The theoretical description for sucralose electrochemical determination on poly(9-triphenylphosphazo) acridine, doped by novel quinolinic amino acids

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Received 15 Oct 2021, Revised 11 Mar 2021, Accepted 26 Apr 2021

Abstract
The sucralose electrochemical determination, assisted by a polymer of a novel acridinic derivative, doped by a novel quinolinicaminoacid, has been theoretically evaluated. The sucralose is capable to interact either with the monomer, or with the dopant, changing the double electric layer (DEL) capacitance and film conductivity. These changes may be responsible for electrochemical instabilities. Nevertheless, the analysis of the model by linear stability theory and bifurcation confirms that this polymer may be applied as an efficient electrode modifier in the sucralose determination in neutral media, being applied for sucralose determination in biological liquids and beverages. The electrochemical response has to be clear and easy to interpret.

Keywords: food safety, sucralose, conducting polymers, electrochemical sensors, stable steady-state

Introduction
Sucralose is one of the most used sweeteners throughout the world [1]. It is considered 3 times as sweet as aspartame, twice as sweet as saccharine and 1000 times as sweet as common sugar.
Even being considered safe, it may present toxic effects like mutagenesis, carcinogenesis, provoke obesity and growth of glycosis levels Moreover, while kept in unappropriate way, it may form dioxines, even more toxic compounds. Therefore, the development of an efficient method for sucralose electrochemical detection is actual [2], and the use of electrochemical methods for it would be very interesting.

As for now, no direct electrochemical methods for sucralose have been developed, except, HPLC with amperometric pulse [3 – 4]. Nevertheless, in some of our works [5 – 6] we have foreseen the possibility for their realization with specific electrode modifiers like overoxidizedpolypyrrole [5] and someacridinic derivatives [6]. An interesting case for electrochemical determination of sucralose electrochemical determination would be described if the phosphazoicacridinic derivative, described in [7], would be electropolymerized in the presence of the novel quinolinicaminoacids, described in [8 – 9]. As the pyridinic nitrogen atoms are present either in the conducting polymer, or in its dopant, both of them are capable to immobilize sucralose efficiently. By this, quaternary salts are formed, the polymer conductivity is altered and double electric layer structure and capacitance is changed, which may cause the electrochemical instabilities, analogous to those observed in [10 – 12]. So the use of the practical use of the electroanalytical system must be preceded by the theoretical investigation, capable to describe in details the behavior of the electroanalytical process. It includes the development and analysis of a correspondent mathematical model.

So, in this work, the mechanistic analysis is given forsucralose possible quantification by the electrode, modified by quinolone-doped poly(9-triphenylphosphazo)acridine. It includes:

- suggestion of the mechanism in the form of reaction consequence, causing the electroanalytical response;
- development of a mathematical model, describing the electroanalytical behavior of this system;
- analysis and interpretation of the model from the electroanalytical point of view with the seek for the possibility of electrochemical instabilities and their cause;
- the behavior comparison between the present electroanalytical process and the similar ones[5 – 7].

Fig. 1. Sucralose
System And Its Modeling

The electropolymerization of (9-triphenylphosphazo) acridine, obtained in [7], has to be realized by application of relatively high anode potentials, due to high acceptor effect of acridinic ring. Even though, the anodic potential will be lower than for other acridinic derivatives, including acridine orange [13 – 14], as the phosphazoic group is relative strong donor. The monomer rings are bind in the positions 2 and 7:

![Polymer Structure](image)

Fig 2. The polymer structure

The doping of the polymer by amioacid is realized by the insertion of the acid to the support electrolyte as sodium salt, yielding the conducting polymer in the charged form, in which either the polymer backbone or the dopant are capable to retain and immobilize sucralose.

If the constant voltage mode is used, the system will be described by a trivariant equation set with the following variables:

- \(c\) – the sucralose concentration in the pre-surface layer;
- \(\theta\) – the sucralose-modified polymer coverage degree;
- \(q\) – the electrode charge density.

Supposing that the reactor is intensively stirred, the background electrolyte is in excess, the diffusion layer is of a constant thickness, equal to \(\delta\), and its concentration profile is linear, we may neglect the convective and migration flow, avoiding the unnecessary (in this case) appearance of complex equations and simplifying the modeling.

Taking into account the mentioned above, we may describe the system behavior by a balance equation set as:
\[ \begin{align*} \frac{dc}{dt} &= \frac{2}{\delta} \frac{A}{\delta} (c_0 - c) - r_{11} - r_{12} \\ \frac{d\theta}{dt} &= \frac{1}{\Gamma} (r_{11} + r_{12} - r_2) \\ \frac{dq}{dt} &= \frac{U}{AR} - i_F \end{align*} \]

in which \( \Delta \) stands for the diffusion coefficient, \( c_0 \) for sucralose bulk concentration, \( \Gamma \) for polymer maximal surface concentration, \( U \) for voltage, \( A \) for electrode area, \( R \) for the resistance, \( i_F \) for Faraday current, and the parameters \( r \) are correspondent reaction rates, defined as:

\[ r_{11} = k_1 \cdot c \cdot (1 - \theta) \exp(\alpha \theta) \]

\[ r_{11} = k_2 \cdot c \cdot (1 - \theta) \exp(\alpha \theta) \]

\[ r_2 = k_2 \cdot \theta \exp \left( \frac{nF \phi_0}{RT} \right) \]

And the faradaic current as:

\[ i_F = nF \cdot k_2 \cdot \theta \exp \left( \frac{nF \phi_0}{RT} \right) \]

Here the parameters \( k \) mean correspondent reaction rate constants, \( n \) is the number of electrons transferred, \( F \) is the Faraday number, \( \phi_0 \) is the DEL potential slope, related to the zero-charge potential, \( R \) is the universal gas constant and \( T \) is the absolute temperature.

In the constant voltage mode the behavior of the system will be more dynamic than for the potentiostatic and even galvanostatic mode. Nevertheless, the process will be electroanalytically efficient, as shown below.

**Results And Discussion**

In order to describe the behavior of the system with the electrochemical determination of sucralose over the electrode, modified by acridinic conducting polymer, doped by quinolinicaminoacid, we analyze the equation-set (3) by means of the linear stability theory. The steady-state Jacobian matrix members for it will be described as:

\[ \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \]

in which:
expressions, we obtain it in the form (16).

\[
a_{11} = \frac{2}{\delta} \left( -\frac{\delta}{\delta} - k_{11}(1 - \theta) \exp(\alpha\theta) - k_{12}c(1 - \theta) \exp(\alpha\theta) \right) (7)
\]

\[
a_{12} = \frac{1}{\gamma} \left( k_{11}c \exp(\alpha\theta) - a k_{11}c(1 - \theta) \exp(\alpha\theta) + k_{12}c \exp(\alpha\theta) - a k_{12}c(1 - \theta) \exp(\alpha\theta) \right) (8)
\]

\[
a_{13} = 0
\]

\[
a_{21} = \frac{1}{\gamma} \left( k_{11}(1 - \theta) \exp(\alpha\theta) + k_{12}(1 - \theta) \exp(\alpha\theta) \right) (9)
\]

\[
a_{22} = \frac{1}{\gamma} \left( -k_{11}c \exp(\alpha\theta) + a k_{11}c(1 - \theta) \exp(\alpha\theta) - k_{12}c \exp(\alpha\theta) + a k_{12}c(1 - \theta) \exp(\alpha\theta) - k_2 \exp \frac{nF\phi_0}{RT} - \xi k_2 \theta \exp \frac{nF\phi_0}{RT} \right) (10)
\]

\[
a_{23} = \frac{1}{\gamma} \left( -\rho k_2 \theta \exp \frac{nF\phi_0}{RT} \right) (11)
\]

\[
a_{31} = 0
\]

\[
a_{32} = -\frac{\mu U}{AR} - k_2 \exp \frac{nF\phi_0}{RT} - \xi k_2 \theta \exp \frac{nF\phi_0}{RT} (12)
\]

\[
a_{33} = -\mu \frac{U}{AR} - k_2 \exp \frac{nF\phi_0}{RT} - \rho k_2 \theta \exp \frac{nF\phi_0}{RT} (13)
\]

Taking into account the expressions (7), (11) and (15), we may observe that the main diagonal elements contain the positive addendums. These addendums are responsible for the positive callback, so the oscillatory behavior in his system is possible. Moreover, it is more probable than for the analogous systems with sucralose determination [5,6] and with use of modifiers with pyridinic nitrogen atoms [5, 7].

Besides of the addendums \(a_{11}c(1 - \theta) \exp(\alpha\theta) > 0\), \(a k_{12}c(1 - \theta) \exp(\alpha\theta) > 0\) if \(\alpha > 0\), describing the oscillatory behavior, caused by influences of the chemical stages on DEL capacitance and structure, like also \(-\xi k_2 \theta \exp \frac{nF\phi_0}{RT} > 0\) if \(\xi < 0\), describing the same influences of the electrochemical stage, the electrochemical oscillations will be also described by the elements: \(-\mu \frac{U}{AR} > 0\) if \(\mu < 0\), describing the oscillatory behavior, accompanying the conductivity decrease during the electrochemical stage, like also \(-\rho k_2 \theta \exp \frac{nF\phi_0}{RT} > 0\) if \(\rho < 0\), describing the influences of the electrochemical stage to the anode charge. Thus, the oscillatory behavior will be more probable than in the analogous systems [5 – 7] with only one to three positive addendums. The oscillations are expected to be frequent and of little amplitude.

In order to investigate the steady-state stability of this system, we apply the Routh-Hurwitz criterion to the equation set (1). Simplifying the Jacobian determinant, in order to avoid the cumbersome expressions, we obtain it in the form (16).

\[
\frac{\delta}{\delta} \begin{vmatrix}
-k - \Omega & \Lambda & 0 \\
\Omega & -\lambda - \Sigma & -\xi \\
0 & -\Pi - \Sigma & -\rho - \Sigma
\end{vmatrix} = 0
\]

(16),

which after the rearrangement will be rewritten as:

\[
-\kappa(\Lambda P + \Lambda \Sigma + \Sigma^2 - \Pi P) - \Omega(\Sigma^2 - \Pi P) < 0
\]
This requirement will be surely satisfied, if the DEL and conductivity influences of the system are relatively weak. Otherwise, the steady-state will be stable and, due to the absence of the side factors, capable to compromise the analyte or modifier stability, it will be electroanalytically efficient, describing the linearity of the dependence between the electrochemical parameter (peak current value) and sucralose concentration. The electroanalytical process will be diffusion-controlled.

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

\[-κ(ΔP + ΔΣ + Σ^2 − ΠP) − Ω(Σ^2 − ΠP) = 0 \tag{18}\]

In the case of *galvanostatic mode*, the oscillatory behavior will be less probable, and the electroanalytical system will be efficient. As the anode current density is fixed, \(\frac{u}{AR} = i₀ = \text{const.}\), the conductivity change won’t provoke the positive callback, so the oscillatory behavior will only be caused by DEL capacitance influences of chemical and electrochemical stages. This case will be described in one of our next works.

**Conclusions**

From the theoretical investigation of sucralose electrochemical determination, assisted by the conducting polymer, in which either monomer or dopant contain piridinic nitrogen atoms (poly(9-triphenylphosphazo)acridine, doped by quinolinicaminoacids) it became possible to conclude that:

- In the constant voltage mode, the behavior of this system will be more dynamic than in galvanostatic and potentiostatic mode. The oscillatory behavior will be more probable than for the analogous systems;
- The sucralose Poly(9-triphenylphosphazo)aridine/Quinolineaminoacid assisted electrochemical determination is an electroanalytically efficient diffusion-controlled system;
- The linearity of the dependence between peak current value and the sucralose concentration is easy to maintain in the vast parameter topological region.

**References**


