



RESEARCH ARTICLE

The mathematical description of dopamine electrochemical oxidation, accompanied by its chemical and electrochemical polymerization

Volodymyr V. Tkach^{1,2*}, Marta V. Kushnir¹, Yana G. Ivanushko³, Svitlana M. Lukanova¹, Silvio C. de Oliveira², Petro I. Yagodynets¹

¹Yuriy Fedkovich Chernivtsi National University, 2 Kotsiubynsky St., Chernivtsi, 58012, Ukraine

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

³Bukovinian State Medical University, 9 Teatralna Sq., Chernivtsi, 58000, Ukraine

Abstract: The electrooxidation of dopamine is accompanied by its chemical and electrochemical polymerization, and in which either the monomer or the polymer may be oxidized to the respective quinonic form, was investigated from the theoretical point of view. Dopamine is one of the important neurotransmitters in human and mammal organisms. It is a precursor to epinephrine, which influences the cardiovascular, hormonal and renal functions. Its lack causes diseases like Parkinson, therefore, dopamine has been used as a drug for their treatment. On the other hand, its excess stimulates the sympatic nervous system yielding the metabolic disorders and even schizophrenia. Thus, the development of the rapid and accurate method for its concentration measurement is very important. Dopamine is very popular analyte in electroanalytical systems. The modified electrodes for its determinations have been developed by many researchers. Dopamine is widely used as a monomer for synthesis of a conducting polymer – polydopamine, whis is used as electrodes' modifier in capacitors and in anticorrosive coatings. The electropolymerization of dopamine into polydopamine proceeds along with its traditional quinone-hydroquinonic oxidation. Both processes give their impact to the electrochemical behavior of dopamine during its electropolymerization. The mechanism's complexity is also responsible for the electrochemical instabilities during electro-oxidation. In order to understand these instabilities it's necessary to develop the mathematical model that is capable to describe the behavior of the system. It also helps us to esteem the influence of the electrochemical instabilities, by which it may be accompanied. The goal of this work is to describe an electrochemical oxidation and polymerization of dopamine that will provide an important connection between the electrochemical detection of biologically active compounds and their electropolymerization for electrode modification.

Keywords: dopamine; polydopamine; electrooxidation; electropolymerization; mathematical model.

Introduction

Dopamine is a hormone and one of the major neurotransmitters in human and mammalian organisms [1-4] that is synthesized in the body. It is a member of the catecholamine family of neurotransmitters in the brain and is a precursor to epinephrine (adrenaline) and norepinephrine (noradrenaline) hormones [5]. Its lack causes

illnesses like Parkinson disease [6], therefore it can be used as a drug in medical protocols [7]. Its excess can cause different effects on sympathic segment of neurosystem, methabolic disturbance and even schizophrenia [8]. Therefore, the development of a novel method that is capable to detect its concentration in a rapid, precise, accurate and sensitive way is very important task.

Chemically modified electrodes have various advantages, the main of which is the affinity between the modifier and the analyte, reason why they are one of the modern, cheap and tunable electroanalytic tools. For example, for detection of hydroquinonic compounds, various electrode modifiers of a different nature and composition were developed [9-15]. Some hydroquinonic and quinonic compounds may also serve as electrode

Received: 03.04.2020

Revised: 10.04.2020

Accepted: 14.05.2020

Published online: 30.06.2020

* Corresponding author. Tel.: +380-50-640-0359;
e-mail: nightwatcher2401@gmail.com (V. V. Tkach)
ORCID: 0000-0001-7696-0954

modifiers [16-17]. Dopamine is a polymerizable compound [18] and its polymer can be used as an electrode modifier similarly as of polyalizarine [19]. Moreover, if the supporting electrolyte contains oxidizing ions, they can promote chemical polymerization of dopamine. In order to evaluate the effect of polymerization by the electrochemical (electroanalytical) process it's necessary to investigate the system with polymerization-accompanied electrochemical oxidation of dopamine from mechanistic point of view.

Therefore, it's important to develop and analyze the mathematical model that is capable to describe the behavior of the system. It will be useful us to evalate the influence of the electrochemical instabilities that can be occurred [20-21].

The goal of this work is to evaluate by mechanistic way the influence of chemical and electrochemical polymerization of dopamine and introduce an important connection between the electrochemical detection of biologically active compounds and their electropolymerization.

System and its modeling

The dopamine polymerization is occured in electrode potential lower than for benzolic compounds. It is due to the presence of donor groups (two hydroxyls and an ethylamine group) in the benzene ring, therefore, the number of chemical oxidants that is capable to promote polymerization, has to be higher compared to benzene. The bond between monomer units is formed either by participation of oxygen, or by creating C-C bond between positions 3 and 6 of the ring.

While the hydroquinonic structure is present (at least in part) in the polymer backbone, the polymer can be also oxidized further to its quinonic form. The oxidation of hydroquinonic monomer units makes the system similar to so called "polythiophene paradox" [22]. The electrochemical oxidation of the dopamine polymer is reversable in nature while overoxidation of the same polymer is irreversible. Therefore we can safely assume that these processes are different.

Taking in account the described assumptions, we are introducing three variables:

c – the dopamine concentration in the pre-surface layer;

θ – dopamine coverage degree;

θ_p – polydopamine (chemically, or electrochemically obtained) coverage degree.

In order to simplify the mathematical model, we introduce several assumptions:

- the background electrolyte is present in an excess, therefore we can disregard the migration flow and the oxidizing dopant concentration change;
- the reactor is intensively stirred, so we can disregard the influence of convection flow;

- the concentration profile of dopamine in the pre-surface layer is linear;

- the thickness of pre-surface layer is constant and equal to δ .

It is possible to demonstrate that the differential equations' set that are describing the electrochemical oxidation system can be defined as following:

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (c_0 - c) + r_{-1} - r_1 \right) \\ \frac{d\theta}{dt} = \frac{1}{G} (r_1 - r_{-1} - r_2 - r_{p1} - r_{p2}) \\ \frac{d\theta_p}{dt} = \frac{1}{J} (r_{p1} + r_{p2} - r_3) \end{cases} \quad (1)$$

where Δ is the dopamine diffusion coefficient to from electrolite to the surface, c_0 is its concentration in the solution, G and J are the maximal surface concentration of the dopamine and its polymer correspondingly, and the parameters r are the dopamine rates of adsorption (r_1), desorption (r_{-1}), electrooxidation (r_2), chemical (r_{p1}) and electrochemical (r_{p2}) polymerization, and the rate of polydopamine oxidation (r_3). These rates can be express as following:

$$r_1 = k_1 c (1 - \theta - \theta_p) \exp(\alpha \theta); \quad (2)$$

$$r_{-1} = k_{-1} \theta \exp(-\alpha \theta); \quad (3)$$

$$r_2 = k_2 \theta \exp\left(\frac{2F\gamma\theta}{RT}\right); \quad (4)$$

$$r_{p1} = k_p \theta^n \exp\left(\frac{zF\gamma\theta}{RT}\right) f(\theta_p); \quad (5)$$

$$r_{p2} = k_p \theta^m f(\theta_p); \quad (6)$$

$$r_3 = k_3 \theta_p \exp\left(\frac{jF\xi\theta_p}{RT}\right) \quad (7)$$

where the parameters k are the correspondent reaction rate constants, parameter α is a variable, which describes the interaction between the dopamine adsorbed molecules, F is the Faraday number, z and j are the numbers of transferred electrons during the polymer formation and oxidation correspondingly, γ and ξ are parameters that describes the influences of the electrochemical processes on the double electric layer (DEL) capacitances, R is the universal gas constant, T is the absolute temperature of the solution, f is the function that describes the autocatalytic reaction of the dopamine polymerization and relates to the polymerization's reaction order.

The electrochemical dopamine polymerization system is similar to “the polythiophene paradox” that combines nearly all variables. Its behavior, however, is slightly different, and will be discussed in the next section.

Results and discussion

In order to understand and investigate the behavior of the electrochemical system that includes dopamine's electrooxidation and polymerization we apply a linear

stability theory to equation set (1). Its steady-state Jacobian matrix members can be described as :

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (8)$$

where variables can be described by Equations 9-17 (Figure 1).

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - k_1(1 - \theta - \theta_p) \exp(\alpha\theta) \right) \quad (9)$$

$$a_{12} = \frac{2}{\delta} \left(k_1 c \exp(\alpha\theta) - \alpha k_1 c (1 - \theta - \theta_p) \exp(\alpha\theta) + k_{-1} \exp(-\alpha\theta) - \alpha k_{-1} \theta \exp(-\alpha\theta) \right) \quad (10)$$

$$a_{13} = \frac{2}{\delta} (k_1 c \exp(\alpha\theta)) \quad (11)$$

$$a_{21} = \frac{1}{G} (k_1 (1 - \theta - \theta_p) \exp(\alpha\theta)) \quad (12)$$

$$a_{22} = \frac{1}{G} \left(-k_1 c \exp(\alpha\theta) + \alpha k_1 c (1 - \theta - \theta_p) \exp(\alpha\theta) - k_{-1} \exp(-\alpha\theta) + \alpha k_{-1} \theta \exp(-\alpha\theta) - \right. \\ \left. -k_2 \exp\left(\frac{2F\gamma\theta}{RT}\right) - \gamma k_2 \theta \exp\left(\frac{2F\gamma\theta}{RT}\right) - nk_p \theta^{n-1} \exp\left(\frac{zF\gamma\theta}{RT}\right) f(\theta_p) - \gamma k_p \theta^n \exp\left(\frac{zF\gamma\theta}{RT}\right) f(\theta_p) \right) \quad (13)$$

$$a_{23} = \frac{1}{G} \left(-k_1 c \exp(\alpha\theta) - f'(\theta_p) (k_p \theta^n \exp\left(\frac{zF\gamma\theta}{RT}\right) + k_p \theta^m) \right) \quad (14)$$

$$a_{31} = 0 \quad (15)$$

$$a_{32} = \frac{1}{J} \left(nk_p \theta^{n-1} \exp\left(\frac{zF\gamma\theta}{RT}\right) f(\theta_p) + \gamma k_p \theta^n \exp\left(\frac{zF\gamma\theta}{RT}\right) f(\theta_p) \right) \quad (16)$$

$$a_{33} = \frac{1}{J} \left(f'(\theta_p) (k_p \theta^n \exp\left(\frac{zF\gamma\theta}{RT}\right) + k_p \theta^m) - k_3 \exp\left(\frac{jF\xi\theta_p}{RT}\right) - \xi k_3 \theta_p \exp\left(\frac{jF\xi\theta_p}{RT}\right) \right) \quad (17)$$

$$(-\xi - \Xi)(\Lambda\Sigma + \Omega\Sigma + P\Sigma + PY + PK - K\Lambda - K\Omega - KP) + \Xi(PY - \Lambda K + \Lambda\Sigma) < 0 \quad (30)$$

$$(-\xi - \Xi)(\Lambda\Sigma + \Omega\Sigma + P\Sigma + PY + PK - K\Lambda - K\Omega - KP) + \Xi(PY - \Lambda K + \Lambda\Sigma) = 0 \quad (31)$$

Figure 1. The series of Equations 9-17 and 30-31.

Observing the expressions (8), (12) and (15), it's possible to demonstrate the *oscillatory behavior* of the system. Moreover, it is even more likely occurrence compare to similar systems [20-21]. It happens because the main matrix diagonal contains more positive elements compare to mathematical models for similar systems [20-21, 23-24].

The oscillatory behavior will be observed under following conditions:

- attraction between the adsorbed molecules that are represented by the positivity of the element $+ak_1c(1-\theta-\theta_p)\exp(\alpha\theta)$ and of $+ak_{-1}\theta\exp(-\alpha\theta)$.

This influence factor is common to all similar systems and represents the surface instability that was described experimentally [20-21] and theoretically [23-24];

- strong influence of electrochemical processes on DEL capacitances. This cause is common to all similar systems and represent the electrochemical instability the oscillation amplitudes and electrolyte's composition [20]. In the case of dopamine three electrochemical processes are taking place that can cause changes to electrolyte's conductivity (increases or decreases). Therefore, the DEL capacitance will have its value altered, which will cause the electrochemical oscillations. Mathematically, they are described by the positivity of the elements

$$-\xi k_3 \theta_p \exp\left(\frac{jF\xi\theta_p}{RT}\right), \quad -\gamma k_2 \theta \exp\left(\frac{2F\gamma\theta}{RT}\right) \quad (18)$$

$$(19)$$

$$\text{and} \quad -\gamma k_p \theta^n \exp\left(\frac{zF\gamma\theta}{RT}\right) f(\theta_p) \quad (20)$$

which make part of the main diagonal elements a_{22} and a_{33} .

- the autocatalysis during polymer formation can occur because of rapid transference of an oligomer and a polymer compare to a monomer. This factor as a cause of the oscillatory behavior occurs during the "polythiophene paradox". Mathematically it can be described by the positivity of the element

$$f'(\theta_p)(k_p \theta^n \exp\left(\frac{zF\gamma\theta}{RT}\right) + k_p \theta^m) \quad (21)$$

The oscillatory behavior has three possible causing factors compare to the two factors that are existing in the general [23]. Their factors are being similar to the polythiophene paradox [24].

In order to evaluate the steady-state stability we apply the Routh-Hurwitz stability criterion to the differential equations' set (1). To avoid the appearance of the cumbersome expressions we introduce new variables:

$$\Delta/\delta = \kappa \quad (22)$$

$$k_1(1-\theta-\theta_p)\exp(\alpha\theta) = \Xi \quad (23)$$

$$k_1c\exp(\alpha\theta) - ak_1c(1-\theta-\theta_p)\exp(\alpha\theta) + k_{-1}\exp(-\alpha\theta) - ak_{-1}\theta\exp(-\alpha\theta) = \Lambda \quad (24)$$

$$k_1c\exp(\alpha\theta) = Y \quad (25)$$

$$k_2\exp\left(\frac{2F\gamma\theta}{RT}\right) + \gamma k_2\theta\exp\left(\frac{2F\gamma\theta}{RT}\right) = \Omega \quad (26)$$

$$nk_p\theta^{n-1}\exp\left(\frac{zF\gamma\theta}{RT}\right)f(\theta_p) + \gamma k_p\theta^n\exp\left(\frac{zF\gamma\theta}{RT}\right)f(\theta_p) = P \quad (27)$$

$$k_3\exp\left(\frac{jF\xi\theta_p}{RT}\right) - \xi k_3\theta_p\exp\left(\frac{jF\xi\theta_p}{RT}\right) = \Sigma \quad (28)$$

so the Jacobian determinant can be described as following:

$$\frac{2}{\delta GJ} \begin{vmatrix} -\kappa - \Xi & \Lambda & Y \\ \Xi & -\Lambda - \Omega - P & -Y - K \\ 0 & P & K - \Sigma \end{vmatrix} \quad (29)$$

Opening the brackets and applying to the determinant the requirement $\text{Det } J < 0$ that is derived from the criterion we can obtain the steady-state stability condition that is described in Equation 30 (Figure 1).

The topological area of satisfaction of the inequation (30) is less than in the similar cases, including even the case of the polythiophene paradox [20-24]. Nevertheless, the steady-state stability is easy to maintain as it will be warranted to be stable if:

- the repulsion between the adsorbed particles that is described by the positivity of the parameter Λ when the parameter α is negative. Together with the satisfaction of the conditions exposed below, the element $\Lambda\Sigma$ is maintained positive, and the left-side expression of the inequation is more negative;

- the influence of the electrochemical processes to the DEL capacitances that is described by the positivities of the parameters Ω , P and Σ . Each parameter corresponds to the certain electrochemical process – electrooxidation (Ω), electropolymerization (P) and the polymer electrooxidation (Σ). In the case of the positivity of the these parameters the expression $\Lambda\Sigma + \Omega\Sigma + P\Sigma + PY$ will have the a positive value, and it will "push" the left-side expression of the

inequation (30) to more negative values, resulting in its satisfaction;

- the absence or fragility of autocatalytic effect during electropolymerization. If the autocatalysis isn't realized, $f(\theta)=\text{const}$ and $f'(\theta)=0$, which annihilates the elements containing the parameter K , the nullity or negativity of which "pushes" the left-side expression of the inequation (30) to more negative values, satisfying the steady-state stability condition.

Depending on dopamine concentration and on electrode's shape the electrochemical process can be diffusion-controlled or adsorption-controlled.

It will correspond to a linear dependence between an electrochemical parameter and a dopamine concentration from the electroanalytical point of view. It will correspond to a polymer formation from electrosynthetic point of view.

The monotonic instability is also probable if the destabilizing and stabilizing influences are equal and it relates to a detection limit from the electroanalytical point of view. It will be caused by an autocatalysis and its conditions can be described by Equation 31 (Figure 2).

Not only dopamine, but also other compounds that are having a hydroquinonic structural characteristics and active sites for electropolymerization can undergo the process that is described in this work. For example, acetaminophen (paracetamol) can be also polymerized [25]. Its electrochemical detection on poly- (aniline blue) electrodes was reported [26] and described theoretically [27]. The section 2 reported electropolymerization that was accompanied by electrochemical detection of paracetamol over polymeric surface. Our model can be used to described polyacetaminophen electrooxidation.

Conclusions

The analysis of dopamine electrooxidation that is accompanied by chemical and electrochemical polymerization allow us to conclude that:

- the stable steady-state, despite to the narrower parameter topological zone, can be easily maintain. The factors, which are warranting the steady-state stability, are repulsion between particles, fragility of DEL influences of electrochemical processes and the absence or fragility of autocatalysis
- depending on dopamine concentration, the electrode area and the presence of active sites, the process will be controlled by diffusion or by adsorption;
- the oscillatory behavior in this case is more probable than in the cases of electropolymerization. It caused by a surface, an electrochemical and an autocatalytical factors;
- the monotonic instability of this system can appear and can be caused by autocatalysis in electropolymerization.

Notes

The authors declare no conflict of interest.

Author contributions. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

References

1. Fellous, J.-M.; Suri, R. E. The Roles of Dopamine. In *The Handbook of Brain Theory and Neural Networks*, 2nd Ed.; Arbib, M. A., Ed.; MIT Press: Cambridge, MA, 2003; pp 361-365.
2. Benes, F. M. Carlsson and the discovery of dopamine. *Trends in Pharmacol. Sci.* **2001**, 22, 46-47.
3. Dopamine, CID=681. In PubChem Database. National Center for Biotechnology Information [Internet]. Available from: <https://pubchem.ncbi.nlm.nih.gov/compound/dopamine#section=Use-and-Manufacturing> (accessed on April 03, 2020).
4. Dopamine, GtoPdb Ligand ID: 940. In IUPHAR Database (IUPHAR-DB) via the Guide to PHARMACOLOGY website [Internet]. Available from: <http://www.guidetopharmacology.org/GRAC/LigandDisplayForward?tab=biochemistry&ligandId=940> (accessed on April 03, 2020).
5. Kirshner, N.; Goodall, M. C. The formation of adrenaline from noradrenaline. *Biochim. Biophys. Acta* **1957**, 24, 658-659.
6. Triarhou, L. C. Dopamine and Parkinson's Disease. In *Madame Curie Bioscience Database* [Internet]. (Austin, TX: Landes Bioscience;) 2000-2013. Available from: <https://www.ncbi.nlm.nih.gov/books/NBK6271/> (accessed on April 03, 2020).
7. Seeman, P. Glutamate and dopamine components in schizophrenia. *J. Psychiatry Neurosci.* **2009**, 34, 143-149.
8. Costa, M. de L.; Loria, A.; Marchetti, M.; Balaszczuk, A. M.; Arranz, C. T. Effects of dopamine and nitric oxide on arterial pressure and renal function in volume expansion. *Clin. Exp. Pharmacol. Physiol.* **2002**, 29, 772-776.
9. Sasso, L.; Heiskanen, A.; Diazi, F.; Dimaki, M.; Castillo, J.; Vergani, M.; Landini, E.; Raiteri, R.; Ferrari, G.; Carminati, M.; Sampietro, M.; Svendsen, W. E.; Emnéus, J. Doped Overoxidized Polypyrrole Microelectrodes as Sensors for the Detection of Dopamine Released from Cell Populations. *Analyst* **2013**, 138, 3651-3659.
10. Scarpetta, A.; Mariño, K.; Bolaños et al. Determination of hydroquinone using a glassy carbon electrode modified with chitosan, multi-wall carbon nano-tubes and ionic liquid. Possible use as sensor. *Rev. Colomb. Cienc. Quim. Farm.* **2015**, 44, 311-321. (In Spanish).
11. Ankireddy, R.; Kim, J. Selective detection of dopamine in the presence of ascorbic acid via fluorescence quenching of InP/ZnS quantum dots. *Int. J. Nanomed.* **2015**, 10, 113-119.
12. Fayemi, O. F.; Adekunle, A. S.; Ebeso, E. E. Metal oxide nanoparticles/multi-walled carbon nanotube nanocomposite modified electrode for the detection of dopamine: comparative electrochemical study. *J. Biosens. Bioelectr.* **2015**, 6, 190-204.
13. Peik-See, T.; Pandikumar, A.; Nay-Ming, H.; Hong-Ngee, L.; Sulaiman, Y. Simultaneous electrochemical detection of dopamine and ascorbic acid using an iron oxide/reduced graphene oxide modified glassy carbon electrode. *Sensors* **2014**, 14, 15227-15243.
14. Vishwanatha, C. C.; Swamy, B. E. K.; Pai, K. V. Electrochemical Studies of Dopamine, Ascorbic Acid and Uric Acid at Lignin Modified Carbon Paste Electrode by Cyclic Voltammetric. *J. Anal. Bioanal. Tech.* **2015**, 6, 237-242.
15. Raoof, J. B.; Kiani, A.; Ojani, R.; Valliolahi, R. Electrochemical determination of dopamine using banana-MWCNTs modified carbon paste electrode. *Anal. Bioanal. Electrochem.* **2011**, 3, 59-66.
16. Ojani, R.; Rahimi, V.; Raoof, J. A new voltammetric sensor for hydrazine based on michael addition reaction using 1-amino-2-naphthol-4-sulfonic acid. *J. Chin. Chem. Soc.* **2015**, 62, 90-96.
17. Khajvand, T.; Ojani, R.; Raoof, J. B. Tetrachloro-ortho-Benzoquinone as Catalyst for Electrocatalytic Oxidation of Sulfite in Acidic Media and its Analytical Application. *Anal. Bioanal. Electrochem.* **2014**, 6, 501-514.
18. Wang, J. L.; Li, B. C.; Li, Z. J. et. al. Electropolymerization of dopamine for surface modification of complex-shaped cardiovascular stents. *Biomaterials* **2014**, 35, 7679-7689.

19. Mahantesha, K. R.; Swamy, B. E. K.; Pai, K. V. Poly (alizarin) Modified glassy carbon electrode for the electrochemical investigation of omeprazole: A voltammetric study. *Anal. Bioanal. Electrochem.* **2014**, 6, 234-244.
20. Das, I., Agrawal, N.R.; Ansari, S. A.; Gupta, S. K. Pattern formation and oscillatory polymerization of thiophene. *Ind. J. Chem.* **2008**, 47A, 1798-1803.
21. Tkach, V.; Nechyporuk, V.; Yagodynets, P. Electropolymerization of heterocyclic compounds. Mathematical models. *Ciênc. Tecn. Mat.* **2012**, 24, 54-58 (In Portuguese).
22. Krische, B.; Zagorska, M. The polythiophene paradox. *Synth. Met.* **1989**, 28, 263-268.
23. Tkach, V.; Nechyporuk, V.; Yagodynets, P. Description matematica de la sintesis electroquimica de polimeros conductores en la presencia de surfactants. *Avances en. Quimica.* **2013**, 8, 9-15 (In Spanish).
24. Tkach, V.; Ojani, R., Nechyporuk, V.; Yagodynets, P. The mathematical description for the sensor of dopamine, based on carbon paste electrode, modified by nanotubes and banana tissues. *Rev. Colomb. Cienc. Quim. Farm.* **2015**, 44, 58-71 (In Portuguese).
25. Li, Y.; Chen, Sh. M. The Electrochemical Properties of Acetaminophen on Bare Glassy Carbon Electrode. *Int. J. Electrochem. Sci.* **2012**, 7, 2175-2187.
26. Vishwanath, C. C.; Swamy, B. E. K. Electrochemical studies of paracetamol at Poly (Aniline Blue) modified carbon paste electrode: A voltammetric study. *Anal. Bioanal. Electrochem.* **2014**, 6, 573-582.
27. Tkach, B. Kumara-Swamy, R. Ojani et al. Paracetamol behavior during the electrocatalytic oxidation of poly (aniline blue) and its mathematical description. *Rev. Colomb. Cienc. Quim. Farm.* **2015**, 44, 148-161 (In Portuguese).

Математичний опис електроокиснення допаміну, що супроводжується його хімічною та електрохімічною полімеризацією

В. В. Ткач^{1,2*}, М. В. Кушнір¹, Я. Г. Іванушко³, С. М. Луканова¹, С. С. де Олівейра², П. І. Ягодинець¹

¹ Чернівецький національний університет імені Юрія Федьковича, вул. Коцюбинського, 2, Чернівці, 58012, Україна

² Федеральний університет штату Мату-Гросу-ду-Сул, просп. Сенадора Філіто Мюллера, 1555, Кампу-Гранді, Мату-Гросу-ду-Сул, 79074-460, Бразилія

³ Буковинський державний медичний університет, пл. Театральна, 2, Чернівці, 58002, Україна

Резюме: Цікавий випадок електроокиснення допаміну, що супроводжується його хімічною та електрохімічною полімеризацією, в умовах якої як мономер, так і полімер можуть електрохімічно окиснюватися, досліджено з теоретичної точки зору. Допамін – один із найважливіших нейротрансмітерів в людських організмах, а також в організмах інших ссавців. Він є прекурсором епінефрину – однієї із найважливіших молекул нейротрансмітерів з важливими впливами на функції серцево-судинної системи, гормонального апарату, нирок тощо. Його нестача стає причиною ряду хвороб – таких, як хвороба Паркінсона. Відтак, допамін використовується як лікарський препарат при їх лікуванні. З іншого боку, надлишок допаміну призводить до стимулювання симпатичної нервової системи, метаболічних порушень і навіть шизофренії. Відтак, розробка методу його визначення точно і швидко – дійсно актуальна задача. Сам по собі допамін є дуже популярним аналітом в електроаналітичних системах. Модифіковані електроди для його визначення були розроблені багатьма вченими. Допамін також широко використовується як мономер провідного полімеру – полідопаміну, який використовується як модифікатор електроду у конденсаторах та як протикорозійне покриття. Оскільки електрополімеризація допаміну іде паралельно з його традиційним окисненням за хінон-гідрохінонним механізмом, обидва процеси вносять свій вклад в електрохімічну поведінку допаміну під час його електрополімеризації. Відтак гібридність механізму теж стає відповідальною за появу електрохімічних нестійкостей при електроокисненні допаміну, що супроводжується його електрополімеризацією. Вони можуть призводити до ускладнення інтерпретації аналітичного сигналу, а також до поломки електрохімічного обладнання. Щоби з'ясувати імовірність появи цих нестійкостей, необхідно априорно дослідити поведінку у даній системі з теоретичної точки зору, що і відбувається у цій роботі. Для цього поведінку в електроаналітичному процесі описується системою трьох балансових диференціальних рівнянь, аналіз якої показує, що: а). Стійкість стаціонарного стану, незважаючи на звуження топологічної області параметрів, яка їй відповідає, підтримується легко. Фактори, що забезпечують стійкість стаціонарного стану – відштовхуюча взаємодія адсорбованих молекул мономеру або полімеру, слабкість впливів електрохімічних процесів на подвійний електричний шар та відсутність або слабкість автокаталізу; б). В залежності від концентрації допаміну та активної площі електроду, електроаналітичний процес може бути дифузійно- або адсорбційно-контрольованим; в). Осциляторна поведінка в цьому випадку стає більш імовірною, ніж в загальних випадках електрополімеризації. Вона спричиняється поверхневими, електрохімічними та автокаталітичними факторами; - монотонна нестійкість в цій системі можлива. Вона спричиняється головню факторами автокаталітичного росту ланцюга.

Ключові слова: допамін; полідопамін; електроокиснення; електрополімеризація; математична модель.