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SHORT COMMUNICATION

The theoretical description for the sucralose electrochemical determination, assisted by poly(safranine) modified electrode

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Abstract: For the first time, sucralose cathodic electrochemical determination, assisted by the safranine-modified electrode has been theoretically described. The correspondent mathematical model has shown that the steady-state stability range is wider than in the most system of electrochemical determination over the pyridinic nitrogen-containing conducting polymer. Moreover, the oscillatory behavior is less probable. Therefore, poly(safranine) is an efficient electrode modifier for sucralose electrochemical determination.

Keywords: sucralose; conducting polymer; safranine; electrochemical sensors; stable steady-state.

Introduction

The use of chemically modified electrodes (CMEs) is a very important step in electroanalytical chemistry [1-4]. Compared to bare electrodes, they have some advantages, such as:

- Rapidity;
- Low cost;
- Exactitude;
- Flexibility;
- Versatility in use;
- Affinity between electrode modifier and analyte.

On the other hand, sucralose [5, 6] is one of the most used sugar substitutes in the world. It is three times sweeter than aspartame, two times sweeter than saccharin, and 800-1000 times sweeter than sucrose [7, 8].

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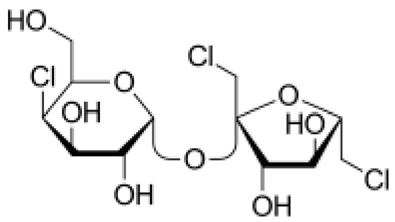

Figure 1. The chemical structure of Sucralose.

Sucralose has been approved for use in the US, Canada, Australia and the European Union [8]. According to its chemical structure, it belongs to carbohydrates. But, the presence of three chlorine atoms can cause a toxic effects like mutagenesis, carcinogenesis, provoke obesity and growth of glycosis levels [7-12]. Moreover, if stored improperly, it can form dioxines, even more toxic compounds [13, 14]. The decomposition of sucralose during baking can lead to the formation of chloropropanoles [15]. Thus, the development of an efficient method for the detection of sucralose is really important [16-18], and the use of electrochemical methods for this would be very interesting.

The possibility of the electrochemical determination of sucralose was already provided theoretically [19-21] and experimentally confirmed [22]. A direct electrooxidation of sucralose was used either in the model or in the experiment. In [19], the immobilization of sucralose on an acridine derivative capable of forming a quaternary salt was proposed. It was assumed that the immobilization of sucralose would be followed by the electrochemical oxidation of the hydroxyl groups of the sucralose units. Another possibility may be the electrochemical reduction of the sucralose salt with the corresponding pyridine nitrogen compound, in which the safranine polymer can be used as a modifier [23-25].

However, the use of new electrode modifiers with new analytes may be impeded by:

- uncertainty about the exact mechanism of the electrochemical reaction;
- the importance to determine the range of parameters corresponding to the most efficient active substance and mediating action;
- the presence of electrochemical instabilities, described for the electrooxidation and reduction of organic compounds [26-28].

These problems can only be solved by analyzing a mathematical model that can adequately describe the electrochemical determination of fluoxetine. Moreover, it is also able compare the behavior of this system with the behavior of similar ones without any experimental essay.

Thus, the purpose of this work is a theoretical and mechanistic analysis of the electrochemical determination of sucralose on a conductive polymer containing pyridine nitrogen atoms. To achieve these goals, we are implement-ting:

- an assumption about the mechanism of the reaction consequence leading to the appearance of an analytical signal;
- development of a mathematical model of the balance equation corresponding to the electroanalytical system;
- analysis and interpretation of the model in terms of electroanalytical use of the system;
- search for the possibility of occurrence of electrochemical instabilities and factors that cause them;
- comparison of the behavior of the specified system with the similar ones [19-21].

System and its Modeling

The safranine fragment, which is already present as a monosalt, reacts with sucralose at the second nitrogen atom in the ring to form a biquaternized derivative, which is thereby reduced electrochemically. The electrochemical conductivity of the polymer augments by reacting with sucralose and diminishes at the electrochemical stage. Schematically, the electrochemical determination of sucralose on a cathode modified with poly(safranine) will be described in Figure 2:

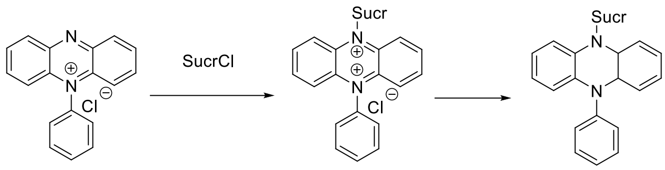

Figure 2. Immobilization of sucralose on safranine and electrochemical reduction of its salt.

Taking this into account, to describe the system´s behavior in the potentiostatic mode, we introduce two options:

s - sucralose concentration in the pre-surface layer;

p - degree of surface coverage with poly(safranine) sucralose salt.

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

It can be shown that the behavior of this system will be described by two balance equations written as:

$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{\Sigma}{\delta}(s_0 - s) - r_s\right) \\ \frac{dp}{dt} = \frac{1}{P}(r_s - r_r) \end{cases} \quad (1)$$

Herein, Σ is the diffusion coefficient of sucralose, s_0 is the volume concentration of sucralose, P is the maximal surface concentration of poly(safranine), and the parameters r are the correspondent reaction rates, calculated as:

$$r_r = k_r p^n \exp\left(-\frac{nF\varphi_0}{RT}\right) \quad (2)$$

$$r_s = k_s(1-p)s^n \exp(-as) \quad (3)$$

Herein, the parameters k are the corresponding reaction rates n is the number of safranine fragments, capable of reacting with sucralose, a is the parameter characterizing the DEL influence of the chemical stage, 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.

Results and Discussion

In order to describe the behavior of the electroanalytical determination of sucralose over a poly(safranine)-modified electrode, we analyze the equation-set (1) by means of linear stability theory and bifurcation analysis. The steady-state Jacobian matrix members for this system may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (4)$$

where:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Sigma}{\delta} - nk_s(1-p)s^{n-1}\exp(-as) + ak_s(1-p)s^n\exp(-as)\right) \quad (5)$$

$$a_{12} = \frac{2}{\delta}(k_s s^n \exp(-as)) \quad (6)$$

$$a_{21} = \frac{1}{P}\left(nk_s(1-p)s^{n-1}\exp(-as) - ak_s(1-p)s^n\exp(-as)\right) \quad (7)$$

$$a_{22} = \frac{1}{P}\left(-k_s s^n \exp(-as) - nk_r p^{n-1}\exp\left(-\frac{nF\varphi_0}{RT}\right) + jk_r p^n \exp\left(-\frac{nF\varphi_0}{RT}\right)\right) \quad (8)$$

General conditions for singular points for bivariant systems are presented in the Table 1.

Table 1. The basic conditions for singular points for the bivariant systems.

Stable steady-state	Tr J<0, Det J>0
Oscillatory behavior	Tr J=0, Det J>0
Monotonic instability	Tr J<0, Det J=0

Avoiding cumbersome expressions, we introduce new variables, rewriting the determinant as (9)

$$\frac{2}{\delta C}\begin{vmatrix} -\kappa - Y & \Lambda \\ Y & -\Lambda - \Omega \end{vmatrix} \quad (9)$$

Taking into account the elements (5) and (8), the appearance of oscillatory behavior is possible in this system. The main Hopf bifurcation condition is realized if the main diagonal contains positive elements related to the positive callback.

In this system, there are two elements responsible for the oscillatory behavior

$+ak_s(1-p)s^n\exp(-as) > 0$, if a>0

and $jk_r p^n \exp\left(-\frac{nF\varphi_0}{RT}\right) > 0$, if j>0,

describing the DEL influences of chemical and electrochemical stages, respectively. The probability of the oscillatory behavior is more expressed than in the simplest cases, but less expressed than in some similar systems [21]. All of the mentioned elements depend on the composition of the background electrolyte, as well as on the amplitude and frequency of oscillations. Mathematically, the condition of oscillatory behavior will be described as (10):

$$\begin{cases} \frac{2}{\delta}(-\kappa - Y) + \frac{1}{P}(-\Lambda - \Omega) = 0 \\ \frac{2}{\delta C}(\kappa\Lambda + \kappa\Omega + Y\Omega) > 0 \end{cases} \quad (10)$$

However, if the mentioned elements are negative, the steady-state stability will be obtained. Opening the brackets and applying the stability requisite, we obtain the steady-state stability condition, which can be described as (11):

$$\begin{cases} \frac{2}{\delta}(-\kappa - Y) + \frac{1}{P}(-\Lambda - \Omega) < 0 \\ \frac{2}{\delta C}(\kappa\Lambda + \kappa\Omega + Y\Omega) > 0 \end{cases} \quad (11)$$

And defines a diffusion-controlled system effective for the determination of sucralose over poly(safranine) in a potentiostatic mode. This condition is satisfied in a relatively wide range of parameters, in which the dependence between the electrode current and copper concentration will be linear.

The monotonic instability corresponding to the detection limit separates stationary stable-states from unstable states. Its condition is mathematically expressed as (12):

$$\begin{cases} \frac{2}{\delta}(-\kappa - Y) + \frac{1}{P}(-\Lambda - \Omega) < 0 \\ \frac{2}{\delta C}(\kappa\Lambda + \kappa\Omega + Y\Omega) > 0 \end{cases} \quad (12)$$

This model is applicable to the determination of sucralose in a neutral enviroment. In acidic media, protons strongly interfere with the electroanalytical process, so a trivariant model has to be used. This model will be described in our next work.

Conclusions

From the theoretical description of the electrochemical determination of sucralose over poly(safranine), we can conclude:

- The mechanism consists of chemical and electrochemical stages leading to a well-defined analytical signal. The polymer can serve as an excellent modifier for the quantitative determination of sucralose. A stable steady-state is easily maintained;
- The system is a diffusion-controlled electroanalytically efficient process;
- In this system, oscillatory behavior is possible, due only to the DEL influences of both electrochemical processes and the chemical stage.

Notes

The authors declare no conflict of interest.

Author contributions. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Теоретична оцінка електроаналітичного визначення сукралози на полімерному електроді, модифікованому сафраніном

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Резюме: Вперше з теоретичної точки зору розглядається можливість електрохімічного визначення сукралози за допомогою модифікованого сафраніном електрода. Аналіз математичної моделі показав, що стаціонарний діапазон стабільності є ширшим, ніж у більшості систем електрохімічного визначення з піридиновим полімерним провідником. Таким чином, полі(сафранін) є ефективним електродним модифікатором.

Ключові слова: сукралоза; провідний полімер; сафранін; електрохімічні сенсори; стійкий стаціонарний стан.