The theoretical description of prodigiosin alkaloids electrochemical determination on triazolic derivatives, reinforced by cobalt and nickel oxyhydroxides

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Abstract

The theoretical description of prodigiosin pigment electrochemical determination, assisted by novel triazolic derivatives, reinforced by cobalt and nickel oxyhydroxides, has been described. It was noticed that both cobalt and nickel oxyhydroxides may serve as efficient electrode modifiers of prodigiosin electrochemical determination in neutral and lightly alkaline media. The electroanalytical process is diffusion-controlled. The oscillatory and monotonic instabilities in the system are possible, being caused by DEL influences on the chemical and electrochemical stages.

Keywords: *natural pigments, electrochemical sensors, cobalt(III) oxyhydroxide, nickel (III)oxyhydroxide, stable steady-state*

Introduction

Prodigiosin is a tripyrrolic bloody-red pigment, synthetized by organisms of genus *Serratia, Pseudomonas* and some other gramnegative bacteria, like *Vibrio psychoerytrus* [1 – 4]. It is appointed as possibly responsible for the known ancient and medieval "bleeding" phenomena like one observed at 332 BC, during the Siege of Tyre by Alexander the Great and also to the Miracle of Bolsena, which gave the origin to the Feast of Corpus Christi. Its structure includes different resonance structures, the most abundant of which is described on the Fig. 1:
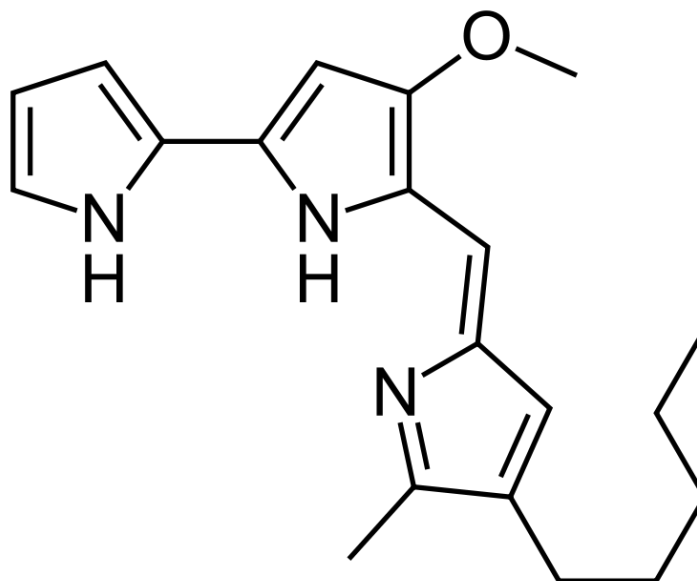
Fig. 1. Prodigiosin (pyrrolo-pyrrolo-isopyrrolic form)

It is potential natural drug with antimalaral, antifungal, immunosuppressant and antibiotic actions, which are dose-related [5 – 8]. Thus, the development of an efficient method of its quantification in different media is important – either from biological and pharmaceutical, or from historical point of view [9 – 12].

For now, no electroanalytical methods for prodigiosin have been developed. Nevertheless, its chemical composition leads to the hypothesis that it has to be electrochemically active with potential use in electroanalytical systems not only as analyte, but also as a monomer for overoxidized-polypyrrole like conjugated polymer and as an electrode modifier [13 – 14].

Being prodigiosin the analyte, it may be efficiently detected by electrochemical oxidation. Two of suggested electrode modifiers, possibly effective for this purpose are cobalt and nickel oxyhydroxides [15 – 18]. These have already gained their use in electrochemical sensors and catalytical systems as both active substances and intermediates.

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

- Thein decision 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 CoO(OH) formation and electrooxidation of different organic molecules [19 – 24], including electrochemical polymerization [22 – 24].

The *apriori* 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 prodigiosine electrochemical determination, assisted by triazolic compounds, reinforced by cobalt and nickel oxyhydroxide:

- Suggestion of the mechanism, presented a as 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 [25 – 26].

System And Its Modeling

Prodigiosin is oxidized initially by losing of two electrons and two protons and forming a dimer. The polymerization with the formation of a polymer composite with interesting tunable properties will be aborded in our next works.

In the presence of oxyhydroxides, the electroanalytical process will be described as:

$$MeO + OH^- - e^- \rightarrow MeO(OH) \qquad (1)$$

$$MeO(OH) + Prod \rightarrow MeO + (Prod)_2 + H_2O \qquad (2)$$
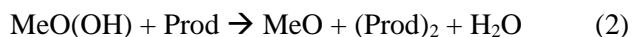
Me = Co, Ni.

The triazolic derivative as described in [27 – 28] on the electrode not only enhances the adhesion, but also stabilizes the oxyhydroxide by coordination (Fig. 2):
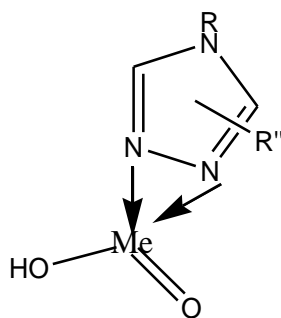

Fig. 2. Metal oxyhydroxyde stabilization effect by triazoles

If the electrode is initially covered by cobalt and nickel oxyhydroxide in equal quantities, in order to describe the system's behavior, we may introduce three variables:

p – prodigiosin pre-surface layer concentration;

κ – the triazole-CoO composite coverage degree;

ν – the triazole-NiO composite 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, equal to δ, and the concentration profile of the analyte and the alkali, to be linear.

Prodigiosin enters the pre-surface layer by means of its diffusion. It is oxidized by the oxyhydroxides, forming a dimer and metal oxides. Thus, the balance equation for its concentration will be rewritten as:

$$\frac{dp}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(p_0 - p) - r_{2c} - r_{2n}\right) \tag{3}$$

in which Δ is diffusion coefficient, p_0 is the bulk concentration of the pigment, r_{2c} and r_{2n} are reaction rates of the interactions between the natural dye and cobalt and nickel oxyhydroxides correspondently.

Both of the oxides are formed by the oxyhydroxides´ reduction by the analyte. They are recuperated on the electrochemical stage. So, their balance equations will be rewritten as:

$$\frac{d\kappa}{dt} = \frac{1}{K}(r_{2c} - r_{1c}) \tag{4}$$

$$\frac{d\nu}{dt} = \frac{1}{N}(r_{2n} - r_{1n}) \tag{5}$$

In which K and N are maximal concentrations of cobalt and niquel oxide correspondently, r_{1c} and r_{1n} are the electrooxidation rates.

The correspondent reaction rates may be calculated as:

$$r_{2c} = k_{2c}p^2(0,5 - \kappa)^2 \exp(\alpha\kappa) \tag{6}$$

$$r_{2n} = k_{2n}p^2(0,5 - \nu)^2 \exp(\beta\nu) \tag{7}$$

$$r_{1c} = k_{1c}\kappa \exp\frac{F\varphi_0}{RT} \tag{8}$$

$$r_{1n} = k_{1c}\nu \exp\frac{F\varphi_0}{RT} \tag{9}$$

in which the parameters k are correspondent rate constants, α and βare parameters, describing the relation between the double electric layer (DEL) capacitance and the oxyhydroxide reduction, 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.

It is possible to see that either the presence of more electroactive compounds, or the presence of more electrochemical stages makes the system's behavior more dynamic. Nevertheless, the system is electroanalytically efficient, which will be shown below.

Results And Discussion

In order to describe the behavior of prodigiosin electroanalytical detection, assisted by CoO(OH) and NiO(OH)-reinforced triazolic derivative, we analyze the equation-set $(3 - 5)$, taking into account the algebraic relations $(6 - 9)$, by means of linear stability theory. The steady-state Jacobian members may be exposed 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:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - 2k_{2c}(0,5 - \kappa)^2 \exp(\alpha\kappa) - 2k_{2v}(0,5 - v)^2 \exp(\beta v)\right) \quad (10)$$

$$a_{12} = \frac{2}{\delta}\left(2k_{2c}p^2(0,5 - \kappa) \quad \exp(\alpha\kappa) - \alpha k_{2c}p^2(0,5 - \kappa)^2 \exp(\alpha\kappa)\right) \quad (11)$$

$$a_{13} = \frac{2}{\delta}\left(2k_{2n}p^2(0,5 - v) \quad \exp(\beta v) - \beta k_{2n}p^2(0,5 - v)^2 \exp(\beta v)\right) \quad (12)$$

$$a_{21} = \frac{1}{K}\left(2k_{2c}(0,5 - \kappa)^2 \exp(\alpha\kappa)\right) \quad (13)$$

$$a_{22} = \frac{1}{K}\left(-2k_{2c}p^2(0,5 - \kappa) \quad \exp(\alpha\kappa) + \alpha k_{2c}p^2(0,5 - \kappa)^2 \exp(\alpha\kappa) - k_{1c}\exp\frac{F\varphi_0}{RT} - jk_{1c}\kappa\exp\frac{F\varphi_0}{RT}\right) \quad (14)$$

$$a_{23} = \frac{1}{K}\left(-uk_{1c}\kappa\exp\frac{F\varphi_0}{RT}\right) \quad (15)$$

$$a_{31} = \frac{1}{N}\left(2k_{2n}(0,5 - v)^2 \exp(\beta v)\right) \quad (16)$$

$$a_{32} = \frac{1}{N}\left(-jk_{1c}v\exp\frac{F\varphi_0}{RT}\right) \quad (17)$$

$$a_{33} = \frac{1}{N}\left(-2k_{2n}p^2(0,5 - v) \quad \exp(\beta v) + \beta k_{2n}p^2(0,5 - v)^2 \exp(\beta v) - k_{1c}\exp\frac{F\varphi_0}{RT} - uk_{1c}v\exp\frac{F\varphi_0}{RT}\right) \quad (18)$$

As it is possible to see from the expressions (10), (14) and (18), the elements $\alpha k_{2c}p^2(0,5 - \kappa)^2 \exp(\alpha\kappa)$, $\beta k_{2n}p^2(0,5 - v)^2 \exp(\beta v)$, $-jk_{1c}v\exp\frac{F\varphi_0}{RT}$ and $-uk_{1c}v\exp\frac{F\varphi_0}{RT}$ may be positive. It

means that the positive callback is possible for this case, so the *oscillatory behavior* for this system is also possible.

The positivity of two first elements appoints the influences, caused by the DEL capacitance changes, caused by the change of the complex configuration on the chemical stage. Two last elements, characteristic for the similar systems , in which CoO(OH) may act as reducent [25] and oxidant [26], describe the DEL influences on the electrochemical stages, leading to the cyclic change of the capacitance and conductivity. The oscillations are expected to be frequent and of small amplitude.

In order to describe the steady-state stability, we apply to the equation-set $(3 - 5)$ the Routh-Hurwitz criterion. Simplifying the determinant analysis, we introduce new variables, so the determinant will be rewritten as:

$$\frac{2}{\delta KN}\begin{vmatrix} -\lambda - \Omega - P & X & Y \\ \Omega & -X - \Pi - \varphi & -\gamma \\ P & -\varphi & -Y - \Phi - \gamma \end{vmatrix} \quad (19)$$

Opening the brackets, we obtaain the steady-state stbility condition, described as:

$$-\lambda(XY + \Pi Y + \varphi Y + X\Phi \quad + \Pi\Phi + \varphi\Phi + \gamma X + \gamma\Pi) - \Omega(\Pi Y + 2\varphi Y + \Pi\Phi + \varphi\Phi + \gamma\Pi) - $$
$$P(X\Phi \quad + \Pi\Phi + \varphi\Phi + 2\gamma X + \gamma\Pi) < 0 (20)$$

Which is the typical steady-state stability condition for a diffusion-controlled electroanalytical system $[25 - 26]$. This condition is warranted to satisfy, in the case of the fragility of DEL influences of chemical and electrochemical stages. Really, in the case of the positivity of the parameters X, φ, Y and γ, correspondent to the fragilty of yet mentioned influences, the left part of the inequation (20) will obtain more negative values, and the steady-state will be more stable.

As neither the analyte, nor the electrode modifier may participate in a side reaction, the system is efficient. This conclusion may be made not only from the analysis of the equation-set $(3 - 5)$, but also from its comparison with the similar systems $[25 - 26]$.

From the electroanalytical point of view, the steady-state stability, as stated, will be correspondent to the linear dependence between the electrochemical parameter and concentration. Both cobalt and nickel oxyhydroxides may serve as efficient electrode modifiers for prodigiosin quantification.

The detection limit is correspondent to the monotonic instability, capable to realize, when the stabilizing and destabilizing influences are equivalent. 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:

$$-\lambda(XY + \Pi Y + \varphi Y + X\Phi \quad + \Pi\Phi + \varphi\Phi + \gamma X + \gamma\Pi) - \Omega(\Pi Y + 2\varphi Y + \Pi\Phi + \varphi\Phi + \gamma\Pi) - $$
$$P(X\Phi \quad + \Pi\Phi + \varphi\Phi + 2\gamma X + \gamma\Pi) = 0 (21)$$

In the case of prodigiosin polymerization, the low-molecular oxidation product participates in the chain propagation, which will be described in one of our next works.

Conclusions

The theoretical description of prodigiosin CoO(OH) – NiO(OH)-assisted electrochemical determination it is possible to conclude that:

- Both cobalt and nickel oxyhydroxides are capable to assist efficiently the prodigiosin electrochemical determination in a diffusion-controlled process;
- Theoscillatorybehaviorinthissystemis more probable than in more common cases, due to the influences of DEL rearrangement not only during the electrochemical, but also during the chemical stage.
- The realization of the oscillatory behavior occurs beyond the detection limit.

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