Orbital: Electron. J. Chem. **2021**, 13(3), 219-222

Orbital The electronic journal of chemistry

the electronic journal of chemistry

Full Paper | http://dx.doi.org/10.17807/orbital.v13i3.1584

The Theoretical Description for a Sucralose Electrochemical Cathodical Determination over a 9-9´-Diacridyl-modified Electrode

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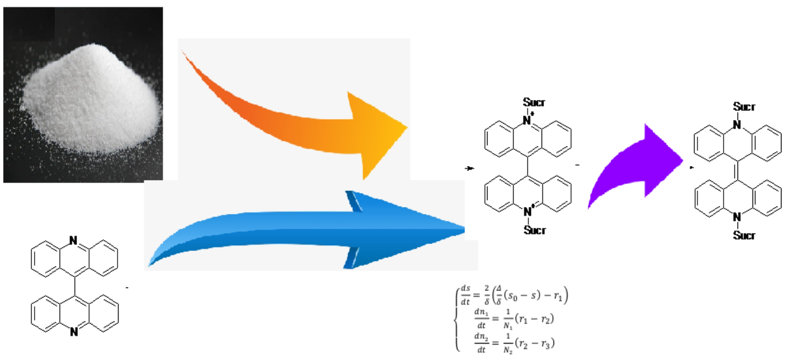
A novel electroanalytical process for sucralose determination has been theoretically suggested. Sucralose is immobilized over an acridine derivative 9-9´-diacridyl, yielding a quaternary salt, which is thereby gradually electrochemically reduced to an *N-N*-disubstituted acridone derivative. The correspondent mathematical model has been developed and analyzed by means of linear stability theory and bifurcation analysis, and this analysis has shown the high probability of the oscillatory and monotonic instabilities, due to the double electric layer structure changes during all of the stages of the process. Nevertheless, it also confirms the efficiency of 9-9´-diacridyl-modified electrode for sucralose determination in an electroanalytical system, which may be coupled with a fluorescent indicator.

Graphical abstract



$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(s_0 - s) - r_1\right) \\ \frac{dn_1}{dt} = \frac{1}{N_1}(r_1 - r_2) \\ \frac{dn_2}{dt} = \frac{1}{N_2}(r_2 - r_3) \end{cases}$$

Keywords

Sucralose, 9-9´-diacridyl
Electrochemical sensors
Electrochemical oscillations
Stable steady-state

Article history

Received 27 December 2020
Revised 15 June 2021
Accepted 27 June 2021
Available online 03 July 2021

Handling Editor: Adilson Beatriz

1. Introduction

The use of chemically modified electrodes (CME) is an especially important step in electroanalytical chemistry [1-4]. Compared to the bare electrodes, they have some advantages, like: rapidity; low cost; precisity; exactity; flexibility; versatility

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in use, and affinity between the electrode modifier and the analyte.

At the other hand, sucralose [5-6] 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 [7-8].

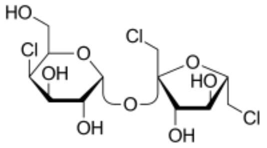

Fig. 1. Sucralose.

It has been approved for use in the USA, in Canada, in Australia and in the European Union [8]. 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 [7-12]. Moreover, while stored in inappropriate way, it may form dioxines, even more toxic compounds [13-14]. The sucralose decomposition during baking may lead to the chloropropanoles formation [15]. So, the development of an efficient method for sucralose detection is really actual [16-18], and the use of electrochemical methods for it would be very interesting.

The possibility of the electrochemical sucralose determination has already been foreseen by us theoretically [19-21] and confirmed experimentally in [22]. A direct electrooxidation of sucralose was used either in the model or in the experiment. In the work [19], sucralose immobilization on an acridinic derivative, capable to form a quaternary salt, has been suggested. The sucralose immobilization was foreseen to be followed by the electrochemical oxidation of hydroxyl groups of the sucralose units. Another opportunity could be an electrochemical reduction of sucralose salt with the correspondent pyridinic nitrogen compound yet realized for paraquat and diquat [23-25].

Nevertheless, the use of novel electrode modifiers with novel analytes may be impeded by:

- the indecision concerning the exact mechanism of electrochemical reaction;

- necessity of determination of the parameter region, correspondent to the most efficient active substance and mediating action;

- the presence of electrochemical instabilities yet described for the electrooxidation and reduction of organic compounds [26-28].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the fluoxetine electrochemical determination. Moreover, 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 sucralose electrochemical determination over a diacridinic compound. In order 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 for the factor, causing them;

- the comparison of the mentioned system´s behavior with the similar ones [19-21]

2. Results and Discussion

2. System and its Modeling

The electroanalytical process may be schematically described as on the Fig. 2.

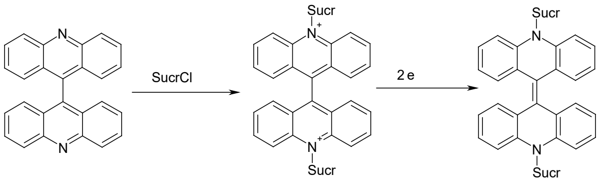

Fig. 2. Sucralose immobilization on 9-9´-diacridyl with the electroreduction of its salt.

The salt electroreduction is gradual, being realized by one quaternary nitrogen atom on each stage. This may provide sucralose selective detection in the natural carbohydrate presence, as natural carbohydrates do not react with biacridinic compounds, yielding salt, as sucralose does.

Taking this into account, two ways to describe the behavior of this system, involving a bi- or trivariant system, are possible. In the last case, the three variables to be introduced are:

s – sucralose concentration in the pre-surface layer;

n_1 – partially reduced salt surface coverage degree;

n_2 – fully reduced salt surface 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 will be described by three balance equations, written as:

$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{\mathit{\Delta}}{\delta}(s_0 - s) - r_1\right) \\ \frac{dn_1}{dt} = \frac{1}{N_1}(r_1 - r_2) \\ \frac{dn_2}{dt} = \frac{1}{N_2}(r_2 - r_3) \end{cases} \tag{1}$$

Herein, $\mathit{\Delta}$ is the diffusion coefficient, s_0 is the sucralose concentration in the pre-surface layer, N_1 and N_2 are the maximal surface concentrations of each one of salts, and the parameters r are the correspondent reaction rates, calculated as:

$$r_1 = k_1(1 - n_1 - n_2)s^2 \exp(-as) \tag{2}$$

$$r_2 = k_2 n_1 \exp\left(-\frac{F\varphi_0}{RT}\right) \tag{3}$$

$$r_3 = k_3 n_2 \exp\left(-\frac{F\varphi_0}{RT}\right) \tag{4}$$

Here the parameters $k$mean correspondent reaction rate constants, F is the Faraday number, ais the parameter, relating the DEL capacitance with the sucralose concentration,φ_0 is the potential slope, related to the zero-charge potential, R is the universal gas constant and T is the absolute temperature.

The behavior of this system is expected to be a bit similar to that observed during the electrochemical determination of paraquat and diquat and the similar compounds with a very probable realization of the oscillatory behavior. Nevertheless, the electroanalytical system is shown to be efficient, as shown below.

3. Material and Methods

In order to describe the sucralose electrochemical determination by the reduction of its quaternary salt, we analyze the equation-set (1) by means of linear stability theory and bifurcation analysis. The steady-state Jacobian matrix members may be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \qquad (5)$$

Where:

$$a_{11} = \frac{2}{\delta}\left(-\frac{4}{\delta} - 2k_1(1-n_1-n_2)s\exp(-as) + ak_1(1-n_1-n_2)s^2\exp(-as)\right) \quad (6)$$

$$a_{12} = \frac{2}{\delta}(k_1 s^2 \exp(-as)) \qquad (7)$$

$$a_{13} = \frac{2}{\delta}(k_1 s^2 \exp(-as)) \qquad (8)$$

$$a_{21} = \frac{1}{N_1}(2k_1(1-n_1-n_2)s\exp(-as) - ak_1(1-n_1-n_2)s^2\exp(-as)) \quad (9)$$

$$a_{22} = \frac{1}{N_1}\left(-k_1 s^2\exp(-as) - k_2\exp\left(-\frac{F\varphi_0}{RT}\right) + jk_2 n_1\exp\left(-\frac{F\varphi_0}{RT}\right)\right) \quad (10)$$

$$a_{23} = \frac{1}{N_1}\left(-k_1 s^2\exp(-as) + lk_2 n_1\exp\left(-\frac{F\varphi_0}{RT}\right)\right) \quad (11)$$

$$a_{31} = 0 \qquad (12)$$

$$a_{32} = \frac{1}{N_2}\left(k_2\exp\left(-\frac{F\varphi_0}{RT}\right) - jk_2 n_1\exp\left(-\frac{F\varphi_0}{RT}\right) + jk_3 n_2\exp\left(-\frac{F\varphi_0}{RT}\right)\right) \quad (13)$$

$$a_{33} = \frac{1}{N_2}\left(-lk_2 n_1\exp\left(-\frac{F\varphi_0}{RT}\right) - k_3\exp\left(-\frac{F\varphi_0}{RT}\right) + lk_3 n_2\exp\left(-\frac{F\varphi_0}{RT}\right)\right) \quad (14)$$

Taking into account the main diagonal elements (6), (10) and (14), we may conclude that the *oscillatory behavior* in this case is possible. Moreover, it will be more probable than for the similar systems, due to the somehow more expressive influence of all of the three reaction stagers to double electric layer and surface conductivity and resistance.

These elements are $lk_3 n_2\exp\left(-\frac{F\varphi_0}{RT}\right) > 0$ if l>0, $+jk_2 n_1\exp\left(-\frac{F\varphi_0}{RT}\right) > 0$ if j>0, describing the DEL influences of two electrochemical stages, and $ak_1(1-n_1-n_2)s^2\exp(-as) > 0$ if a>0, describing the analogous influences of the chemical stage.

The oscillations frequency and amplitude are dependent on the background electrolyte composition, directly related to DEL structure and conductivity. Nevertheless, the proper oscillations are expected to be frequent and of small amplitude.

In order to investigate the *steady-state stability,* we apply the Routh-Hurwitz criterion to the equation-set (1). Avoiding the cumbersome expressions, we introduce new variables, describing the matrix determinant as:

$$\frac{2}{\delta N_1 N_2}\begin{vmatrix} -\kappa - \Xi & \Sigma & \Sigma \\ \Xi & -\Gamma - \Sigma & -T - \Sigma \\ 0 & -\Phi - \Gamma & -\Omega - T - \Sigma \end{vmatrix} \qquad (15)$$

Opening the brackets and applying the requisite Det J<0, salient from the criterion, we obtain the steady-state stability condition, exposed as:

$$-\kappa(\Gamma\Omega + \Sigma\Omega + \Sigma T + \Sigma^2 - \Phi T - \Phi\Sigma) - \Xi(\Gamma\Omega + \Sigma\Omega + \Sigma T - \Phi T + \Phi\Sigma) < 0 \qquad (16)$$

This describes an electroanalytically efficient process, which is either diffusion or kinetically controlled. The transition to diffusion or kinetically controlled mode is realized by changing the electrolyte composition, analyte concentration and electrode shape.

The steady-state stability topological zone has to be narrower than in the simpler cases, described in [19-21]. Nevertheless, it remains relatively wide, providing a wide concentration interval of sensitive sucralose determination. As no side reactions, capable to compromise the analyte or modifier stability are typical for this case, the steady-state stability will be correspondent to the linear dependence between the analyte concentration and electrochemical parameter.

As the acridinic derivatives tend to be fluorescent, the fluorescence intensity and wavelength change during the reaction will be another analytical signal to be observed during the reaction.

As for the detection limit, it will be described by the monotonic instability. It delimits the stable steady-states from unstable states, and its condition will be Det J=0, or (17):

$$-\kappa(\Gamma\Omega + \Sigma\Omega + \Sigma T + \Sigma^2 - \Phi T - \Phi\Sigma) - \Xi(\Gamma\Omega + \Sigma\Omega + \Sigma T - \Phi T + \Phi\Sigma) = 0 \qquad (17)$$

This reaction may also be realized in assisted mode, in which sucralose is present in the solution in the form of a quaternary salt. By this, the electrochemical determination will become similar to that of paraquat, diquat and abametapir protonized form.

Also, if the reaction is realized in acidic media, sucralose fragment tends to dehalogenize, yielding a chloride ion. This case will be described in our next works.

4. Conclusions

From the theoretical description of sucralose electrochemical determination over a 9-9´-diacridyl-modified cathode it has been possible to conclude that:

- The mechanism consists on the chemical and two gradual electrochemical stages, leading to the appearance of a clearly determined analytical signal. 9-9´-diacridyl may serve as an excellent modifier for sucralose quantification. The stable steady-state is maintained easily.

- The system is electroanalytically efficient, depending on the electrolyte composition, electrode size and on analyte concentration, the process may be diffusion-controlled or kinetically controlled.
- The oscillatory behavior in this system is possible, being caused only by DEL influences of both of electrochemical processes, like also of the chemical stage.

Author Contributions

Volodymyr V. Tkach (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing); Marta V. Kushnir (Data Curation, Conceptualization, Investigation); Sílvio C. de Oliveira (Conceptualization, Investigation, Supervision, Formal Analysis), Mykhailo P. Zavhorodnii (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Oleksandr A. Brazhko (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Maryna M. Kornet (Investigatioon, Conceptualization, Data Curation, Methodology, Validation, Visualization), Olga V. Luganska (Conceptualization, Investigation, Data Curation, Methodology, Validation, Visualization, Formal Analysis), Vira V. Kopiika (Conceptualization, Investigation, Supervision, Formal Analysis), Yana G. Ivanushko (Conceptualization, Investigation, Supervision, Formal Analysis), Oleksandra V. Ahafonova (Conceptualization, Investigation, Formal Analysis), Mariia P. Mytchenok (Conceptualization, Investigation, Formal Analysis), Petro I. Yagodynets´ (Investigation, Conceptualization, Methodology, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing), Zholt O. Kormosh (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing), Lucinda Vaz dos Reis (Data Curation, Conceptualization, Investigation).

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How to cite this article

Tkach, V. V.; Kushnir, M. V.; Oliveira, S. C.; Zavhorodnii, M. P.; Brazhko, O. A.; Kornet, M. M.; Luganska, O. V.; Kopiika, V. V.; Ivanushko, Y. G.; Mytchenok, M. P.; Ahafonova, O. V.; Yagodynets', P. I.; Kormosh, Z. O.; Reis, L. V. *Orbital: Electron. J. Chem*. **2021**, *13*, 219. **http://dx.doi.org/10.17807/orbital.v13i3.1584**