









Theoretical Description for Orellanin Electroreductive Determination in the Presence of Paraquat Pesticide over Vanadium (III) Oxyhydroxide–poly(5-amino-1,4-dihydroxynaphthalene) Composite

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Abstract: The system with the electrochemical determination of orellanin alongside paraquat pesticide has been evaluated. Theoretically, the correspondent mathematical model has been developed and analyzed using linear stability theory and bifurcation analysis. It has been shown that the electrochemical reduction of orellanin and paraquat will influence the double electric layer (DEL) in different manners, as the transformation of ionic forms will reduce only one compound. This makes the oscillatory behavior probability more probable than for the simplest case but less probable than for the case of paraquat and diquat simultaneous electroreduction. In the case of orellanin, an N-oxide, an initial pyridinic form is yielded with the reduction by an oxygen atom. Yet, for the paraquat reduction, a formation of a quinonic structure without structural changes is typical. The electroanalytical process has to be diffusion-controlled, and the linear dependence between the concentration and electrochemical parameters will be satisfied on a vast parameter zone.

Keywords: orellanin; paraquat; electrochemical sensor; vanadium (III) oxyhydroxide; poly(5-amino-1,4-dihydroxynaphthalene); stable steady-state.

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1. Introduction

Orellanin (2-2' (3,4,3'4'-tetrahydroxy)dipyridyl-N,N-dioxide, Fig. 1 to the left) is the main toxin of poisonous mushrooms *Orellani* (foolish webcaps) [1–4]. The orellanin poisoning leads to digestive failure, followed by kidney failures. The death becomes imminent if the intoxication is untreated.

On the other hand, paraquat (4-4' dipyridilium dichloride, Fig. 1. To the right) [5–8] is one of the most poisonous non-selective herbicides. It has already been used even as a chemical weapon. Nowadays, its use is prohibited in the US and the EU countries, but some countries like Brazil still approve of its use. Thus, the development of a rapid, sensitive and exact method for determining both compounds is actual [9–12].

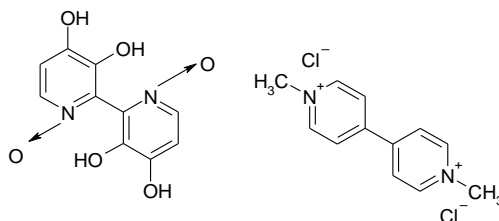


Figure 1. Orellanin and Paraquat.

Both of the compounds possess a positively charged nitrogen heteroatom, the reason why they are electrochemically active, being easily reduced on the cathode. As for orellanin, it may also be oxidized by a hydroquinone-like mechanism [13–15]. Nevertheless, the cathodic electrochemical reduction is strongly recommended to realize the simultaneous determination of both toxins, and vanadium (III) oxyhydroxide, deposited over a conducting polymer as electrode modifier, could be an interesting, sensitive coating for electroanalytical reduction of both of the compounds.

Nevertheless, the development of novel electroanalytical methods requires an *a priori* theoretical investigation. It helps to detect the conditions for the efficient electrochemical determination of the analyte [15-21] and the possibility for the electrochemical instabilities, typical for the organic electrooxidation, including electropolymerization [16 - 19].

Therefore, this work aims to evaluate the possibility of vanadium (III) oxyhydroxide-assisted orellanin electrochemical determination in the presence of paraquat. It includes the suggestion of the mechanism of the appearance of the analytical signal, the development and analysis (in terms of stability) of the correspondent mathematical model, the derivation of the conditions and requirements for the stability and the electrochemical instabilities, and the comparison of the behavior of this system with that of the similar processes [20 - 21].

2. Materials and Methods

Orellanin is reduced by oxygen atoms attached to the nitrogen heteroatom, transforming it into a pyridinic one. Yet paraquat is reduced without changing its atomic composition, but with the charge and bonding structure change. In neutral media, both heterocyclic nitrogen compounds formed on the chemical stages aren't protonized. Moreover, the ionic force decreases due to the disappearance of the paraquat ionic form.

Thus, the influence of each one of the electroanalytical processes on the double electric layer (DEL) will be different. As for the electroanalytical process, it will be schematically depicted as on Fig. 2.

Taking this into account, to describe the behavior of this system, we introduce three variables:

- o – orellanin concentration in the pre-surface layer;
- p – paraquat concentration in the pre-surface layer;
- v – vanadium (IV) oxide surface coverage degree.

Accepting certain assumptions [20 – 21], electrochemical system behavior will be described by the trivariant equation-set (1):

$$\begin{cases} \frac{do}{dt} = \frac{2}{\delta} \left(\frac{o}{\delta} (o_0 - o) - r_1 \right) \\ \frac{dp}{dt} = \frac{2}{\delta} \left(\frac{p}{\delta} (p_0 - p) - r_2 \right) \\ \frac{dv}{dt} = \frac{1}{V} (r_1 + r_2 - r_3) \end{cases} \quad (1)$$

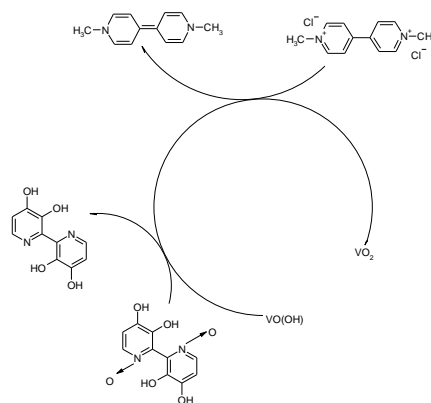


Figure 2. The scheme of the electroanalytical process.

Herein, O and P are analyte diffusion coefficients, o_0 and p_0 are their bulk concentrations, V is the vanadium dioxide maximal surface coverage degree, and the parameters r are correspondent reaction rates, calculated as (2 – 4):

$$r_1 = k_1 o (1 - v)^2 \quad (2)$$

$$r_2 = k_2 p (1 - v)^2 \exp(-ap) \quad (3)$$

$$r_3 = k_3 r \exp\left(-\frac{F\varphi_0}{RT}\right) \quad (4)$$

Herein, the parameters k are the correspondent reaction rate constants, a is the parameter relating the DEL capacitance with the paraquat deionization, F is the Faraday number, φ_0 is the potential slope in DEL, related to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature of the solution.

Taking into account paraquat deionization and its influence on DEL ionic force, the oscillatory and monotonic instabilities will be more probable for this system than for the simplest case but less probable than for two salts reduction. This shan't impede this system from being electroanalytical efficient, as shown below.

3. Results and Discussion

To describe the system with the orellanin and paraquat simultaneous cathodically electrochemical detection over a $VO(OH)/Poly(5\text{-amino-}1,4\text{-dihydroxynaphthalene})$ - modified electrode, we analyze the equation-set (1) using linear stability theory. The steady-state Jacobian matrix members may be described as (5)

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (5)$$

herein:

$$a_{11} = \frac{2}{\delta} \left(-\frac{o}{\delta} - k_1 (1 - v)^2 \right) \quad (6)$$

$$a_{12} = 0 \quad (7)$$

$$a_{13} = \frac{2}{\delta} (2k_1 o(1 - v)) \quad (8)$$

$$a_{21} = 0 \quad (9)$$

$$a_{22} = \frac{2}{\delta} \left(-\frac{P}{\delta} - k_2(1 - v)^2 \exp(-ap) + ak_2p(1 - v)^2 \exp(-ap) \right) \quad (10)$$

$$a_{23} = \frac{2}{\delta} (2k_2p(1 - v) \exp(-ap)) \quad (11)$$

$$a_{31} = \frac{1}{v} (k_1(1 - v)^2) \quad (12)$$

$$a_{32} = \frac{1}{v} (k_2(1 - v)^2 \exp(-ap) - ak_2p(1 - v)^2 \exp(-ap)) \quad (13)$$

$$a_{33} = \frac{1}{v} \left(-2k_1 o(1 - v) - 2k_2p(1 - v) \exp(-ap) - k_3 \exp\left(-\frac{F\phi_0}{RT}\right) + jk_3r \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (14)$$

Taking into account the main diagonal elements (6), (10), and (14), it is possible to conclude that the positive callback may be realized in this system, as these elements possess positive addendums corresponding to this callback. As the positive callback is tightly related with the Hopf bifurcation condition, correspondent to the oscillatory behavior, this behavior is possible, being a bit more probable than for similar systems [20,21].

Two elements describing the positive callback may describe the oscillatory behavior. These elements are $ak_2p(1 - v)^2 \exp(-ap) > 0$, if $a > 0$, describing the DEL influences of the nitrogen atom protonation, and $jk_3r \exp\left(-\frac{F\phi_0}{RT}\right) > 0$ if $j > 0$, describing the DEL impact of the electrochemical stage. The oscillation amplitude will strongly depend on the background electrolyte content and will augment with the decrease of pH, as protons participate directly in both chemical and electrochemical stages.

Despite being more probable than for the simplest case, the oscillatory behavior in this system will be less probable than for the case with two salts electrochemical reduction. In that case, two strong electrolytes instead of one are reduced, provoking more impact on the DEL ionic force.

As for the steady-state stability, it is warranted if the above-cited conditions are not satisfied. To investigate the steady-state stability, we apply the Routh-Hurwitz criterion to the equation-set (1). Simplifying the system, we introduce new variables, rewriting the determinant as (15):

$$\frac{4}{\delta^2 V} \begin{vmatrix} -\kappa_1 - \varepsilon & 0 & P \\ 0 & -\kappa_2 - \Sigma & T \\ \varepsilon & \Sigma & -P - T - \Omega \end{vmatrix} \quad (15)$$

Opening the straight brackets and applying the criterion $\text{Det } J < 0$, salient from the criterion, we obtain the stability requisite exposed as (16):

$$-\kappa_1(\kappa_2 P + \kappa_2 T + \kappa_2 \Omega + \Sigma P + \Sigma \Omega) - \varepsilon(\kappa_2 T + \kappa_2 \Omega + \Sigma \Omega) < 0 \quad (16)$$

which is readily satisfied if the variables Σ and Ω are positive. Really, if these variables are positive, taking into account the positivity of the rest of the variables, the left side of the inequation (16) will be driven to more negative values, stabilizing the system. The positivity of the mentioned variables is correspondent to the fragility of DEL influences of the electrochemical stage and the chemical stage involving paraquat

Taking into account the kinetic properties of the system, like also the presence of both of the diffusion parameters κ_1 and κ_2 in the majority of the addendums of the expression, it is possible to conclude that the electroanalytical process will be diffusion controlled.

As no side reaction capable of compromising the analyte and modifier stability is realized in this system, the steady-state stability is electroanalytical efficient. By this, the steady-state stability corresponds to the linear dependence between the concentration and the electric current in the system, which will be satisfied for a wide parameter topological region, separated from the unstable states by a monotonic instability.

This instability is correspondent to the detection limit, being its condition $\text{Det } J=0$, or:

$$-\kappa_1(\kappa_2P + \kappa_2T + \kappa_2\Omega + \Sigma P + \Sigma\Omega) - \mathcal{E}(\kappa_2T + \kappa_2\Omega + \Sigma\Omega) = 0 \quad (16)$$

This model is valid for two analytes, like paraquat and orellanin, aren't capable of reacting with each other. In that case, the reaction rate should be included in both of the first equations of the model. This case may have different behavior, depending on the nature of the mentioned reaction, and it will be evaluated in our next works.

4. Conclusions

From the theoretical model evaluation of CP-VO(OH)-assisted orellanin and paraquat simultaneous electrochemical determination in neutral media, it has been possible to conclude that it is an efficient electroanalytical process. The linear dependence between the analytes' concentrations and electrochemical parameters is easily maintained. In its turn, the oscillatory behavior is expected to be relatively probable and highly dependent on the solution background electrolyte composition. Nevertheless, the oscillatory behavior is less probable than two salts simultaneous reduction due to less expressed DEL ionic force influence.

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Conflicts of Interest

The authors declare no conflict of interest.

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