].

Nevertheless, the introduction of new modifiers may confront the problems like:

- the indecision in the modifier mechanism of action;
- the compatibility of the modifier with the analyte;
- the presence of electrochemical instabilities, accompanying both electropolymerization and overoxidation processes [20–25].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the electroanalytical system. By modeling it is also capable compare the behavior of this system with that for the similar ones without any experimental essay.

So, the goal of this work is the mechanistic theoretic analysis of the possibility of sucralose overoxidized-polypyrrol-assisted electrochemical quantification. In order to achieve it, we realize the specific goals:

- suggestion of the mechanism of the immobilization and electroanalytical reaction, 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 for the factor, causing them;
- the comparison of the mentioned system's behavior with the similar ones [26 - 28].

2. SYSTEM AND ITS MODELING

According to [17], contrarily to the neutral polypyrrole, the overoxidized polymer contains pyridinic nitrogen heteroatoms, capable to react selectively with chlormethyl groups of sucralose, forming quaternary salt. This salt is more conducting than the overoxidized polypyrrole, and this may be used as analytical signal. It may also provoke double electric layer (DEL) influences, discussed below. Other reactions between sucralose and overoxidized polypyrrole, without the chlorine atom participation and without DEL influences, are also possible, and they are also included.

Supposing that, on the beginning of the reaction, the overoxidized polymer covers the entire electrode surface, we introduce two variables:

c —sucralose concentration in the pre-surface layer;

θ —the quaternary salt coverage degree.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we assume that the background electrolyte is in excess, so we can neglect the migration flow. The diffusion layer is supposed to be of a constant thickness, equal to δ , and the concentration profile in it is supposed to be linear.

It is possible to show that the behavior of this system may be described by the classical bivariant equation set, described as:

$$\left\{ \begin{array}{l} \frac{dc}{dt} = \frac{2}{\delta} \left(\frac{D}{\delta} (c_0 - c) - r_1 - r_2 \right) \\ \frac{d\theta}{dt} = \frac{1}{G} (r_1 + r_2 - r_3) \end{array} \right. \quad (1)$$

In which D is the diffusion coefficient, c_0 , is its bulk concentration, G is the adduct maximal surface concentration, r_1 , r_2 and r_3 are the reaction rates, which may be calculated as:

$$r_1 = k_1 c (1 - \theta) \exp(\gamma \theta) \quad (2)$$

$$r_2 = k_2 c (1 - \theta) \quad (3)$$

$$r_3 = k_3 \theta \exp \frac{nF\gamma\theta}{RT} \quad (4)$$

In which the parameters k are correspondent reaction rate constants, F is the Faraday number, γ is the parameter, relating the DEL potential slope in the double, related to the zero-charge potential, with the quaternized polymer coverage degree R is the universal gas constant and T is the absolute temperature.

Although the model seems to be equal to that described in [26], there are differences in the system behavior, related to the DEL influences of the quaternization, which will be discussed below.

3. RESULTS AND DISCUSSION

In order to describe the behavior of the system with sucralose electrochemical detection by immobilization on the overoxidized polypyrrole, we analyze the equation set (1) by means of the linear stability theory. The steady-state Jacobian functional matrix elements for this system may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (5)$$

in which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - k_1(1 - \theta) \exp(\gamma\theta) - k_2(1 - \theta) \right) \quad (6)$$

$$a_{12} = \frac{2}{\delta} (k_1c \exp(\gamma\theta) - \gamma k_1c(1 - \theta) \exp(\gamma\theta) + k_2c) \quad (7)$$

$$a_{21} = \frac{1}{G} (k_1(1 - \theta) \exp(\gamma\theta) + k_2(1 - \theta)) \quad (8)$$

$$a_{22} = \frac{1}{G} \left(-k_1c \exp(\gamma\theta) + \gamma k_1c(1 - \theta) \exp(\gamma\theta) - k_2c - k_3 \exp \frac{nF\gamma\theta}{RT} - \gamma k_3\theta \exp \frac{nF\gamma\theta}{RT} \right) \quad (9)$$

In order to simplify the analysis of the matrix, we introduce new variables, so the matrix determinant will be described as:

$$\frac{2}{\delta G} \begin{vmatrix} -\kappa_1 - \mathcal{E} & \Omega \\ \mathcal{E} & -\Omega - \Lambda \end{vmatrix} \quad (10),$$

In which

$$\kappa_1 = \frac{\Delta}{\delta} \quad (11)$$

$$\mathcal{E} = k_1(1 - \theta) \exp(\gamma\theta) + k_2(1 - \theta) \quad (12)$$

$$\Omega = k_1c \exp(\gamma\theta) - \gamma k_1c(1 - \theta) \exp(\gamma\theta) + k_2c \quad (13)$$

$$\Lambda = k_3 \exp \frac{nF\gamma\theta}{RT} + \gamma k_3\theta \exp \frac{nF\gamma\theta}{RT} \quad (14)$$

The main conditions for bivariant systems are described in the Table 1:

Table 1. The main conditions for bivariant systems

Steady-state stability	Tr J<0, Det J>0
Oscillatory instability	Tr J=0, Det J>0
Monotonic instability	Tr J<0, Det J=0

Observing the expressions (6) and (9), it is possible to see that the *oscillatory behavior* in this system is more probable than in the simplest cases [26–27], approaching in this feature the case, described in [28], as there is more than one process influencing DEL.

Besides of the DEL influences of the electrochemical synthesis, described by the positivity of $-\gamma k_3 \theta \exp \frac{nF\gamma\theta}{RT}$, the oscillatory behavior may be also caused by the influences of the sucralose immobilization by quaternization, leading to the formation of a more conducting product. These influences are described by the positivity of $\gamma k_1 c(1 - \theta) \exp(\gamma\theta)$.

The steady-state stability condition for a two-dimensional system may be described as: $\text{Tr } J < 0$, $\text{Det } J > 0$. Opening the brackets with the inclusion of the variables introduced in (11–14), we obtain the steady-state stability condition as:

$$\begin{cases} -\kappa - \Xi - \Omega - \Lambda < 0 \\ \kappa\Omega + \kappa\Lambda + \Xi\Lambda > 0 \end{cases} \quad (15)$$

And it is warranted to be satisfied in the case of the positivity of Ω , describing the fragility of DEL influences of the electrochemical process. The process is diffusion-controlled, tending to be reaction-controlled in the case of the relatively small electrodes and relatively high analyte concentrations (see the Table 2).

Table 2. The steady-state stability for sucralose OPPy-assisted quantification

Analyte concentration	Electrode size	Steady-state stability defining process
Low	Small	Diffusion or reaction
High		Reaction
Low	Large	Diffusion
High		Diffusion or reaction

For the electroanalytical effects the steady-state stability is correspondent to the linear dependence between the electrochemical parameter and analyte concentration, or, better saying, to the electroanalytical efficiency. It isn't compromised even by radical recombination effects, if they do not provoke side reactions.

The *monotonic instability* in this system is possible, being caused by the equality between the stabilizing influences and the destabilizing ones of the electrochemical process influences on DEL. It is correspondent to the detection limit and its condition may be described as:

$$\begin{cases} -\kappa - \Xi - \Omega - \Lambda < 0 \\ \kappa\Omega + \kappa\Lambda + \Xi\Lambda > 0 \end{cases} \quad (16)$$

It is also possible to modify the overoxidized polypyrrole before its use, or use specifically modified neutral or doped conducting polymer for sucralose immobilization. These cases will be described in our next works.

4. CONCLUSION

The theoretical analysis of the system with daclatasvir electrochemical detection let us conclude that the oscillatory behavior for this case is possible, being even more probable, than for general case of CP-based electrochemical sensor. It may be caused by DEL-influences of electrochemical and chemical stage. Also, the steady-state stability is warranted by the fragility of DEL-influences of two reactions. Nevertheless, the topological stability zone is vast, and the sensor is very sensitive. Moreover, the process is, in general, diffusion-controlled and electroanalytically efficient, permitting us use of higher pH values, up to neutral in daclatasvir electrochemical detection in these conditions.

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