The theoretical description for the electrochemical determination of 4-4'-dihydroxyazobenzene, assisted by a composite of squaraine dye with cobalt (iii) oxyhydroxide in pair with cobalt (iv) oxide

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Abstract
The theoretical description for 4-4'-dihydroxyazobenzene CoO(OH) – assisted electrochemical determination in mushroom pulp, food and biological liquids has been described. In this system, a squaraine dye is used as a Cobalt(III)oxyhydroxide stabilizer and electron transfer mediator. It is shown that, contrarily to the great part of the systems with cobalt (III) oxyhydroxide, this system will behave in a more stable manner, providing an efficient diffusion-controlled process. On the other hand, the oscillatory and monotonic instabilities, although possible, are caused by the double electric layer influences of either chemical or electrochemical stage.

Keywords: food safety, Agaricus xanthodermus, 4-4'-dihydroxyazobenzene, cobalt(III)oxyhydroxide, squaraine dye, electrochemical sensors, stable steady-state

Introduction
Agaricus is the most cultivated and consumed genus of mushrooms in Western and Northern Europe [1 – 4]. Its principal and most known representants are button mushroom (Agaricus bisporus) and field mushroom (Agaricus campestris). Both of them are edible and are cultivated in the special farms.

Nevertheless, alongside with the edible species, this genus includes also some poisonous species. The most common of them is the so called yellow stainer (Agaricus xanthodermus). It may readily grow among the edible Agaricus mushrooms and even compart the same mycelium, so it is easy to be confounded with the button and field mushrooms. Of those who gather Agaricus mushrooms, the yellow stainer poisoning cases are nearly the half of the total of the mushroom intoxications. The yellow...
stainer may be discriminated among the rest of the Agaricus mushroom by color and a disgusting smell, which becomes even more intense on cooking. Either the color or the smell or the toxic effects of the mushroom for the most people are explained by the presence of the phenolic compounds in it. The most toxic of these phenolic compounds [5-8] is the 4-4´-dihydroxyazobenzene, which in fact is responsible for the color of the mushroom. It was the first naturally found endogenous azo-dye:

![Fig. 1. 4-4´-dihydroxyazobenzene](image)

In the mushroom pulp, the phenolic compounds act as antioxidants, detaining the metabolic oxidation processes. Nevertheless, containing a strongly accepting azo-group, this compound becomes much more acidic, while compared to the simplest phenol, and its ingestion may cause gastric problems. Moreover, the 4-4´-dihydroxyazobenzene has also a potential to be used as an industrial dye, being intentionally or unintentionally added into food. Thus, the development of the determination methods for 4-4´-dihydroxyazobenzene is really actual.

As for now, no chemical or electrochemical methods, capable to determinate specifically the 4-4´-dihydroxyazobenzene have been described. Nevertheless, from the chemical composition of the compound it is possible to foresee that, as other phenolic and hydroquinonic compounds, it will be electrochemically active [9–14] for either cathodic or anodic determination. Its behavior has to be similar to that of either Sudan dyes or hydroquinonic compounds.

For the case of anodic oxidation, the use of the cobalt (III) oxyhydroxide may be suggested. It is a p-type semiconductor, proposed by some researchers as an alternative to titanium dioxide [15–18], but with more flexible electrochemical behavior. Possessing trivalent cobalt, it may act either as an oxidant or as a reductant. Both redox pair may be applied to the phenolic compounds. Its electroanalytical behavior has been analyzed by either experimental [19–22] or theoretical [23–26] means.

For stability reasons, cobalt (III) oxyhydroxide may be used as a part of composite material with the conducting polymer, carbon material or a squaraine dye. Thus, the cobalt (III) oxyhydroxide acts as an active substance, and the conjugated material, as a mediator.

Nevertheless, the use of novel electrode modifiers with novel analytes may be impeded by:
- the indecision concerning the exact mechanism of electrochemical reaction;
- necessity of determination of the parameter region, correspondent to the most efficient active substance and mediating action;
- the presence of electrochemical instabilities, yet described for the CoO(OH) synthesis [27-28].
The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the neotame electrochemical determination. Moreover, it is also capable to 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 4-4'-dihydroxyazobenzene electrochemical determination, assisted by CoO(OH) – Squaraine dye composite. 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 [23 – 28].

Two types of the behavior are possible, depending on the redox role of cobalt(III)oxyhydroxide. In this work, the use of CoO(OH) – CoO\(_2\) redox pair is analyzed. The behavior in this case will be more interesting than in the case of the use of CoO(OH) as oxidant.

**System And Its Modeling**

In the case of the use of CoO(OH) – CoO\(_2\) redox pair, both quinonic oxidation and assisted polymerization of the 4-4'-dihydroxyazobenzene are possible. Thus, the electroanalytical process will be schematically described as on the Fig. 2. In the simplest case, both participation of the quinonic compound in the polymerization process and the polymer oxidation aren’t included.
Fig. 2. The scheme of the electroanalytical process

For the potentiostatic mode, the electroanalytical process will be described by the balance differential equation set of two variables:

- \( p \) – phenolic compound concentration in the pre-surface layer;
- \( c \) – cobalt (III) oxyhydroxide – dye composite surface 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 \( \delta \), and the concentration profile in it is supposed to be linear.

It is possible to show that the behavior of this system will be described by the equation set (1):

\[
\begin{align*}
\frac{dp}{dt} &= \frac{2}{\delta} \left( \frac{p}{\delta} (p_0 - p) - r_1 - r_p \right) \\
\frac{dc}{dt} &= \frac{1}{C} (r_1 + r_p - r_2)
\end{align*}
\]
in which P stands for the diffusion coefficient, \( p_0 \) is the bulk concentration of the phenolic compound, C is the CoO maximal concentration in the pre-surface layer; \( i \) is the Faradaic current and the parameters \( r \) are the correspondent reaction rates, which may be calculated as:

\[
\begin{align*}
  r_1 & = k_1 p (1-c)^2 \exp(-ap) \\
  r_p & = k_p p^x (1-c)^y \exp(-ap) \\
  r_2 & = k_2 c \exp \frac{\varphi_0}{RT}
\end{align*}
\]

in which the parameters \( k \) are the correspondent rate constants, \( \alpha \) describes the DEL influence of the transformation of a more ionic phenolic compound to a less ionic quinonic form, which is significant for the relatively acidic phenols, \( F \) is the Faraday number, \( R \) is the universal gas constant and \( T \) is the absolute temperature.

While compared to the use of the CoO(OH) – CoO redox pair, the tetravalent cobalt will be far much more active. Even for the simplest case, the oscillatory and monotonic instabilities will be more probable, as there are more processes influencing the double electric layer, as shown below.

Results And Discussions

In order to investigate the steady-state stability of the system with the 4-4’-dihydroxyazobenzenem, assisted by cobalt (III) oxyhydroxide in pair with cobalt dioxide, we analyze the equation-set (1) by means of the linear stability theory. The steady-state Jacobian matrix members may be exposed as:

\[
\begin{pmatrix}
  a_{11} & a_{12} \\
  a_{21} & a_{22}
\end{pmatrix}
\]

in which:

\[
\begin{align*}
  a_{11} & = \frac{2}{\delta} ( - \frac{p}{\delta} - k_1 (1-c)^2 \exp(-ap) + ak_1 p (1-c)^2 \exp(-ap) - xk_p p^{x-1} (1-c)^y \exp(-ap) + ak_p p^x (1-c)^y \exp(-ap) ) \\
  a_{12} & = \frac{2}{\delta} ( 2k_1 p(1-c) \exp(-ap) + yk_p p^x (1-c)^y \exp(-ap) ) \\
  a_{21} & = \frac{1}{c} ( k_1 (1-c)^2 \exp(-ap) - ak_1 p (1-c)^2 \exp(-ap) + xk_p p^{x-1} (1-c)^y \exp(-ap) - ak_p p^x (1-c)^y \exp(-ap) ) \\
  a_{22} & = \frac{1}{c} ( -2k_1 p(1-c) \exp(-ap) - yk_p p^x (1-c)^y \exp(-ap) - k_2 \exp \frac{\varphi_0}{RT} - jk_2 c \exp \frac{\varphi_0}{RT} )
\end{align*}
\]

All the three reactions (both of the chemical stages and the electrochemical stage) influence the double electric layer capacitance. These influences may include the positive callback, responsible for the oscillatory behavior.

According to Hopf bifurcation conditions, the oscillatory behavior is realized if \( \text{Tr} J=0 \) and \( \text{Det} J>0 \). The first condition may be realized if the main diagonal contains at least one positive element. In this system, there are three positive elements - \( ak_1 p (1-c)^2 \exp(-ap) > 0 \) and \( ak_p p^x (1-c)^y \exp(-ap) > 0 \), if \( \alpha>0 \), describing the DEL influences of the chemical stages and \( -jk_2 c \exp \frac{\varphi_0}{RT} > 0 \) if \( j < 0 \), describing the DEL capacitance changes of the electrochemical reaction. The intensity of all of these influences strongly depends on support electrolyte composition. Nevertheless, in general feature,
the oscillations are frequent and of small amplitude. Mathematically, the oscillatory behavior condition will be described as:

\[
\begin{align*}
-\frac{2}{\delta}(\kappa + \Xi) - \frac{1}{M}(P + \Omega) &= 0 \\
\kappa P + \Xi P + \kappa \Omega &> 0
\end{align*}
\] (10),

Where:

\[
P = \kappa (11)
\]

\[
k_1(1 - c)^2 \exp(-ap) - \alpha k_1 p (1 - c)^2 \exp(-ap) + xk_p p^{x-1}(1 - c)^y \exp(-ap) - \frac{a k_p p^x (1 - c)^y \exp(-ap)}{\exp(-\alpha p)} = \Xi (12)
\]

\[
2k_1 p (1 - c) \exp(-ap) + y k_p p^x (1 - c)^y - 1 \exp(-ap) = P (13)
\]

\[
k_2 \exp \frac{\varphi_{\alpha}}{RT} - j k_2 c \exp \frac{\varphi_{\alpha}}{RT} = \Omega (14)
\]

In order to obtain the steady-state stability requirement, we apply the general condition \( \text{Tr} J < 0, \text{Det} J > 0 \). For this system it will be exposed as (16):

\[
\begin{align*}
-\frac{2}{\delta}(\kappa + \Xi) - \frac{1}{M}(P + \Omega) &< 0 \\
\kappa P + \Xi P + \kappa \Omega &> 0
\end{align*}
\] (15)

As the parameters \( \kappa \) and \( \Xi \) may only have positive values, the condition (16) is readily satisfied, if the parameters \( P \) and \( \Omega \) are also positive. It occurs if the DEL capacitance impacts aren’t strong enough to destabilize the system.

Really, if \( P > 0 \) and \( \Omega > 0 \), the first expression will maintain negative values, and the second expression will remain positive, describing a diffusion-controlled electroanalytical system with a vast parameter region, correspondent to the linear dependence between the concentration of the phenolic compound and the electrochemical parameter (system current). The electroanalytical process may be used in different media including the mushroom pulp, food and dye samples and biological liquids. Nevertheless, for the electroanalytical purposes the use of CoO(OH) – CoO redox pair will be a bit more efficient.

On the other hand, taking into account the polymerization scenario, this system may be used either for electroanalytical or for electrosynthetic purposes. The surface of squaraine dye/CoO(OH)/poly(4,4-dihydroxyazobenzene) is to be highly conductive and well developed. The morphology of the resulting composite will be centered near Cobalt(III) oxyhydroxide activated sites. The monotonic instability, correspondent to the N-shaped part of voltammogram, delimits the margin between the stable steady-states and unstable states. Its condition for the bivariant systems is \( \text{Tr} J < 0,\ \text{Det} J = 0 \).

\[
\begin{align*}
-\frac{2}{\delta}(\kappa + \Xi) - \frac{1}{M}(P + \Omega) &< 0 \\
\kappa P + \Xi P + \kappa \Omega &> 0
\end{align*}
\] (16)

Two factors, not included into the simplest model, may also influence the system’s behavior.

In the case of the participation of the quinonic product in the chain propagation and interruption, the third equation will be added to the equation-set (1). The polymerization rate equation will also be altered. Yet if the polymer, yielded during the phenolic compound oxidation is also oxidized (which is similar to yet known “polythiophene paradox”), the third equation of other type is also added. Both of the cases will be evaluated in our next works.
Conclusions

From the theoretical analysis of the electrochemical determination of the 4,4´-dihydroxyazobenzene, assisted by the CoO(OH) composite with a squaraine dye, with the use of CoO(OH) – CoO2 redox pair, it was possible to conclude that:

- the electroanalytical process is highly stable, and the linear dependence between the concentration and electrochemical parameter is realized in a wide parameter range. Nevertheless, comparing to the CoO(OH) – CoO redox pair, the stability is lower;  
- the electroanalytical process is controlled by the diffusion of the phenolic analyte;  
- this system may be used for both electroanalytical and electrosynthesitical purposes, yielding a well-developed and highly conductive polymer composite;  
- the electroanalytical process is efficient and suitable for the determination of 4,4´-dihydroxyazobenzene in different media, including mushroom pulp, food and biological liquids;  
- the oscillatory behavior in this system is possible, being caused by DEL influences of both chemical and electrochemical reactions. The oscillation characteristic will be highly dependent on the nature of the supporting electrolyte.

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