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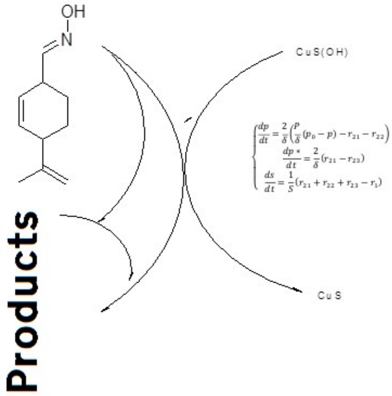
The Theoretical Description for the Perylaldehyde Aldoxyme Anodic Electrochemical Determination, Assisted by the Novel Squaraine Dye Composite with Copper(ii) Sulfide Nanoparticles

Volodymyr V. Tkach* [a], Marta V. Kushnir [a], Yana G. Ivanushko [c], Sílvio C. De Oliveira [b], Petro I. Yagodynets´ [a], Zholt O. Kormosh [d], and Lucinda Vaz dos Reis [e]

In this work the perillaldehyde aldoxime electrochemical determination on an anode, modified by squaraine dye composite with copper sulfide nanoparticles is analyzed. The electroanalytical process involves the formation of trivalent copper species, capable to oxidize the analyte by two parallel mechanisms. The correspondent mathematical model, correspondent to both of them, has been developed and analyzed by means of linear stability theory and bifurcation analysis. The model analysis clearly shows that the composite of a squaraine dye in organic phase and bivalent copper sulfide in the inorganic phase may be an efficient electrode modifier for perillaldehyde aldoxime electrochemical determination on an anode. The electroanalytical process will be mostly kinetically-controlled with the possibility of the transfer to diffusion-controlled mode. On the other hand, both oscillatory and monotonic instabilities may be realized in the electroanalytical process, and their probability will depend on the direction of the electroanalytical scenario in the concrete conditions, due to the possibility of the formation of ionic compounds in the pre-surface layer.

Graphical abstract



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1. Introduction

Perillartine (**Fig. 1**) (perillaldehyde *anti*-aldoxime) is a natural sugar substitute, extracted from Japanese perilla

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[a] Chernivtsi National University, 58000, Kotsyubyns´ky Str. 2, Chernivtsi, Ukraine. [b] Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller, 1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil. [c] Bukovinian State Medical University, 58000, Teatral´na Sq. 9, Chernivtsi, Ukraine. [d] East Ukrainian National University, 43000, Voli Ave., 13, Lutsk, Ukraine. [e] Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801, Folhadela, Vila Real, Portugal. Corresponding author. E-mail: **nightwatcher2401@gmail.com**

(shiso) leaves [1–4]. It is considered twice as sweet as sucralose, four times as sweet as saccharine and 2000 times as sweet as sucrose.

Besides of the proper perillartine, its ether derivative is also used, despite of being much less sweet than the proper perillartine (possessing the sweetness, nearly equal to that of aspartame).

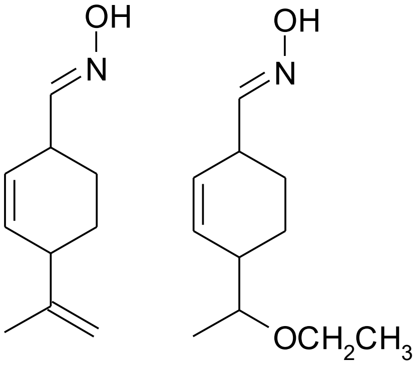

Fig. 1. Perillartine and its ether derivative.

This oxime is bioavailable and biodegradable, contrarily to the synthetic sweeteners like aspartame, saccharine and sucralose. Moreover, it isn´t considered toxic or dangerous for the environment.

Nevertheless, it may be allergic for people allergic to shiso herb [5–6]. Also, some toxic nitrogen derivatives like hydroxylamine may form during its metabolism in some people. It is important to mention that perillaldehyde aldoxyme and its derivatives are rarely used as sweeteners outside Japan, so this statement may be used in investigation of falsification of allegedly Japanese product claimed to contain the perillartine. Thus, the development of an efficient, exact and rapid method for perillartine determination is really actual task, and the electroanalytical methods would give it a good service [7–15].

As for now, no electrochemical methods for perillartine determination have been developed. Nevertheless, the aldoxime may be electrochemically active, being capable either to reduce or to oxidize. In both cases, the chemically modified electrodes are preferred to use, as they diminish the overvoltage and augment the electrode sensitivity and efficiency, due to the modifier affinity to analyte [16–30].

Both cathodic and anodic processes may be applicable to perillartine. In the last case, strong oxidants have to be used as specific and selective oxidants, as the oxime molecule possesses strong electron acceptors, enhancing the analyte oxidation potential and overvoltage.

In [31], an interesting anodic process for inositol electrochemical determination has been suggested. Therein, copper sulfide nanoparticles were used as electrode modifiers in alkaline media, providing the efficient electrooxidation with the relatively low detection limit and relatively wide linear range. The copper sulfide nanoparticles, at their turn, may be used as inorganic phase of a composite material, in which the organic phase role may be attributed to a conducting polymer, carbon material or squaraine dye (as monomer or polymerized) [32–35]. Therefore, the composite material will be either an active substance or a mediator.

Nevertheless, the electroanalytical processes of the likely substances tend to be accompanied by electrochemical instabilities [36–39], the electrochemical instabilities (oscillatory and monotonic) are highly probable to appear. They are capable to strongly influence the analytical signal, leading the sensing result to be misinterpreted.

Thus, in order to avoid or minimize the negative influences of the electrochemical instabilities or use their positive influences, if any, the theoretical *a priori* investigation of the system´s behavior is necessary. This investigation is realized by the development and analysis of the mathematical model, based on a most probable mechanism of the chemical and electrochemical reactions, causing the analytical signal. Moreover, the modeling permits us to compare behavior of the systems without experimental essays.

So, the main goal of our work is to investigate theoretically the behavior of the system with the electrochemical determination of perillartine on an anode, modified by CuS-Squaraine dye composite. In order to achieve it, we realize the specific goals like:

- Development of a mechanism, capable to describe the electrochemical behavior of the electroanalytical system;
- Development of a balance equation mathematical model, correspondent to the mechanism;
- Analysis of the model with the interpretation of the main results in terms of the electroanalytical process;
- Investigation of the steady-state stability requirements and oscillatory and monotonic instability conditions;
- Comparison of the behavior of the system with the similar ones [40–42].

2. Material and Methods

In the work [31] the electrochemical oxidation of the 1,2,3,4,5,6-cyclohexanehexole (inositol), assisted by copper sulfide nanoparticles, has been conducted in strongly alkaline media (pH=13). In this media, copper sulfide will be electrochemically oxidized (1):

$$CuS + OH^{-} - e^{-} \rightarrow CuS(OH) \qquad (1)$$

The copper(III)sulfohydroxide has the similar structure to that of cobalt(III) oxyhydroxide, but is highly energetic. Therefore, it will be strong oxidant, transforming perillartine according to a hybrid mechanism (**Fig. 2**).

In basic media, the alkene fragments tend to be oxidized by Wagner reaction, yielding the correspondent glycol. Nevertheless, in the presence of trivalent copper, the glycol is immediately oxidized to form carbonyl compounds. On the other hand, the oxime is oxidized to form the acy-nitroform of the nitrocompound (the pseudoacid ion), which augments the double electric layer (DEL) ionic force, capacitance and conductivity.

Taking into account that the oxyme oxidation will be realized more quickly than the oxidation of the double-bond fragments, we consider the mechanism as depicted on the Fig. 2 and describe the system´s behavior by introducing three variables:

p – peryllartin concentration in the pre-surface layer;

p* - pseudoacid ion concentration in the pre-surface layer;

s – copper sulfide matrix surface coverage degree.

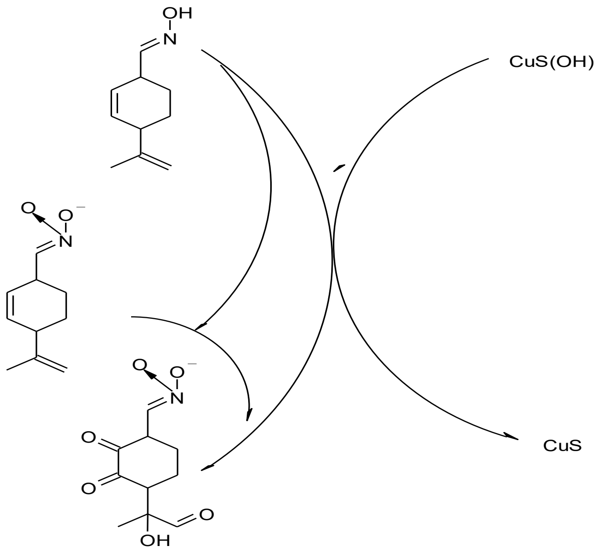

Fig. 2. Peryllartin oxidation mechanism

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 and equal to δ, and the concentration profile of the analyte to be linear. Also, we assume that on the initial moment of the reaction, copper (III) sulfohydroxide covers the entire squaraine dye matrix surface.

It is possible to show that the behavior of the electroanalytical process will be described by a trivariant equation set as (2):

$$\begin{cases} \dfrac{dp}{dt} = \dfrac{2}{\delta}\left(\dfrac{P}{\delta}(p_0 - p) - r_{21} - r_{22}\right) \\ \dfrac{dp*}{dt} = \dfrac{2}{\delta}(r_{21} - r_{23}) \\ \dfrac{ds}{dt} = \dfrac{1}{S}(r_{21} + r_{22} + r_{23} - r_1) \end{cases} \tag{2}$$

in which P is the diffusion coefficient, p_0 is the sweetener bulk concentration, S is the copper (II) sulfide maximal surface coverage degree, and the parameters r are the correspondent reaction rates, calculated as:

$$r_1 = k_1 s \exp\left(\frac{F\varphi_0}{RT}\right) \tag{3}$$

$$r_{21} = k_{21} p (1-s)^2 \exp(-\alpha p) \tag{4}$$

$$r_{22} = k_{22} p (1-s)^7 \exp(-\alpha p) \tag{5}$$

$$r_{23} = k_{23} p * (1-s)^5 \exp(-\beta p *) \tag{6}$$

in which the parameters k are rate constants of the reactions, parameters α and β describe the double electric layer capacitance and ionic force influences of the formation of ionogenic (primary amine) and ionic (vanadyl-ion) compounds, F is the Faraday number, φ_0 is the potential slope in DEL, relative to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature.

This model is very similar to that described in [40], also involving the oxidation of a nitrogen compound (hydrazine) on a trivalent copper. Nevertheless, the pseudoacid ions formation and transformation cause cyclic changes in DEL ionic forces and conductivities. These changes may be responsible for the oscillatory and monotonic instabilities, as shown below.

3. Results and Discussion

In order to investigate theoretically the electroanalytical determination of perillartine, assisted by squaraine dye – CuS composite, we analyze the equation-set (2) and algebraic relations (3–6) by means of linear stability theory. The steady-state Jacobian matrix members will be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{7}$$

in which:

$$\begin{aligned} a_{11} = \frac{2}{\delta}\Big(-\frac{P}{\delta} - k_{21}(1-s)^2 \exp(-\alpha p) \\ + \alpha k_{21} p (1-s)^2 \exp(-\alpha p) \\ - k_{22}(1-s)^7 \exp(-\alpha p) \\ + \alpha k_{22} p (1-s)^7 \exp(-\alpha p)\Big) \end{aligned} \tag{8}$$

$$a_{12} = 0 \tag{9}$$

$$\begin{aligned} a_{13} = \frac{2}{\delta}(2k_{21}p(1-s)\exp(-\alpha p) + 7\,k_{22}p(1 \\ - s)^6 \exp(-\alpha p)) \end{aligned} \tag{10}$$

$$\begin{aligned} a_{21} = \frac{2}{\delta}(k_{21}(1-s)^2 \exp(-\alpha p) \\ - \alpha k_{21} p (1-s)^2 \exp(-\alpha p)) \end{aligned} \tag{11}$$

$$\begin{aligned} a_{22} = \frac{2}{\delta}(-k_{23}(1-s)^5 \exp(-\beta p *) + \beta k_{23} p \\ * (1-s)^5 \exp(-\beta p *)) \end{aligned} \tag{12}$$

$$\begin{aligned} a_{23} = \frac{2}{\delta}\big(-2k_{21}p(1-s) \quad \exp(-\alpha p) + 5k_{23}p \\ * (1-s)^4 \exp(-\beta p *)\big) \end{aligned} \tag{13}$$

$$\begin{aligned} a_{31} = \frac{1}{S}(k_{21}(1-s)^2 \exp(-\alpha p) \\ - \alpha k_{21} p (1-s)^2 \exp(-\alpha p) \\ + k_{22}(1-s)^7 \exp(-\alpha p) \\ - \alpha k_{22} p (1-s)^7 \exp(-\alpha p)) \end{aligned} \tag{14}$$

$$\begin{aligned} a_{32} = \frac{1}{S}\Big(k_{23}(1-s)^5 \exp(-\beta p *) - \beta k_{23} p \\ * (1-s)^5 \exp(-\beta p *) \\ - m k_1 s \exp\left(\frac{F\varphi_0}{RT}\right)\Big) \end{aligned} \tag{15}$$

$$\begin{aligned} a_{33} = \frac{1}{S}\Big(-2k_{21}p(1 \\ - s)\exp(-\alpha p) - 7\,k_{22}p(1 \\ - s)^6 \exp(-\alpha p) - 5k_{23}p \\ * (1-s)^4 \exp(-\beta p *) \\ - k_1 \exp\left(\frac{F\varphi_0}{RT}\right) - j k_1 s \exp\left(\frac{F\varphi_0}{RT}\right)\Big) \end{aligned} \tag{16}$$

in order to investigate the *steady-state stability* in this system, we apply the Routh-Hurwitz criterion to the equation-set (2). Avoiding the cumbersome expressions, we introduce new variables, so the Jacobian determinant will be presented as:

$$\frac{4}{\delta^2 S}\begin{vmatrix} -\sigma-\Sigma-T & 0 & \Phi \\ \Sigma & -P & H-\Phi \\ \Sigma+T & P-\omega & -H-\Phi-\xi \end{vmatrix} \quad (17)$$

Opening the brackets and applying the Det J<0 requirement, salient from the criterion, we obtain the steady-state stability requirement, exposed as (18):

$$-\sigma(2P\Phi+P\xi+\omega H-\omega\Phi)-\Sigma(2P\Phi+P\xi+\omega H) - T(P\Phi+P\xi+\omega H-\omega\Phi)<0 \quad (18)$$

Describing a system, very close to that described in [36,40] (hydrazine electrochemical determination, involving the trivalent copper). As in the mentioned publications, the system tends to be either diffusion or kinetically controlled, but the kinetically-controlled mode tends to be more probable here than in [36,40], due to the formation of more ionic compounds than hydrazine, hydroxylamine and free nitrogen. These ionic compounds alter the ionic force of the solution, changing cyclically the conductivity of the pre-surface layer.

Nevertheless, as no side reactions, capable to compromise the modifier or analyte stability are observed here, the composite will be electroanalytically efficient. As in [31], the linear dependence range will be relatively vast and the detection limit, relatively low.

The detection limit is described by the *monotonic instability,* serving as margin between the stable steady-states and unstable states. Its realization condition is Det J=0, or

$$-\sigma(2P\Phi+P\xi+\omega H-\omega\Phi)-\Sigma(2P\Phi+P\xi+\omega H)- T(P\Phi+P\xi+\omega H-\omega\Phi)=0 \quad (19)$$

The oscillatory behavior in this system is possible, as the Jacobian main diagonal elements possess addendums, capable to be positive. Their positivity describes the positive callback (autocatalytic and self-promoting behavior), which is essential for the Hopf bifurcation, correspondent to the oscillatory behavior.

The oscillatory behavior in this system is more probable than in [40], but less probable than for cathodic reduction scenario with use of vanadium oxyhydroxide. Besides of the element $-jk_1 s\exp\left(\frac{F\varphi_0}{RT}\right)>0$ if j<0, defining the DEL influence of the surface conductivity change during the electrochemical reaction, the elements $\alpha k_{21}p(1-s)^2\exp(-\alpha p)>0$ and $\alpha k_{22}p(1-s)^7\exp(-\alpha p)>0$ if $\alpha>0$ and $\beta k_{23}p*(1-s)^5\exp(-\beta p*)>0$ if $\beta>0$, which describe the DEL ionic force influences of the formation and transformation of pseudoacid ions during the chemical stages also describe the oscillatory behavior.

The oscillations are expected to be frequent and of small amplitude, resembling those observed experimentally [36–37] and confirmed theoretically [40–42].

The same model (with some rectifications), is capable to describe the electrochemical determination of perillartine, assisted by cobalt(III) oxyhydroxide as inorganic phase. As CuS, CoO(OH) will act as reducent, yielding a highly energetic CoO_2 during the electrochemical stage.

Cobalt (IV) oxide, as a strong oxidant with confirmed peroxidase-like activity [32] easily oxidizes the alkene fragments to dicarbonyl compounds and oximes to pseudoacids. Thus, the electroanalytical process with its participation will be easily described by the present model. This model confirms the efficiency of $CoO(OH)/CoO_2$ redox pair in perillartine determination.

4. Conclusions

From the analysis of the system with the perillartine electrochemical determination as an anodic process, assisted by CuS – Squaraine Dye composite it is possible to conclude that:

- The system's behavior is more dynamic, while compared to the similar system with hydrazine determination, but less dynamic than in the case of the cathodic process, assisted by VO(OH);
- The electroanalytical process tends to be mostly kinetically controlled with the possibility of easy transition to the diffusion controlled mode;
- The oscillatory behavior tends to have more probability to be realized than in similar systems, but it is less probable than in the case of VO(OH)-assisted electrochemical determination of the same compound. It is caused by the DEL influences of the electrochemical stage and of the pseudoacid ions formations and transformations.

Author Contributions

Volodymyr V. Tkach (investigation, conceptualization, supervision, validation, writing – original draft, writing – review and editing); Marta V. Kushnir (data curation, conceptualization, investigation); Silvio C. de Oliveira (conceptualization, supervision, investigation, formal analysis); Yana G. Ivanushko (conceptualization, investigation, formal analysis, data curation); Petro I. Yagodynets (investigation, conceptualization, 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 (investigation, conceptualization, supervision, validation, writing – original draft, writing – review and editing)

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