FULL PAPER

The Theoretical Description for the Perylaldehyde Aldoxime Electrochemical Determination, Assisted by the Novel Squaraine Dye – VO(OH) - Composite

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Abstract:

For the first time, the perillaldehyde aldoxime electrochemical determination has been evaluated from the theoretical point of view. The correspondent mathematical model, including different scenarios of the electroanalytical process, 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 vanadium oxyhydroxide in the inorganic phase may be an efficient electrode modifier for perillaldehyde aldoxime electrochemical determination. On the other hand, both oscillatory and monotonic instabilities may be realized in the electroanalytical process, and their probability will strongly depend on the direction of the electroanalytical scenario in the concrete conditions

Keywords: perillaldehyde aldoxime; sugar substitute; food safety; electrochemical sensor; electrochemical oscillations; stable steady-state

1. Introduction

Perillartine (Fig.1) (perillaldehyde *anti-*aldoxime) is a natural sugar substitute, extracted from Japanese perilla (shiso) leaves [1-4]. It is considered twice as sweet as sucralose, four times as sweet as saccharine and 2000 times as sweet as common sugar.

Although this oxime isn´t considered toxic or dangerous for the environment, 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 is rarely used as sweetener outside Japan, so this statement may be used in investigation of falsification of allegedly Japanese product. 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].
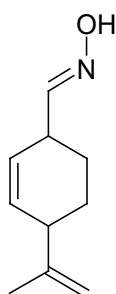

Figure 1. Perillartine.

In the case of perillartine, cathodic reduction is preferable, as oxime group is easy to reduce. Thus, the cathodic process would be conducted efficiently by an electrode, modified by a hybrid composite, in which a conducting polymer or squaraine dye [31-35] could be used as matrix for an inorganic oxide or oxyhydroxide with strongly reducing properties. Vanadium (III) oxyhydroxide [36-38] is suitable candidate for this role.

Nevertheless, the electroanalytical process of VO(OH)-assisted reduction of perillaldehyde, depending on solution pH, may be realized by different scenario. For example, VO(OH) may be oxidized either to VO_2, or to VO^{2+}. On the other hand, perillaldehyde may also be reduced yielding different products. Taking this into account, it is possible to foresee that, analogously to the similar cases [39-44], the electrochemical instabilities (oscillatory and monotonic) are highly probable to appear. They may influence strongly the interpretation of the analytical signal, causing strong behavioral changes not only in the system, but also in the equipment function mode.

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, assisted by VO(OH)-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 [45-49].

2. Material and Methods

2.1 System and its Modeling

In this work we develop and analyze the general model, describing different behavior scenarios, realizing during the VO(OH)-Squaraine dye-assisted electrochemical determination of perillartine for 3<pH≤7. All of them are joined on the Fig. 2.
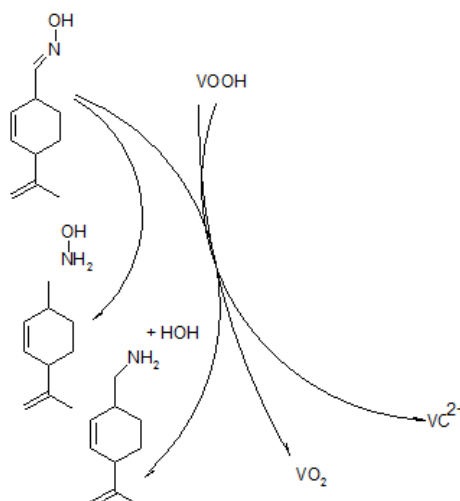

Figure 2. The general interaction mechanism for VO(OH)-assisted perillartine determination.

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In general, there are four different interaction possibilities for perillartine determination. More acidic is the solution, more possible is vanadyl formation. Nevertheless, if the pH<3, VO(OH) will be dissolved, according to the equation:

$$VO(OH) + 3H^+ \rightarrow V^{3+} + 2H_2O \quad (1),$$
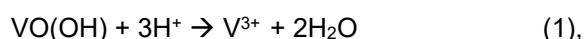
destroying the modifying material [36 – 38]. Thus the neutral, mildly and moderately acidic solutions are to be used in this case.

Taking this into account, we analyze the behavior of the system with perillartine determination, using three variables:

s – perillartine concentration in the pre-surface layer;

v_1 – vanadium dioxide surface coverage degree;

v_2 – vanadyl derivative surface coverage degree.

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, vanadium (III) oxyhydroxide covers the entire squaraine dye matrix surface.

Thus, the behavior of this system will be described by the balance equation-set (2):

$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{\Sigma}{\delta}(s_0 - s) - r_{11} - r_{12} - r_{11h} - r_{12h}\right) \\ \frac{dv_1}{dt} = \frac{1}{V_1}(r_{11} + r_{11h} - r_{21}) \\ \frac{dv_2}{dt} = \frac{1}{V_2}(r_{12} + r_{12h} - r_{22}) \end{cases} \quad (2)$$

in which Σ is the sugar substitute diffusion coefficient, s_0 is its bulk concentration, V_1 and V_2 are maximal surface concentrations of each form of the tetravalent vanadium, and the parameters

r are correspondent reaction rates for non-hydrolytic and hydrolytic processes. They may be calculated as (3 – 8):

$$r_{11} = k_{11}s(1 - v_1 - v_2)^4 \quad (3)$$

$$r_{11h} = k_{11h}s(1 - v_1 - v_2)^4 \exp(-\alpha s) \quad (4)$$

$$r_{12} = k_{12}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \quad 5)$$

$$r_{12h} = k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s) \quad (6)$$

$$r_{21} = k_{21}v_1 \exp -\frac{F\varphi_0}{RT} \quad (7)$$

$$r_{22} = k_{22}v_2 \exp -\frac{F\varphi_0}{RT} \quad (8)$$

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 includes four possible chemical stages and two electrochemical stages. Therefore, the behavior of the system will be much more dynamic than in the similar cases [45-49], as it is strongly influenced by either electrochemical and chemical stages, as shown below.

3. Results and Discussion

In order to investigate theoretically the electroanalytical determination of perillartine, assisted by squaraine dye – VO(OH) composite, we analyze the equation-set (2) and algebraic relations (3-8) by means of linear stability theory. The steady-state Jacobian matrix members will be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (9)$$

In which:

$a_{11} = \frac{2}{\delta}\left(-\frac{\Sigma}{\delta} - k_{11}(1 - v_1 - v_2)^4 - k_{11h}(1 - v_1 - v_2)^4 \exp(-\alpha s) + \alpha k_{11h}s(1 - v_1 - v_2)^4 \exp(-\alpha s) - k_{12}(1 - v_1 - v_2)^4 \exp(\beta v_2) - k_{12h}(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s) + \alpha k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s)\right)$ (10)

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$a_{12} = \frac{2}{\delta}(4k_{11}s(1 - v_1 - v_2)^3 + 4k_{11h}s(1 - v_1 - v_2)^3 \exp(-\alpha s) + 4k_{12}s(1 - v_1 - v_2)^3 \exp(\beta v_2) + 4k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s))$ (11)

$a_{13} = \frac{2}{\delta}(4k_{11}s(1 - v_1 - v_2)^3 + 4k_{11h}s(1 - v_1 - v_2)^3 \exp(-\alpha s) + 4k_{12}s(1 - v_1 - v_2)^3 \exp(\beta v_2) + 4k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s) - \beta(k_{12}s(1 - v_1 - v_2)^4 \exp(\beta v_2) + k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s)))$ (12)

$a_{21} = \frac{1}{V_1}(k_{11}(1 - v_1 - v_2)^4 + k_{11h}(1 - v_1 - v_2)^4 \exp(-\alpha s) - \alpha k_{11h}s(1 - v_1 - v_2)^4 \exp(-\alpha s))$ (13)

$a_{22} = \frac{1}{V_1}\left(-4k_{11}s(1 - v_1 - v_2)^3 - 4k_{11h}s(1 - v_1 - v_2)^3 \exp(-\alpha s) - k_{21}\exp-\frac{F\varphi_0}{RT} - jk_{21}v_1 \exp-\frac{F\varphi_0}{RT}\right)$ (14)

$a_{23} = \frac{1}{V_1}(-4k_{11}s(1 - v_1 - v_2)^3 - 4k_{11h}s(1 - v_1 - v_2)^3 \exp(-\alpha s))$ (15)

$a_{31} = \frac{1}{V_2}(k_{12}(1 - v_1 - v_2)^4 \exp(\beta v_2) + k_{12h}(1 - v_1 - v_2)^4 \exp(\beta v_2)\exp(-\alpha s) - \alpha k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s))$ (16)

$a_{32} = \frac{1}{V_2}(-4k_{12}s(1 - v_1 - v_2)^3 \exp(\beta v_2) = 4k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2)\exp(-\alpha s))$ (17)

$a_{33} = \frac{1}{V_2}\left(-4k_{12}s(1 - v_1 - v_2)^3 \exp(\beta v_2) - 4k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2)\exp(-\alpha s) + \beta(k_{12}s(1 - v_1 - v_2)^4 \exp(\beta v_2) + k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2)\exp(-\alpha s)) - k_{22}\exp-\frac{F\varphi_0}{RT} - jk_{22}v_2 \exp-\frac{F\varphi_0}{RT}\right)$ (18)

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:

$$\frac{2}{\delta V_1 V_2}\begin{vmatrix} -\kappa - \Lambda_1 - \Lambda_2 & X_1 + X_2 & X_1 + X_2 + \omega \\ \Lambda_1 & -X_1 - \Xi_1 & -X_1 \\ \Lambda_2 & -X_1 & -X_2 - \Xi_2 - \omega \end{vmatrix}$$
(19)

Opening the brackets and applying the Det J<0 requirement, salient from the criterion, we obtain the steady-state stability requirement, exposed as (20):

$-\kappa(X_1\Xi_2 + X_1\omega + \Xi_1 X_2 + \Xi_1\Xi_2 + \Xi_1\omega) - \Lambda_1(\Xi_1 X_2 + \Xi_1\Xi_2 + \Xi_1\omega - X_1\Xi_2 - X_2\Xi_2) - \Lambda_1(X_1\Xi_2 + X_1\omega + \Xi_1\Xi_2 + X_1 X_2) < 0$ (20)

Which indicates that, comparing this system with the similar ones [45-49], involving vanadium (III) oxyhydroxide and (or) conjugated compound as electrode modifier, the topological region of the steady-state stability will be narrower. In other words, it will be satisfied will have less probability than in the above-mentioned similar works [45-49].

On the other hand, the instabilities will be more probable. Nevertheless, their satisfaction is correspondent to the parameter values, which lie beyond the detection limit. Thus, taking also into account that no side reaction, compromising the material or analyte stability is possible in the model conditions, it is possible to conclude that the linear dependence between the analyte concentration and the electrochemical parameter will be satisfied within the steady-state stability region, making the analytical signal easy to interpret. The electroanalytical process will be either diffusion or kinetically controlled.

The detection limit is correspondent to the *monotonic instability*, serving as a margin between the stable steady-states and instable states. Its realization condition is Det J =0 (21):

$-\kappa(X_1\Xi_2 + X_1\omega + \Xi_1 X_2 + \Xi_1\Xi_2 + \Xi_1\omega) - \Lambda_1(\Xi_1 X_2 + \Xi_1\Xi_2 + \Xi_1\omega - X_1\Xi_2 - X_2\Xi_2) - \Lambda_1(X_1\Xi_2 + X_1\omega + \Xi_1\Xi_2 + X_1 X_2) = 0$ (21)

What about the *oscillatory behavior*, in this system it will be more probable than in the similar systems [45 – 49], as the double electric layer capacitance, conductivity and ionic force suffer strong influences on two electrochemical and three of four chemical stages as described below.

As known, the Hopf bifurcation is realized if the Jacobian matrix main diagonal elements have positive elements, responsible to the positive callback. In these systems, elements, which may be positive are:

$\alpha k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s) > 0$ if α>0, describing the DEL influence of the transformation of an oxyme (weak base) into a primary amine (strong base). The amine, as a ionogenic compounds will interact with ions yet present in DEL, altering its structure and contributing to the cyclic changes in its capacitance, conductivity and ionic force;

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$(k_{12}s(1 - v_1 - v_2)^4 \exp(\beta v_2) + k_{12h}s(1 - v_1 - v_2)^4 \exp(\beta v_2) \exp(-\alpha s)) > 0$, if β>0, describing the DEL influence of the formation and disappearance of an ionic compound (vanadyl derivative) on a squaraine matrix, leading to an effect, analogous to that described above;

$$-jk_{21}v_1 \exp -\frac{F\varphi_0}{RT} > 0 \qquad \text{and}$$

$-jk_{22}v_2 \exp -\frac{F\varphi_0}{RT} > 0$, if j<0, describing the DEL influences of the electrochemical stages on DEL capacitance, conductivity and ionic force, like also the surface doping degree and resistance.

All of the three factors are characteristic for the similar systems [45 – 49] or are analogous to them, as the similar systems also represent the DEL influences of electrochemical and (or) chemical stages, responsible for oscillatory behavior.

This model describes the general case of the perillartine VO(OH)-Squaraine dye assisted determination. It is characteristic for the pH values, in which both tetravalent vanadium forms are yielded. If only one of the is on the electrode, the variable, correspondent to the second form will be annulated, and the trivariant system will be transformed into a bivariant.

4. Conclusions

From the analysis of the system with the perillaldehyde aldoxime cathodic electrochemical determination on VO(OH)-squaraine dye composite it is possible to conclude that:

- The system's behavior is more dynamic, while compared to the similar ones, as there are five reactions influencing double electric layer capacitance, conductivity and ionic force, like also surface doping degree and conductivity – more than in similar systems;

- The electroanalytical process tends to be either diffusion or kinetically controlled;

- The oscillatory behavior tends to have more probability to be realized than in similar systems. It is caused by three factors;

- Despite of this, the linear dependence between the electrochemical parameter and concentration is observed in a vast parameter region, defining that the VO(OH) – Squaraine

Dye composite is an efficient electrode modifier for perillartine electrochemical detection.

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