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The mathematical evaluation of the electrochemical determination of paraquat, on conducting polymer, modified by VO₂/ VO₂⁺ oxidation pair

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ABSTRACT

The possibility of paraquat electrochemical detection, realized by conducting polymer electrode, doped by vanadium dioxide, was analyzed by theoretical point of view. It was shown, that the conducting polymer composite with VO₂ may serve as an excellent electrode modifier for paraquat electrochemical detection. The steady-state may be maintained stable in the vast parameter region. The possibility for electrochemical instabilities in this system has also been studied.

Keywords: *food safety, intoxication prevention, paraquat, vanadium dioxide, electrochemical detection, electrochemical sensing, stable steady-state.*

INTRODUCTION

Paraquat is one of the most efficient non-selective herbicides [1 – 4], killing green plants on contact. It is also used in modeling of oxidizing stress [5]. Nevertheless, besides of its toxicity for plants, it is highly toxic for humans and animals [2, 6 – 7], and it is frequently used as mean of suicide and murder. Moreover, its action in organism may be associated with Parkinson disease [8], and there is no known specific antidote for it. That fact led it to be forbidden in the European Union [9] and in South Korea

[10], where the prohibition of paraquat has influenced the suicide and murder profile, and limited in the US [11], but it is still used in 120 countries, mostly developing and with agrarian-related economy. Thus, the development of an exact, precise, sensitive and rapid method of its detection is really an actual problem [11 – 13].

As paraquat is a redox-active substance, the electrochemical methods may be applicable to it. Nevertheless, it acts as an oxidant, and the the use of cathodic processes in electroanalytics isn´t very frequent [14 – 15]. However, chemically modified electrodes, yet used for other substances [16 – 17], may serve good the detection of paraquat [18] and its related compound diquat [19] (Fig. 1).
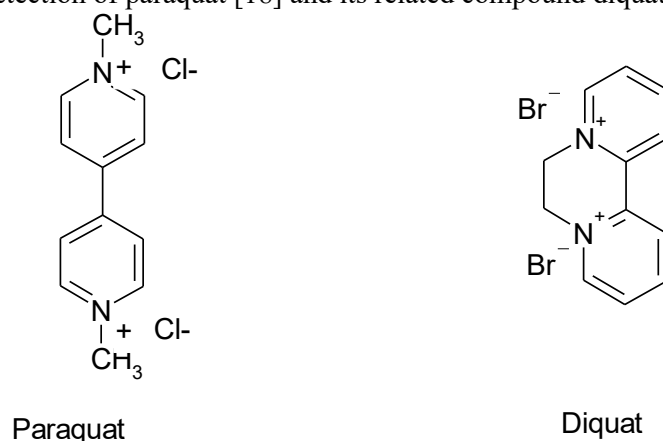

Fig. 1. Paraquat and diquat

One of the substances, frequently used to assist electrochemical and non-electrochemical analytical methods is vanadium dioxide [20 – 21]. It is also formed in the catalyzed sulfate acid synthesis [22 - 23]. But, in the case of paraquat, no electrochemical detection method involving it, or other vanadium compounds, has been developed, and it leads he research to resolve the problems like:

- Indefinition in the modifier mechanism of action with paraquat;
- The possible presence of electrochemical instabilities, accompanying the system, like oscillatory behavior.

Their resolution is impossible without development of a mathematical model, capable to describe adequately the system´s behavior. The modeling also lets us compare it with the behavior of other, similar systems.

So, the goal of our work is the mechanistic investigation for VO_2-assisted paraquat electrochemical determination. For its purpose, we reach specific objectives like:

- the mechanism suggestion for paraquat electrochemical reduction on vanadium dioxide;
- the development of mathematical model, correspondent to this mechanism;
- the analysis and interpretation of the model;
  The comparison of the system´s behavior with that for the similar ones [24 – 28].

System And Its Modeling

The mechanism of the electrochemical action of VO_2 in the determination of paraquat may be described as:

$$2VO_2 + PQ^{2+} \rightarrow 2VO_2^+ + PQ \tag{1}$$
$$VO_2^+ + e^- \rightarrow VO_2 \tag{2}$$

The electrode reversibility is maintained by short-time pervanadyl-ion formation, and its efficiency for paraquat reduction is maintained in neutral pH, so for the modeling purposes it will be used.

For the behavior of neutral-media paraquat electrochemical reduction, assisted by vanadium compounds, it is possible to suggest the balance-equation model, involving two variables:

c – paraquat pre-surface layer electrochemical detection;
v – pervanadyl coverage degree.

In order 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 δ, and the concentration profile in it is supposed to be linear. It is also supposed that at the null-moment of the reaction vanadium dioxide covers the entire cathode surface.

It is possible to show that the balance equations, describing the system's behavior, may be expressed as:

$$\begin{cases} \dfrac{dc}{dt} = \dfrac{2}{\delta}\left(\dfrac{\Delta}{\delta}(c_0 - c) - r_1 \right) \\ \dfrac{dv}{dt} = \dfrac{1}{V}(r_1 - r_2) \end{cases} \tag{3}$$

in which r_1 and r_2 are correspondent reaction rates for the reactions (1) and (2), c_0 is paraquat bulk concentration, V is pervandyl maximal surface concentration and Δ is its diffusion coefficient.

The reaction rates may be calculated as:

$$r_1 = k_1 c(1-v) \qquad\qquad r_2 = k_2 v \exp\left(-\dfrac{Fjv}{RT} \right) \tag{4 – 5},$$

In which the parameters k are rate constants of the correspondent reactions, F is the Faraday number, j is the coefficient, describing the influence of the electrochemical process to the double electric layer (DEL) capacitance, R is the universal gas constant and T is the absolute temperature.

The model is very similar to that observed for the cases of the use of CoO(OH) and ferrocene derivatives. The common and different features of their behavior will be discussed below.

Results And Discussion

To describe the behavior of the system with VO_2-assisted electrochemical detection of paraquat, we investigate the equation set (3) by means of linear stability theory. The steady-state Jacobi functional matrix elements for this system may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{6},$$

in which:

$$a_{11} = \frac{2}{\delta}\left(-k_1(1-v)-\frac{\Delta}{\delta}\right) \tag{7}$$

$$a_{12} = \frac{2}{\delta}(k_1 c) \tag{8}$$

$$a_{21} = \frac{1}{V}(k_1(1-v)) \tag{9}$$

$$a_{22} = \frac{1}{V}\left(-k_1 c - k_2 \exp\left(-\frac{Fjv}{RT}\right) + jk_2 v \exp\left(-\frac{Fjv}{RT}\right)\right) \tag{10}$$

It is possible to observe that the *oscillatory behavior*, whose main condition is Tr J = 0, in which Tr J = a_{11} + a_{22}, is possible, because one of the main diagonal addendums $jk_2 v \exp\left(-\dfrac{Fjv}{RT}\right) > 0$ may

be positive. The positivity of this element is responsible for the positive callback, characteristic for self-accelerated systems.

As in the similar systems [24 – 28], the electrochemical influences of the DEL capacitances' changes are responsible for the oscillatory behavior. As in this system the adsorption, desorption and sollubilization processes are absent, those influences are the unique factor, causing the oscillations.

The oscillations have to be frequent and of little amplitude, due to the instability of pentavalent vanadium compounds in the system's conditions.

The steady-state stability requisite for the two-dimension system is Tr J<0, Det J>0, in which Det J = $a_{11}a_{22}$-$a_{21}a_{12}$. As the first requirement is easy to satisfy, the main condition is the second one. To avoid the cumbersome expressions, we introduce new variables, for the Jacobian determinant to be rewritten as:

$$\frac{2}{\delta V}\begin{vmatrix} -\kappa_1 - V_1 & \Omega_1 \\ V_1 & -\Omega_1 - \Omega_2 \end{vmatrix} \tag{11}$$

Opening the brackets and applying the condition of Det J>0, we obtain the main steady-state stability condition as:

$$\kappa_1(\Omega_1 + \Omega_2) > -V_1\Omega_2 \tag{12}$$

This requirement is easy to be satisfied. Moreover, it is warrantly satisfied in the case of the positivity of electrochemical reaction parameter Ω_2, defining the absence or fragility of influences of the electrochemical reaction on DEL capacitances, leading to the positive callback.

The steady-state is maintained stable by easy manner. The linear dependence between the paraquat concentration and electrochemical parameter (current) is maintained in the vast concentration range, due to steady-state stability. The process is kinetically controlled, but in small analyte concentrations may be considered diffusion-controlled.

The detection limit is corresponding to the steady-state stability margin, defined by the *monotonic instability*. For this system, its main condition is Det J=0, or

$$\kappa_1(\Omega_1 + \Omega_2) = -V_1\Omega_2 \tag{12'}$$

In this case, the system exists in the multiplicity of steady-states, from which it chooses one. It is destroyed, whilst the system conditions are changed.

In the *galvanostatic and potentiodynamic modes* the system behavior may be accomplished and compromised by the possibility of the further tetravalent vanadium reduction to the trivalent, bivalent or metallic form. The model, presented in the research, is capable to describe the behavior of an amperometric or conductometric sensor in potentiostatic mode, and in the case of the galvanostatic and potentiodynamic modes new addendums, corresponding to the further vanadium reduction and potential change are added.

In the case of the possible *solubilization* of pervanadyl-cation, the reactions of its formation and reduction are accompanied by surface phenomena and they are responsible for the oscillatory behavior.

CONCLUSIONS

The theoretical investigation for the vanadium dioxide-assisted electrochemical detection of paraquat let us conclude that:

- VO$_2$ may serve as an excellent cathode modifier for paraquat electrochemical reduction.
- The steady-state in the system is easy to maintain. The linear dependence between the paraquat concentration and electrochemical parameter (current) is maintained in the vast concentration range, due to steady-state stability.

- The process is kinetically controlled, but in small analyte concentrations may be considered diffusion-controlled.
- The oscillatory behavior in the system is possible, being caused only by influences of the electrochemical reaction on DEL capacitances, leading to the positive callback.
- The oscillations have to be frequent and of little amplitude, due to the instability of pentavalent vanadium compounds in the system's conditions.
- In the *galvanostatic and potentiodynamic modes* the system behavior may be accomplished and compromised by the possibility of the further tetravalent vanadium reduction to the trivalent, bivalent or metallic form.
- In the case of the possible solubilization of pervanadyl-cation, the reactions of its formation and reduction are accompanied by adsorption phenomena responsible for the oscillatory behavior.

Conflict of interest

The authors declare that there is no conflict of interests regarding this publication

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