THE MATHEMATICAL DESCRIPTION OF STEVIOL ELECTROCHEMICAL OXIDATION ON CARBON ELECTRODES IN NEUTRAL MEDIA

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Received 01 Jul 2022, Revised 30 Aug 2022, Accepted 30 Sep 2022

Abstract

The steviol electrochemical oxidation, realized for electroanalytical purposes, was theoretically evaluated. The mechanism for steviol electrooxidation has been suggested, and the correspondent mathematical model has been evaluated by means of the linear stability theory and bifurcation analysis. It was shown that, despite of the possibility of Kolbe electrochemical decarboxylation and its influences, the steady-state stability is easy to maintain. The oscillatory and monotonic instabilities for this case are more probable than for the similar ones.

Keywords: electrochemical sensors, steviol, electrooxidation, electrochemical oscillations, stable steady-state
Introduction

The use of chemically modified electrodes (CME) is a very important step in electroanalytical chemistry [1 – 4]. Compared to the bare electrodes, they have some advantages, like:

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

On the other hand, steviol is a diterpene first isolated from the plant *Stevia rebaudiana* in 1931[5]. Its chemical structure was not fully elucidated until 1960.[6]

Fig. 1. Steviol

Steviol occurs in the plant as steviol glycosides, sweet compounds that have found widespread use as sugar substitutes [7 - 10]. The glycoside complex of stevia contains 8 glycosides, which differ in carbohydrate fragment, but have a steviol fragment as a common part. Separately, they are 50 to 450 times as sweet as sugar. They are heat-stable, pH-stable and don’t ferment, so they can be used by people with diabetes. However, its excessive use may be linked with side effects like male infertility and even provoke cancer [11 – 14]. Thus, the development of an efficient method of its quantification is really actual task [15 – 20] and the electrochemical methods for it may give it an interesting solution.

Nevertheless, the development of the new electrochemical methods for new analytes and(or) modifiers confronts different obstacles like:

- the indecision concerning steviol electrooxidation mechanism;
- the possibility of additional stages, like Kolbe electrochemical decarboxylation in alkaline media [21 – 23]
the presence of electrochemical instabilities, accompanying the electrochemical oxidation of organic molecules (including electrochemical polymerization of heterocyclic compounds) [24 - 29].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the steviol electrooxidation, main reaction in 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 steviol electrooxidation. 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 [30 – 35].

System And Its Modeling

In alkaline media, the steviol electrooxidation may be given either by double bond, or by Kolbe decarboxylation, yielding a radical recombination adduct. This adduct may be also oxidized with the participation of the remaining hydroxyl groups (Fig. 2).

![Fig. 2. Steviol electrooxidation in alkaline solution](image-url)
So, taking into account the alkali excess, in order to describe this system, we introduce three variables;
c – steviol pre-surface layer concentration;
θ – steviol surface coverage degree;
θ* - steviol Kolbe decarboxylation product 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 electroanalytical process will be described by the three-dimensional equation set, exposed as:

\[
\begin{align*}
\frac{dc}{dt} &= \frac{2}{\delta} \left( \frac{\Delta}{\delta} (c_0 - c) - r_1 + r_{-1} \right) \\
\frac{d\theta}{dt} &= \frac{1}{G} (r_1 - r_{-1} - r_2 - r_3) \\
\frac{d\theta^*}{dt} &= \frac{1}{G^*} (r_3 - r_4)
\end{align*}
\]

In which Δ is the diffusion coefficient, \(c_0\) is the steviol bulk concentration, G and G* are steviol and adduct maximal surface concentrations and the parameters \(r\) are adsorption, desorption and reaction rates, which may be calculated as:

\[
\begin{align*}
r_1 &= k_1 c (1 - \theta - \theta^*) \exp(\alpha \theta) \\
r_{-1} &= k_{-1} \theta \exp(-\alpha \theta) \\
r_2 &= k_2 \theta \exp\left(\frac{2F \gamma \theta}{RT}\right) \\
r_3 &= k_3 \theta^2 \exp\left(\frac{2F \gamma \theta}{RT}\right) \\
r_4 &= k_4 \theta^* \exp\left(\frac{4F \gamma^* \theta}{RT}\right)
\end{align*}
\]

In which the parameters \(k\) are the correspondent rate constants, \(F\) is the Faraday number, \(\gamma\) and \(\gamma^*\) are mutually dependent coefficients, describing the influences of the electrochemical reactions in the double electric layer (DEL), \(R\) is the universal gas constant and \(T\) is the absolute temperature.

The presence of the complex chain of the electrochemical processes, including Kolbe reaction, makes the system’s behavior more dynamic, and it will be discussed below.
Results And Discussion

In order to investigate the steviol electrooxidation in alkaline solutions, we analyze the equation set (1) by means of linear stability theory. The Jacobian steady-state elements may be described as:

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

in which:

\[
a_{11} = \frac{2}{δ} \left( -\frac{4}{δ}(c_0 - c) - k_1(1 - θ - θ*) exp(αθ) \right)
\] (8)

\[
a_{12} = \frac{2}{δ} (k_{-1} exp(-αθ) - αk_{-1}θ exp(-αθ) + k_1c exp(αθ) - αk_1c(1 - θ - θ*) exp(αθ))
\] (9)

\[
a_{13} = \frac{2}{δ} (k_1c exp(αθ))
\] (10)

\[
a_{21} = \frac{1}{G} (k_1(1 - θ - θ*) exp(αθ))
\] (11)

\[
a_{22} = \frac{1}{G} \left( -k_{-1} exp(-αθ) + αk_{-1}θ exp(-αθ) - k_1c exp(αθ) + αk_1c(1 - θ - θ*) exp(αθ) - k_2 exp \left( \frac{2Fγθ}{RT} \right) - k_2θ \exp \left( \frac{2Fγθ}{RT} \right) - 2k_3θ \exp \left( \frac{2Fγθ}{RT} \right) - γk_3θ^2 \exp \left( \frac{2Fγθ}{RT} \right) \right)
\] (12)

\[
a_{23} = \frac{1}{G} \left( k_1c \exp(αθ) - γ * k_2θ \exp \left( \frac{2Fγθ}{RT} \right) - γ * k_3θ^2 \exp \left( \frac{2Fγθ}{RT} \right) \right)
\] (13)

\[
a_{31} = 0
\] (14)

\[
a_{32} = \frac{1}{G} \left( 2k_3θ \exp \left( \frac{2Fγθ}{RT} \right) + γk_3θ^2 \exp \left( \frac{2Fγθ}{RT} \right) - γk_4θ^* \exp \left( \frac{4Fγθ^*}{RT} \right) \right)
\] (15)

\[
a_{33} = \frac{1}{G} \left( γ * k_2θ \exp \left( \frac{2Fγθ}{RT} \right) + γ * k_3θ^2 \exp \left( \frac{2Fγθ}{RT} \right) - k_4 \exp \left( \frac{4Fγθ^*}{RT} \right) - γ * k_4θ^* \exp \left( \frac{4Fγθ^*}{RT} \right) \right)
\] (16)

Taking into account the expressions (8), (12) and (16), it is possible to observe that the oscillatory behavior in this system is possible, as the main diagonal contains positive elements, responsible for the positive callback. Moreover, it is more probable than in the similar systems [30 – 35].

Both surface and electrochemical instabilities are possible for this case. Nevertheless, as there is more than one electrochemical stage, the electrochemical instabilities are more probable to be realized, enhancing the possibility of the oscillatory behavior. The oscillations are expected to be frequent and of little amplitude.

In order to investigate the steady-state stability in this system, we apply the Routh-Hurwitz criterion to the equation set (1). Avoiding the cumbersome expressions, we introduce new variables, for the Jacobian determinant to be rewritten as:
Opening the brackets and applying to the determinant the requirement $\text{Det } J < 0$, derived from the criterion, we obtain the steady-state stability condition described as:

\[
\left( -\xi - \Xi \right) \left( \Lambda \Sigma + \Omega \Sigma + P \Sigma + PY + PK - K \Lambda - K \Omega - KP \right) + \Xi (PY - \Lambda K + \Lambda \Sigma) < 0
\]  

(18)

Besides of the narrowness of the steady-state stability topological zone, the steady-state is easy to maintain, as the requirement (18) is satisfied whilst the DEL- and surface influences of the processes are fragile. The dependence between the concentration and electrochemical parameter is linear, and the system is electroanalytically efficient.

Depending on the steviol concentration, electrode area and the presence of the active sites, the reaction may be diffusion-, adsorption- and reaction-controlled.

The monotonic instability, correspondent to the detection limit from the electroanalytical point of view, is also probable, if the destabilizing and stabilizing influences are equal. Its conditions will be described as:

\[
\left( -\xi - \Xi \right) \left( \Lambda \Sigma + \Omega \Sigma + P \Sigma + PY + PK - K \Lambda - K \Omega - KP \right) + \Xi (PY - \Lambda K + \Lambda \Sigma) = 0
\]  

(19)

The steviol behavior in the presence of a chemically modified electrode will depend on the nature of the modifier. The evaluation of the use of some modifiers to steviol will be made furtherly.

Conclusions

The analysis of the system’s behavior with the steviol electrooxidation let us conclude that:

- the stable steady-state, despite of being correspondent to the narrower parameter topological zone, is easy to maintain. The factors, warranting the steady-state stability are repulsion between the particles, fragility of DEL influences of electrochemical processes and the absence or fragility of autocatalysis
- depending on the steviol concentration, on electrode area and on the presence of the active sites of the reaction, the process will be controlled by diffusion, adsorption or reaction;
- the oscillatory behavior in this case is more probable than in common cases of electrooxidation and electropolymerization, being caused by surface and electrochemical;
- the monotonic instability in this system may appear.

Conflict of interest

The authors declare that there is no conflict of interests regarding this publication.
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