The theoretical determination of purpurogallin in the presence of transition metal cations, assisted by a new schiff base

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Abstract

The possibility of purpurogallin electrochemical determination on an anode, modified by a new triazolic Schiff base, has been theoretically evaluated. The correspondent mathematical model has been developed and analyzed by means of linear stability theory and bifurcation analysis. It was shown that the Schiff base provides an efficient purpurogallin electrochemical determination in the presence of transition metal cations, forming complex. The proper basicity of Schiff base and triazolic ring favors the process. The steady-state stability is easy to establish. The oscillatory behavior, in this case, is possible, due to the double electric layer influences of the electrochemical stage.

Keywords: purpurogallin, electrochemical sensors, chemically modified electrodes, triazole, stable steady-state

Introduction

Purpurogallin is a red, crystalline compound [1 – 2]. It is anaglycon of several glycosides from nutgalls and oak barks.[1] It can inhibit 2-hydroxy and 4-hydroxypurpurogallin methylation by catechol-O-methyltransferase.[2] It potently and specifically inhibits TLR1/TLR2 activation pathway, reason why it is used as a hepatoprotector and antioxidant in animals and humans.
Purpurogallin has confirmed biologic activity, which is dose-related. Moreover, its excess may cause adverse effects like nausea, vomiting, diarrhea, intense urinating and changed urine color. So, the development of an efficient and rapid purpurogallin determination method is really an actual task, and the electrochemical methods could help us in its resolution.

For now, only some methods of purpurogallin electrochemical determination have been developed – none of them are electrochemical [3 – 5]. Nevertheless, this molecule contains quinone-hydroquinonic system, which have already used either in electrode modifiers, or in analytes [6 – 12].

On the other hand, the use of the principally new analytes and electrode modifiers requires an a priori mechanistic theoretical analysis of the electroanalytical system. It would help us to resolve some problems like:

- The indecision in interaction of the electrode with the analyte and on its role in electroanalytical system;
- The possibility of the appearance of electrochemical instabilities in similar systems with electrooxidation of different organic molecules [13 – 14], including electrochemical polymerization [15].

The a priori theoretical investigation provides us the possibility to resolve the mentioned problems during the elaboration of the sensor. Such an investigation includes the development and analysis of a mathematical model, capable to describe adequately the electroanalytical system. So, the principal objective of this work is the mechanistic investigation of an electroanalytical system with purpurogallin electrochemical determination, assisted by a newly synthetized triazolic Schiff base. It is realized by achieving the specific goals like:

- Suggestion of the mechanism, presented as a sequence of chemical and electrochemical transformations, leading to the appearance of analytical signal;
- Development of a mathematical model, based on this mechanism;
- Analyze the model, obtaining the steady-state stability conditions (correspondent to the electroanalytical efficiency of the process) and of the oscillatory and monotonic instability;
- Compare the behavior of this system with that of the analogous systems [16 – 17].
System And Its Modeling

Materials and reagents. 5-(4-tert-butylphenyl)-4-amino-1,2,4-triazol-3-thiole has been provided as a courtesy by Zaporizhzhya State Medical University, and 5-phenylazosalicylic aldehyde has been used from the deposit of Chernivtsi National University. Ethanol, ether and DMF have been acquired from Sfera Sim™ (Lviv, Ukraine) and used without further purification. The $^1$H NMR experiment has been carried out in Karabük University (Turkey), by Varian Mercury 400 spectrometer (400 MHz) in DMSO-$d_6$. The reaction has been realized as in the Fig. 2:

![Fig. 2. Synthesis of Schiff base](image)

The mixture of 0.57 mol (0.0025 mol) of 5-phenylazosalicylic aldehyde with 0.62 g (0.0025 mol) 5-(4-tert-butylphenyl)-4-amino-1,2,4-triazol-3-thiole in 20 ml of ethanol was reflux for 2 hours. The reaction mixture was kept for 12 hours. The 0.2 g (17%) crude product has been filtered out and rinsed by ether. Melting poing 232 – 234°C. Chrystallized from DMF – H₂O mixture. Found: C: 65.52%, H 5.16%, N 18.22%. C_{25}H_{24}N_{6}OS. Calculated: C: 65.77%, H 5.30%, N 18.41%. The $^1$H NMR shifts may be depicted on the Fig. 3:

![Fig. 3. The PMR shifts of the new Schiff base](image)
The yield of the Schiff base in these conditions is relatively low, but it is in accord with other syntheses, based on the same triazolic derivative [18 – 19].

In the presence of metal cations in the background electrolyte (which is in excess), either purpurogallin, or the Schiff base are capable to form complex compounds. So, purpurogallin may enter the pre-surface layer in the form of a complex like:

![Fig. 4. The copper complex with purpurogallin](image)

This form of the complex is the most preferable, due to the presence of carbonyl in purpurogallin groups. This complex compound has the oxidation potential even lower than that of purpurogallin, so it may be either oxidized by the Schiff base with proton transfer, (realized either via Schiff bond, or via azo bond) or coordinate also with the metal cation and Schiff base on the surface, enhancing its oxidation and polymerization capacities. The complex, in the case, could be written down as:

![Fig. 5. The copper complex with purpurogallin and Schiff base](image)
Taking into account that the Schiff base is incorporated into a polymer, for galvanostatic mode, we introduce three variables:

\( c \) – purpurogallin complex concentration in the pre-surface layer;

\( \theta \) – the modified polymer coverage degree;

\( q \) – the charge of the electrode.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we suppose that the background electrolyte is in excess, so we can neglect the migration flow. The pre-surface layer thickness is assumed to be constant, equal to \( \delta \), and the concentration profile of the analyte and the alkali, to be linear.

It is possible to show that the system’s behavior will be described by the tridimensional equation-set described as:

\[
\begin{align*}
\frac{dc}{dt} &= \frac{2}{\delta} \left( \frac{\Delta}{\delta} (c_0 - c) - r_{11} - r_{12} - r_{13} \right) \\
\frac{d\theta}{dt} &= \frac{1}{\delta} \left( r_{11} + r_{12} + r_{13} - r_2 \right) \\
\frac{dq}{dt} &= i - i_F
\end{align*}
\]

In which \( c_0 \) is purpurogallin bulk concentration, \( \Delta \) is the diffusion coefficient, \( G \) is the reduced polymer maximal surface concentration, \( i_F \) is the Faraday current, and the parameters \( r \) are the rates of the correspondent chemical and electrochemical stages, capable to be calculated as:

\[
\begin{align*}
 r_{11} &= k_{11} c (1 - \theta) \\
 r_{12} &= k_{12} c (1 - \theta) \\
 r_{13} &= k_{13} c (1 - \theta) \exp(-\alpha \theta) \\
 r_2 &= k_2 \theta \exp \left( \frac{2F\varphi_0}{RT} \right) \\
 i_F &= 2Fk_2 \theta \exp \left( \frac{2F\varphi_0}{RT} \right)
\end{align*}
\]

In which the parameters \( k \) stand for the correspondent rate constants, \( \alpha \) is the parameter, relating the DEL capacitance to the complex recoordination, \( F \) is the Faraday number, \( \varphi_0 \) is the potential slope related to the zero-charge potential, \( R \) is the universal gas constant and \( T \) is the absolute temperature.

Although accomplished, while compared to the simple case, the behavior in this electroanalytical process will be efficient. Nevertheless, compared to the potentiostatic mode, the galvanostatic behavior will be more dynamic, which will be shown below.
Results and Discussion

In order to describe the purpurogallin galvanostatic electrochemical determination, assisted by a new triazolic derivative in the presence of the metal cations, we analyze the equation set (1) by means of linear stability theory. The steady-state Jacobian matrix members may be described as:

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

In which:

\[
a_{11} = \frac{2}{\delta} \left( -\frac{4}{\delta} k_{11} (1 - \theta) - k_{12} (1 - \theta) - k_{13} (1 - \theta) \exp(-\alpha \theta) \right)
\]

\[
a_{12} = \frac{2}{\delta} (k_{11} c + k_{12} c + k_{13} c \exp(-\alpha \theta) - \alpha k_{13} c (1 - \theta) \exp(-\alpha \theta))
\]

\[
a_{13} = 0
\]

\[
a_{21} = \frac{1}{\delta} (k_{11} (1 - \theta) - k_{12} (1 - \theta) - k_{13} (1 - \theta) \exp(-\alpha \theta))
\]

\[
a_{22} = \frac{1}{\delta} \left( -k_{11} c - k_{12} c - k_{13} c \exp(-\alpha \theta) + \alpha k_{13} c (1 - \theta) \exp(-\alpha \theta) - k_2 \exp\left(\frac{2F\varphi_0}{RT}\right) - \xi k_2 \theta \exp\left(\frac{2F\varphi_0}{RT}\right) \right)
\]

\[
a_{23} = \frac{1}{\delta} \left( -\mu k_2 \theta \exp\left(\frac{2F\varphi_0}{RT}\right) \right)
\]

\[
a_{31} = 0
\]

\[
a_{32} = 2F \left( k_2 \exp\left(\frac{2F\varphi_0}{RT}\right) + \xi k_2 \theta \exp\left(\frac{2F\varphi_0}{RT}\right) \right)
\]

\[
a_{33} = 2F \left( \mu k_2 \theta \exp\left(\frac{2F\varphi_0}{RT}\right) \right)
\]

Observing the expressions (8), (12) and (16), it is possible to show that in the galvanostatic mode the oscillatory behavior is even more probable than in the potentiostatic mode, as more positive addends, describing the positive callback, are present in the main diagonal elements. The DEL changes of the electrochemical stage, described by the element \( -\xi k_2 \theta \exp\left(\frac{2F\varphi_0}{RT}\right) > 0 \) typical for the similar systems [16 – 17], also influence the electrode charge density, and these influences are described by the positivity of \( \mu k_2 \theta \exp\left(\frac{2F\varphi_0}{RT}\right) > 0 \). Moreover, the DEL influences of the chemical stage also may cause the oscillatory behavior, if \( \alpha k_{13} c(1 - \theta) \exp(-\alpha \theta) > 0 \). The oscillations are realized beyond the detection limit and are expected to be frequent and of small amplitude.

The steady-state stability will be investigated by Routh-Hurwitz criterion. In order to apply it for the equation set (1), avoiding cumbersome expressions, we introduce new variables, for the Jacobian determinant to be described as:

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Opening the brackets and applying the Det J<0 inequation, the steady-state stability requirement will be described as:

\[-\kappa_1 \Pi_2 M < 0\] (18)

Which is warranted to be satisfied if both of the kinetic parameters \(\Pi_2\) and \(M\) are simultaneously negative (which succeeds for grand majority of cases). In these conditions the steady-state stability will be correspondent to the linearity of the dependence between electrochemical parameter or concentration (as no factors, compromising the side-reaction stability of analyte and electrode modifier are present). The electroanalytical process will be diffusion-controlled.

The detection limit is correspondent to the monotonic instability, capable to realize, if one of the kinetic parameters \(\Pi_2\) or \(M\) becomes equal to nil. By this way, the main condition for static bifurcation, which is Det J = 0 is satisfied, separating the stable steady-states from unstable states by:

\[-\kappa_1 \Pi_2 M = 0\] (19)

The same compound may also be used for the retention and determination of heavy-metal ions – not only in potentiostatic, but also in galvanostatic mode, which will be shown in one of our next publications.

**Conclusions**

The theoretical analysis of the purpurogallin electrochemical determination, assisted by a new Schiff base in the presence of metal cations, let us conclude that:

- it may be an excellent electrode modifier for purpurogallin electroanalytical electrooxidative quantification. The system is electroanalytically efficient, as the steady-state stability is easy to obtain and maintain;
- The electroanalytical process in galvanostatic mode is mostly diffusion-controlled.
- The oscillatory behavior in this system in galvanostatic mode is more probable than in potentiostatic mode, due to the influences of DEL rearrangement not only to the DEL capacity, but also to the faradaic current;
- Other case of the oscillatory behavior are the DEL influences of the chemical stage;
- The realization of the oscillatory behavior occurs beyond the detection limit.

REFERENCES