Full Paper

The Theoretical Evaluation of Propoxur Electrochemical Determination over a Conducting Polymer, Saturated With Radical Centers

Volodymyr V. Tkach,[1,2,]* Sílvio C. de Oliveira,[2] Yana G. Ivanushko,[1] Svitlana M. Lukanova,[1] Lyudmyla V. Romaniv,[1] Olena I. Aksimentyeva,[3] Reza Ojani[4] and Petro I. Yagodynets´[1]

[1]Chernivtsi National University, 58012, Kotsyubyns'ky Str., 2, Chernivtsi, Ukraine

[2]Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller, 1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil

[3]Lviv National University, 79005, Kyryl and Mefodiy Str., 6, L´viv, Ukraine

[4]University of Mazandaran, 47416-95447, 3rd km. Air Force Road, Babolsar, Islamic Republic of Iran

*Corresponding Author, Tel.: +380506400359; Fax: +5521991809675

E-Mail: nightwatcher2401@gmail.com

Abstract- The possibility of the electrochemical detection of propoxur pesticide over a conducting polymer, saturated by radical sites, was described from theoretical mechanistic point of view. The correspondent mathematical model was developed and analyzed by means of linear stability theory and bifurcation analysis. It was shown that, despite of the effects of radical coupling, the radical sites saturated conducting polymers may serve as an efficient electrode modifier for propoxur electrochemical detection. The reaction is expected to be diffusion controlled. The oscillatory behavior in this system is possible and may be caused by surface and electrochemical reaction factors.

Keywords- Propoxur, Food safety, Electrochemical sensors, Conducting polymers, Stable steady-state

1. INTRODUCTION

The use of electrochemical methods has been advanced recently in the electrochemical detection of pesticides [1-4], due to several advantages of electrochemical analytical methods, comparing to the rest of them. These advantages are rapidity, low cost and efficiency.

On the other hand, propoxur Propoxur (2-isopropoxyphenyl-N-methylcarbamate), sold as Baygon®, was introduced in 1959 and is one of the most used carbamate pesticides [5]. It has been applied to control numerous species of insects, including *Aedes Aegypti,* transmitting dengue, chikungunya and zika fevers [6-8]. Nevertheless, studies conducted on rats showed that PPX is a carcinogen [9], and exposure to carbamate pesticides during the prenatal period may be associated with leukaemia [10]. Being found on cereal grains and pasture crops due to the steps taken to prevent pest infestations, it is inserted in the food chain of cattle, which can contaminate its milk [11,12]. It acts on both central and peripheral nervous systems by inhibiting the acetylcholinesterase (AChE) enzyme, reducing its biological activity and leading to a range of health problems [13,14] because AChE removes the excess neurotransmitter acetylcholine, which interrupts the nerve synapse [15]. Despite of the mentioned health effects, it is still used, so the development of a method, capable to detect its presence and concentration in different media remains an actual and important problem [16-18].

As propoxur is electrochemically active, the electrochemical methods may be applied to it [16,19-23]. The electrodes, doped with boron [16] and carbon materials [19-23] have been used for its detection, and the use of conducting polymers, combining the properties of plastics with metallic conductivity and being easy to modify [24-29] would be an interesting solution of this problem.

Nevertheless, their application to electrochemical detection of propoxur may confront some difficulties, like:

- The indecision about the mechanism of propoxur electrochemical oxidation and about the recommended strategy of the development of the electroanalytical technique;
- The possibilities of electrochemical instabilities, yet observed during the conducting polymer synthesis and CP-based sensing [30-35];
- Possible influence of radical-cation behavior on the electroanalytical process.

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the electroanalytical system. By modeling it is also capable compare the behavior of this system with that for the similar ones without experimental essays.

So, the general objective of our work is to evaluate, from the mechanistic theoretical point of view, the electrochemical detection of propoxur on radically pretreated conducting polymers. To achieve it, we realize the specific goals:

- Suggestion of the mechanism of the electroanalytical 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 [36-42].

2. SYSTEM AND ITS MODELING

Taking into account the reaction kinetics [16,19-23], it is possible to suggest the mechanism of propoxur electrochemical oxidation as represented on the Fig. 1:
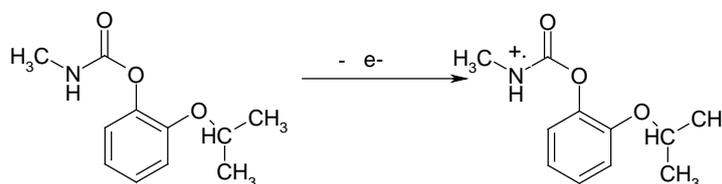

Fig. 1. Propoxur electrochemical oxidation, yielding a cation-radical

The formed cation-radicals are then coupled one with another, and two protons are formed, yielding a low-molecular product, leaving the surface. But when the reaction is realized over radically pretreated conducting polymers, they are also capable to recombine with radical sites present on the polymer structure, modifying the macromolecule. The similar process has been observed in the case of carbendazim electrochemical oxidation, in which the NH – CO – group also undergoes the radical formation (in the initial stage) in the similar conditions [43-45].

The aromatic fragment may also be oxidized, and its product, bearing a radical site is even capable to promote the polymerization.

Taking into account the mentioned statements, to describe this system mathematically, we introduce three variables:

c – propoxur concentration in the pre-surface layer;

θ – propoxur surface coverage degree on polymer layer;

θ^* – propoxur radical-cation coverage degree on polymer layer.

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.

It is possible to show that the system will be represented by a classic model, similar to that represented in the section 2 of the work [46]:

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) + r_{-1} - r_1\right) \\ \quad \frac{d\theta}{dt} = \frac{1}{G}(r_1 - r_{-1} - r_2) \\ \quad \frac{d\theta*}{dt} = \frac{1}{G}(r_2 - r_{31} - r_{32}) \end{cases} \tag{1}$$

In which Δ is the diffusion coefficient, c_0 is propoxur bulk concentration r_{-1} and r_1 are its desorption and adsorption rates, G is its maximal surface concentration, r_2 is its electrochemical oxidation rate, r_{31} and r_{32} are radical recombination rates.

The case, in which the propoxur electrochemical oxidation may be described by the models, represented in [46], like also by those valid for the similar systems [47-49] will be described below.

The correspondent reaction rates may be calculated as:

$$r_1 = k_1 c (1 - \theta - \theta*) \exp(\alpha\theta) \tag{2}$$
$$r_{-1} = k_{-1}\theta \exp(-\alpha\theta) \tag{3}$$
$$r_2 = k_2\theta \exp\left(\frac{F\gamma\theta}{RT}\right) \tag{4}$$
$$r_{31} = k_{31}\theta^{*2} \exp(-\beta\theta*) \tag{5}$$
$$r_{32} = k_{31}\theta^* \exp(-\varepsilon\theta*) \tag{6}$$

In which the parameters k are the rate constants of corresponding reactions, the parameter α is describing the interaction of propoxur adsorbed particles, β, the mutual interaction of its cation-radicals, ε, the radicals´ interaction with the radical sites on the polymer surface, F is the Faraday number, γ is the parameter, describing the DEL influences of the electrochemical oxidation, R is the universal gas constant and T is the absolute temperature.

In general, this model may be considered similar to those, observed for the carbendazim electrochemical detection [45] or for the chain propagation of conducting polymers on the first stage [46]. Nevertheless, the factor of the solubilization of the low-molecular recombination products, like also the interactions of the radicals with the polymer surface influence the system's behavior strongly, making its behavior slightly different, which will be discussed below.

3. RESULTS AND DISCUSSION

To investigate the behavior of the electrochemical oxidation of propoxur on radically-pretreated polymer layer, we analyze the differential equation set (1) by means of linear stability theory. The Jacobian functional matrix steady-state elements, in this case, may be exposed as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{7}$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_1(1 - \theta - \theta*)\exp(\alpha\theta)\right) \tag{8}$$

$$a_{12} = \frac{2}{\delta}(k_{-1}\exp(-\alpha\theta) - \alpha k_{-1}\theta\exp(-\alpha\theta) + k_1 c\exp(\alpha\theta) - \alpha k_1 c(1 - \theta - \theta*)\exp(\alpha\theta)) \tag{9}$$

$$a_{13} = \frac{2}{\delta}(k_1 c\exp(\alpha\theta) \quad) \tag{10}$$

$$a_{21} = \frac{1}{G}(k_1(1 - \theta - \theta*)\exp(\alpha\theta)) \tag{11}$$

$$a_{22} = \frac{1}{G}\left(-k_{-1}\exp(-\alpha\theta) + \alpha k_{-1}\theta\exp(-\alpha\theta) - k_1 c\exp(\alpha\theta) + \alpha k_1 c(1 - \theta - \right.$$
$$\left. \theta*)\exp(\alpha\theta) - k_2\exp\left(\frac{F\gamma\theta}{RT}\right) - \gamma k_2\theta\exp\left(\frac{F\gamma\theta}{RT}\right)\right) \tag{12}$$

$$a_{23} = \frac{1}{G}(-k_1 c\exp(\alpha\theta) \quad) \tag{13}$$

$$a_{31} = 0 \tag{14}$$

$$a_{32} = \frac{1}{G}\left(k_2\exp\left(\frac{F\gamma\theta}{RT}\right) + \gamma k_2\theta\exp\left(\frac{F\gamma\theta}{RT}\right)\right) \tag{15}$$

$$a_{33} = \frac{1}{G}(-2k_{31}\theta^*\exp(-\beta\theta*) + \beta k_{31}\theta^{*2}\exp(-\beta\theta*) - k_{32}\exp(-\varepsilon\theta*) + \varepsilon k_{32}\exp(-\varepsilon\theta*)) \tag{16}$$

Taking into account the expressions (8), (12) and (16), the Jacobian main diagonal elements, we may see, that they contain the addendums, capable to be positive. Those addendums describe the positive callback in the system, so the *oscillatory behavior* is possible in it. Moreover, it is more probable, than in similar systems, either with electrochemical detection [3045], or with electrochemical polymerization [46-49].

Besides of the *attraction of the adsorbed particles,* described by the positivity of $\alpha k_{-1}\theta\exp(-\alpha\theta)$ and $\alpha k_1 c(1 - \theta - \theta*)\exp(\alpha\theta)$, and of the *DEL influences of propoxur electrooxidation,* described by the positivity of $-\gamma k_2\theta\exp\left(\frac{F\gamma\theta}{RT}\right)$, other factors, causing oscillatory behavior in this system are *the radicals' attraction* with the desorption of low-molecular coupling product, described by the positivity of $\beta k_{31}\theta^{*2}\exp(-\beta\theta*)$ and also *the attraction between radicals and the polymer surface,* accelerating their modification, which is described by the positivity of $\varepsilon k_{32}\exp(-\varepsilon\theta*)$. The oscillations are expected to be frequent and of little amplitude.

To investigate the *steady-state stability,* we apply the Routh-Hurwitz criterion to the equation set (1). To simplify the modeling, we introduce new variables, so the Jacobian determinant will be described as:

$$\frac{2}{\delta G^2}\begin{vmatrix} -\kappa_1 - \Xi & X & \xi \\ \Xi & -X - \Lambda & -\xi \\ 0 & \Lambda & -\Sigma \end{vmatrix} \tag{17}$$

Opening the brackets and applying the requisite Det J<0, salient from the criterion, we obtain the stability condition described as:

$$(-\kappa_1 - \Xi)(X\Sigma + \Lambda X + \Lambda \xi) + \Xi(\Lambda \xi + X\Sigma) < 0 \qquad (18)$$

The rearrangement with the successive annihilation of the opposite-sign elements with equal module will transform the requisite (18) into:

$$(-\kappa_1)(X\Sigma + \Lambda X + \Lambda \xi) - \Xi\Lambda X < 0 \qquad (19)$$

The inequation is always satisfied, if the parameters X, Λ and Σ, describing surface and electrochemical influences of the systems, are positive, describing the fragility of the above mentioned influences. So, the steady-state is easy to maintain.

This steady-state stability condition is typical for the similar systems [30-42]. For the electroanalytical means it is correspondent to the linear dependence between the electrochemical parameter and the concentration, so the sensing has to be efficient, and the analytical signal has to be clear. The electroanalytical process is diffusion-controlled, in rare cases, reaction-controlled.

When the destabilizing influences of surface and electrochemical factors are equal, *the monotonic instability* is realized. Being correspondent to the detection limit, it is described as:

$$(-\kappa_1)(X\Sigma + \Lambda X + \Lambda \xi) - \Xi\Lambda X = 0 \qquad (20)$$

It caused, mostly, by surface influences.

In the case of the *application of the potential of the oxidation of the aromatic moiety,* the radical center appears in it. The reaction is capable to yield either low-molecular products, or polymers, so for this case the system will be described by common-case electropolymerization models, described in [46-49].

Yet, in the case of the *application of the potential of the oxidation of the aromatic moiety, with the use of basic solutions,* the pesticide is hydrolyzed before the reaction product's polymerization. This case will be observed in one of our next works.

4. CONCLUSIONS

The mathematical evaluation for the propoxur electrochemical detection on radically pretreated polymer surface let us conclude that:
-   Despite of the presence of many destabilizing factors during the propoxur electrochemical detection, the stable steady-state is easy to maintain and is electroanalytically efficient;
-   The electrochemical response is clear and easy to interpret. The linear dependence between the concentration and electrochemical parameter is observed in vast parameter region;
- The electroanalytical process is diffusion-controlled, or, in some cases, reaction-controlled;

- The oscillatory behavior in this system is possible. Moreover, it is more probable, than in the similar systems, being caused by more factors, than in the common case;
- The oscillations are expected to be frequent and of small amplitude;
- The monotonic instability in this system is possible and may be caused, mostly, by surface influences;
- In the case of the application of the potential of the oxidation of the aromatic moiety, the radical center appears in it, leading to its polymerization, so the system will be described by a convenient electropolymerization model.

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