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The Theoretical Description for Ledol and Ethanol Electrochemical Determination in Honey-Based Alcoholic Drinks

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Abstract: For the first time, the electroanalytical system for ledol and electrochemical determination in honey and honey-based alcoholic drinks over cobalt (III) oxyhydroxide has been described. As ledol is a tertiary cyclopropane-based alcohol, its electrooxidation will be given at a higher potential. The analysis of the electroanalytical process by linear stability theory and bifurcation analysis confirms that the neutral medium is the most suitable for ledol and ethanol quantification in honey and honey-based beverages.

Keywords: honey; ledol; ethanol; electrochemical sensor; cobalt (III) oxyhydroxide; stable steady-state.

1. Introduction

Honey [1–4] is one of the food products known to people since the Stone Age. It is usually accepted to call "honey" a viscous and intensely sweet liquid, which is a product of honey bees' enzymatic processing of nectar. Honey is widely used in cosmetics and in popular medicine, as it contains carbohydrates and polyphenolic compounds acting as antioxidants. Also, the production of honey-based alcohol drinks (including honey beer, honey wine, and honey-based strong alcoholic beverages) is widespread in the moderate climate countries of Europe, Asia, and the Americas [3,4].

In most cases, the honey is safe. Nevertheless, some of the flowers, pollinated by the honey bees and used to produce honey, including rhododendron (*L. palustre*), contain toxic compounds for human organisms, including the highly toxic tertiary alcohol, known as ledol (Figure 1).

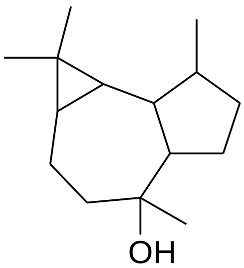

Figure 1. Ledol.

Consumption of honey containing high ledol concentrations leads to intoxication [5–7], manifested by muscular spasms, gastrointestinal problems, hallucinations, and even delirium, the reason why it is popularly known as "drunken honey" (in Ukraine) and "mad honey" (in Portugal and Brazil). If its concentration in honey exceeds the 15% threshold, this honey is considered unsafe and improper for human consumption. Also, the presence of ledol in honey-based alcoholic drinks may intensify the toxic effects of both ledol and ethanol.

On the other hand, ledol is also found in some Brazilian natural oils, like priprioca oil [8], in which its concentration reaches 4%. For these and other reasons, the development of a method capable of detecting its concentration with and without ethanol is really actual [9–12].

As for now, no electroanalytical method for ledol electrochemical detection has been developed. On the other hand, the electroanalytical methods frequently used in food and beverage analysis [13–21] may be easily applied to ledol electrooxidation with or without ethanol, as both compounds are electrochemically active.

Nevertheless, before the practical use of an electroanalytical process for the new analyte, it is necessary to evaluate the electrochemical behavior of ledol in the presence of ethanol from the theoretical mechanistic point of view, revealing the most probable mechanism for the process and, with that, the conditions for the most efficient sensing and the possibility of the electrochemical instabilities.

Therefore, this work aims to theoretically evaluate the system's behavior with ledol and electrochemical determination on cobalt (III) oxyhydroxide-modified electrodes for the first time. The theoretical evaluation includes the most probable mechanism suggestion, model development, analysis, and comparison of the behavior of this system with that of similar electroanalytical processes [24–28].

2. Materials and Methods

Ethanol is oxidized by cobalt (III) oxyhydroxide according to the reaction (1):

$$2CoO(OH) + C_2H_5OH \rightarrow CH_3COH + 2CoO + 2H_2O \quad (1)$$

As for ledol, it is oxidized via the cyclopropane ring first. This oxidation is thereby followed by proton and electron loss by the corresponding polyol (Figure 2).

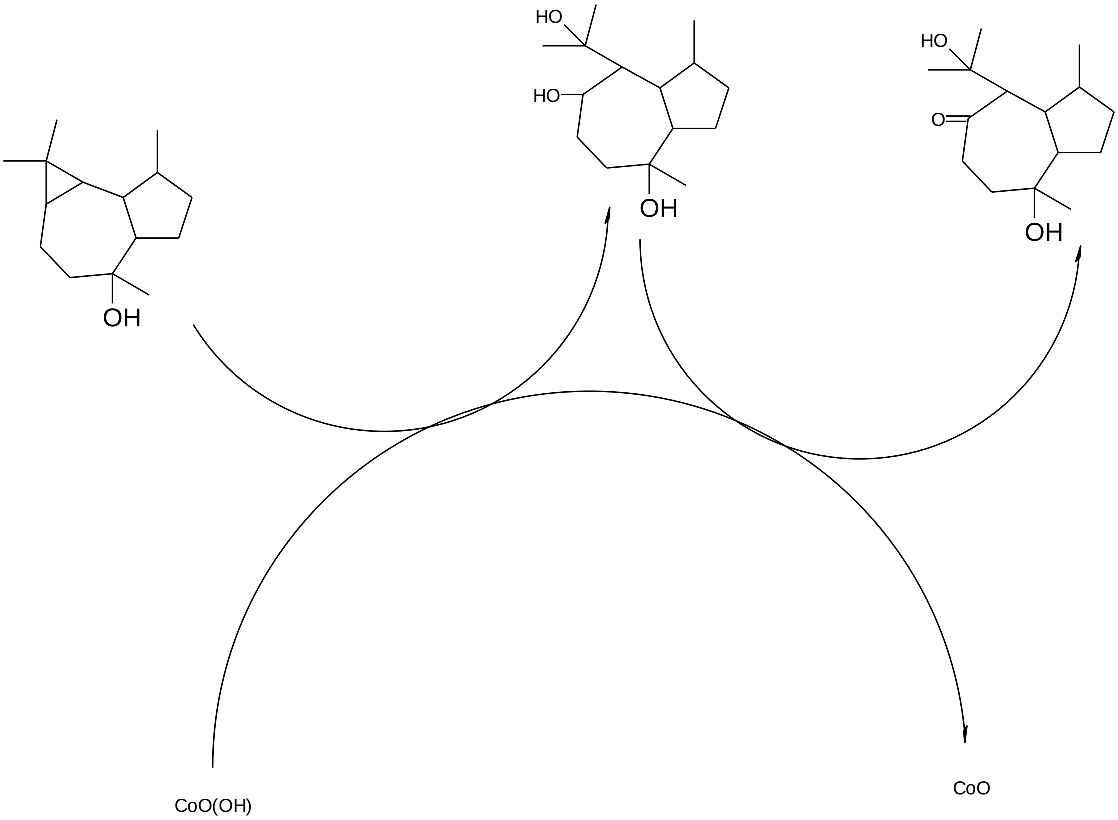

Figure 2. The scheme for CoO(OH)-assisted ledol electrooxidation.

Therefore, considering certain assumptions [27,28], we describe the behavior of this system by a trivariant equation set (2):

$$\begin{cases} \frac{da}{dt} = \frac{2}{\delta}\left(\frac{A}{\delta}(a_0 - a) - r_a\right) \\ \frac{dl}{dt} = \frac{2}{\delta}\left(\frac{L}{\delta}(l_0 - l) - r_l\right) \\ \frac{dc}{dt} = \frac{1}{C}(r_l + r_a - r_o) \end{cases} \quad (2)$$

Herein, a and l are correspondent to ethanol and ledol pre-surface concentration, a_0 and l_0 are the correspondent bulk concentrations, A and L are their diffusion coefficients, c is cobalt (II) oxide surface coverage degree, C is its maximal surface concentration, and the parameters r stand for the correspondent reaction rates, computed as (3 – 5):

$$r_a = k_a a(1-c)^2 \quad (3)$$
$$r_l = k_l l(1-c)^4 \quad (4)$$
$$r_o = k_o c \exp\left(\frac{F\varphi_0}{RT}\right) \quad (5)$$

Herein, the parameters k are the corresponding reaction rate constants, F stands for the Faraday number, φ_0 is the zero-charge-related DEL potential slope, R is the universal gas constant, and T is the solution absolute temperature.

This system will correspond to the anodic equivalent of sucralose and chloropicrin electrochemical determination, assisted by a conducting polymer, with the only difference being that the chemical stages do not affect DEL. Therefore, the system will be more stable, as shown below.

3. Results and Discussion

To investigate the CoO(OH)-assisted electrochemical determination of ledol and ethanol in honey-based drinks, we analyze the equation set (2) by linear stability theory, exposing the Jacobian steady-state elements as (6):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{6}$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{A}{\delta} - k_a(1-c)^2\right) \tag{7}$$

$$a_{12} = 0 \tag{8}$$

$$a_{13} = \frac{2}{\delta}(\mathbf{2}k_a a(1-c)) \tag{9}$$

$$a_{21} = 0 \tag{10}$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{L}{\delta} - k_a(1-c)^4\right) \tag{11}$$

$$a_{23} = \frac{2}{\delta}(\mathbf{4}k_a a(1-c)^3) \tag{12}$$

$$a_{31} = \frac{1}{C}(k_a(1-c)^2) \tag{13}$$

$$a_{32} = \frac{2}{\delta}(k_a(1-c)^4) \tag{14}$$

$$a_{33} = \frac{2}{\delta}\left(-\mathbf{2}k_a a(1-c) - \mathbf{4}k_a a(1-c)^3 - k_o \exp\left(\frac{F\varphi_0}{RT}\right) + jk_o c \exp\left(\frac{F\varphi_0}{RT}\right)\right) \tag{15}$$

Similar systems with CoO(OH)-assisted electrochemical determination of two analytes with the simple oxidation scheme that do not react with each other have already been described in our previous works [27, 28]. Taking into account that both honey and honey-based alcoholic beverages possess mildly acidic pH, and, therefore, both of the alcohols are less ionized, this case will correspond to the simplest system, corresponding to an efficient diffusion-controlled electroanalytical process.

In neutral media, the chemical stage does not affect the double electric layer, which is why the oscillatory behavior will be caused by the only factor of DEL impact of the electrochemical stage, described by the positivity of $jk_c c \exp\left(\frac{F\varphi_0}{RT}\right) > 0$, if j>0. This factor is common for all similar systems [22–28] and also defines the dependence of the oscillation frequency and amplitude on the background electrolyte composition.

Avoiding the cumbersome expression during the determinant analysis, we introduce new variables and rewrite the determinant as (16):

$$\frac{4}{\delta^2 V}\begin{vmatrix} -\kappa_1 - \Xi & 0 & \Lambda \\ 0 & -\kappa_2 - \Sigma & P \\ \Xi & \Sigma & -\Lambda - P - \Omega \end{vmatrix} \tag{16}$$

Opening the brackets, applying the Det J<0 requisite, salient from the criterion, and changing the signs to the opposite, we describe the stability requirement as (17):

$$\kappa_1(\kappa_2\Lambda + \kappa_2 P + \kappa_2\Omega + \Sigma\Lambda + \Sigma\Omega) + \Xi(\kappa_2\Lambda + \kappa_2 P + \Sigma\Omega) > 0 \tag{17}$$

Describing an efficient diffusion-controlled process in which the stable steady-state is easily formed. The inequation (17) is warranted to be satisfied if the electrokinetic parameter Ω is positive, which occurs in the majority of the cases. By this, the left side of the inequality (17) is driven towards more positive values, stabilizing the system. Taking into account that ledol and ethanol in the analysis conditions (in beverages and/or honey) do not react with each other and that the steady-state stability is easy to obtain and maintain, it is possible to conclude that this process may also serve for electroanalytical purpose, and the steady-state stability will be thereby correspondent to the linear dependence between concentration and current.

As for the monotonic instability, it delimits the margin for steady-state stability and, for electroanalytical effects, the detection limit. Its condition corresponds to the nullity of the determinant, or (18).

$$\kappa_1(\kappa_2\Lambda + \kappa_2 P + \kappa_2\Omega + \Sigma\Lambda + \Sigma\Omega) + \Xi(\kappa_2\Lambda + \kappa_2 P + \Sigma\Omega) = 0 \tag{18}$$

The electroanalytical process may be interfered with by compounds like: Furfural and its 5-hydroxymethyl derivative [12]; Lactic acid; Phenolic and polyphenolic compounds (including apigenin); Terpenols.

Cobalt (III) oxyhydroxide, in this case, may separate the peaks of two analytes and of the interfering compound. Moreover, in certain conditions, it may assist in the determination of the concentration relation between the mentioned compounds. Depending on the ionization degree, the behavior of this system will correspond to the model (2) or to similar models, including analyte ionization during the chemical stage.

4. Conclusions

The analysis of the system with ledol and ethanol electrochemical determination in beverages lets us conclude that this process is an efficient diffusion-controlled system with an electroanalytical function, providing facile analytical signal interpretation due to the easy steady-state stabilization. As for the oscillatory behavior, it may be caused by the only factor of the DEL influence on the electrochemical stage.

Author Contributions

All authors have read and agreed to the published version of the manuscript.

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Data supporting the findings of this study are available upon reasonable request from the corresponding author.

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Conflicts of Interest

The authors declare no conflict of interest.

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