Full Paper

The Mathematical Description for the Hydrazine Detection by Michael Reaction with Naphtholaminosulphonic Acids

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Abstract- The electroanalytical system with the hydrazine detection by Michael addition reaction with naphthlaminosulphonic acids was mathematically described. The corresponding mathematical model has been developed and analyzed by linear stability theory and bifurcation analysis. The steady-state stability conditions, corresponding to the better response, were developed. The presence of oscillatory and monotonic instabilities was also confirmed.

Keywords- Hydrazine, Naphtholaminosulphonic acid, Electrochemical sensors, Electrochemical oscillations, Steady-states stability

1. INTRODUCTION

Hydrazine, as a simplest diamine with the formula N_2H_4. Due to its basic properties and nucleophilicity, it is widely used as a starting compound and a catalyst in organic synthesis [1-3], for example, of heterocyclic compounds. The proper compound and its derivatives may

be used in the preparation of fuels (for missiles and fuel cells), explosives, pesticides and corrosion inhibitors. At the other hand, it is toxic compound, capable to be absorbed by the skin, affecting blood production and causing kidney and liver damages [4–6]. Its effect in each of mentioned class of systems depends on its concentration, thus, the search of the hydrazine detection method capable to determinate it by rapid, efficient and precise way is, without a doubt, an actual problem [7].

Many analytical non-electrochemical [8–10] and electrochemical [11–14] techniques have been suggested for the hydrazine detection and the electrochemical techniques represent as an advantage their rapidity, simplicity, high sensitivity, reproducibility and clear response [15,16].

Unfortunately, there are several difficulties in realizing the direct hydrazine oxidation, like the overvoltage, appearing during the electrooxidation on metal bare electrodes [17], oscillatory and monotonic instabilities, supporting the process [18] and difficulty to detect the exact oxidation mechanism for a concrete media [19]. Two promising approaches may be used in purpose to reduce the overvoltage. One of them is the use of specific electrode material, like carbon paste and glassy carbon [20–40], titanium dioxide [41], or conducting polymers [42–50], and the use of specific electron transfer mediator, like curcumin [51], iron phthalocyanine [52], hematoxylin [53], catechin [54], dyes and complex compounds [55–58], metal oxide nanoparticles [59] and ferrocene derivatives [60–70].

Nonetheless, as it was mentioned, the problem of the overpotential and overvoltage isn´t unique in the aspect and even when it´s resolved, the problem of electrochemical instabilities, capable to appear during the oxidation of different organic compounds ([71–80], including the electropolymerization systems) may remain and its resolution needs finding the causes and reason of their appearance.

A phenomenological explanation, usually given to these occurrences, may be based on logical facts, but it hasn´t a rigid theoretical foundation, which may be only given by the development and analysis of a mathematical model, capable to describe adequately the processes in the system. Also it helps to resolve the third problem, because gives the possibility to detect the most probable behavior scenario. Besides of this, the modeling has prognostic function, because it helps to predict the electroanalytical behavior of the systems, that haven´t analyzed.

In the work [81], a new voltammetric sensor for hydrazine, based on Michael reaction, using aminonaphtholsulphoacid, has been described. So, the goal of this work is to continue the investigation, begun in [81], and to confirm mathematically the phenomenological mechanism, suggested in the mentioned work, we develop and analyze its mathematical model. It is also a mean to compare the mentioned system with other similar electroanalytical systems, based on conducting polymers, ferrocene and copper oxide nanoparticles, described in [82–97].

2. SYSTEM AND ITS MODELING

The general mechanism of the electroanalytical function of quinonic systems may be described like:

Anal (Init.) + Q → Anal (Ox.) + H$_2$Q   (1)

H$_2$Q – 2e$^-$ → Q + 2H$^+$ (2)
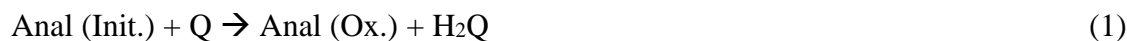
But in the system of [81], the system is more complicated and we may call it *double respiration quinonic electroanalytical scenario,* using the term of avian biology [98].

H$_2$Q – 2e$^-$ → Q + 2H$^+$ (3)

Q + H$_2$An → H$_2$QAn   (4)

H$_2$QAn – 2e$^-$ → QAn + 2H$^+$ (5)

As the conjugated system in the compound, modified by Michael reaction (4), is longer (due to the lone pairs of nitrogen atoms), and the positive mesomer effect is more intensive, than the negative inductive effect, the reaction (5) occurs in lower potential, than the reaction (3).

Such a mechanism is pH-dependent, so the presence of protons, or other interfering particles may provoke side reactions. So, the best pH value for the sensor function has to be equal to 7, and in order to describe mathematically the behavior of the system (3–5), in neutral media and in absence of other interfering compounds, we introduce three variables:
c – hydrazine concentration in pre-surface layer;

Q – the coverage degree of the Q-form of the quinonic (or, better, quinoneiminic) compound of the equation (4);

Θ – the coverage degree of the Michael adduct H$_2$QAn.

In order 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 (containing the main dopant) is in excess, so we can neglect the migration flow. The concentration profile of the monomer and the alkali in pre-surface layer (with constant thickness, equal to δ) is supposed to be linear. Also we suppose, that at the very beginning, the H$_2$Q form covers the entire electrode surface.

The analyte Enters the pre-surface layer by diffusion and leaves it, entering in the Michael reaction with the Q-form of the quinonic compound. So, taking in account the first Fick law, and the bimolecular pre-surface layer modeling coefficient, we may describe the hydrazine balance equation as:

$$\frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_2\right)$$ (6)

In which Δ is analyte diffusion coefficient, c_0 its bulk concentration and r_2 is the Michael reaction rate.

The quinonic compound Appears by oxidation of an initial, hidroquinonic form, and then enters in the Michael reaction, forming an adduct. So, its balance equation may be described as:

$$\frac{dQ}{dt} = \frac{1}{G}(r_1 - r_2) \tag{7}$$

in which G is the quinonic compound maximal surface concentration, r_1 is the initial form oxidation rate.

The analyte modified hydroquinonic compound is a Michael adduct, that is formed by Michael reaction and then oxidized to its final quinonic form. Thus, its balance equation may be written like:

$$\frac{d\Theta}{dt} = \frac{1}{H}(r_2 - r_3) \tag{8}$$

In which H is the adduct maximal surface concentration and r_3 is an adduct oxidation rate. The reaction rates may be calculated as:

$$r_1 = k_1(1 - Q - \Theta) \exp\left(\frac{2F\varphi_0}{RT}\right) \tag{9}$$

$$r_2 = k_2 cQ \tag{10}$$

$$r_3 = k_1 \Theta \exp\left(\frac{2F\varphi_0}{RT}\right) \tag{11}$$

in which the parameters k are the rate constants of respective reactions, F is Faraday number, φ_0 is the potential slope in DEL (double electric layer), relative to zero-charge potential, R is universal gas constant and T is absolute temperature.

The model is very similar to these described for conducting polymers [82–92], ferrocene [93–95] and metal nanoparticles [96–97] which confirms the third theorem of similarity (the similar systems are described by similar equations). But now, as the system is more complicated and adapted to the electrochemical and chemical behavior of participating compounds, and the differences between the following system and the yet described will be exposed in the next section.

3. RESULTS AND DISCUSSION

To investigate the behavior of the system, described by the reactions (3–5), we have to analyze the equation set (6–8), taking in account the algebraic equations (9–11) by linear

stability theory. The Jacobi functional matrix, the members of which are calculated for a steady-state may be described as:

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

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_2 Q\right) \tag{13}$$

$$a_{12} = \frac{2}{\delta}(-k_2 c) \tag{14}$$

$$a_{13} = 0 \tag{15}$$

$$a_{21} = \frac{1}{G}(-k_2 Q) \tag{16}$$

$$a_{22} = \frac{1}{G}\left(-k_1 \exp\left(\frac{2F\varphi_0}{RT}\right) - a_1 k_1 (1 - Q - \Theta) \exp\left(\frac{2F\varphi_0}{RT}\right) - k_2 c\right) \tag{17}$$

$$a_{23} = \frac{1}{G}\left(-k_1 \exp\left(\frac{2F\varphi_0}{RT}\right) - a_2 k_1 (1 - Q - \Theta) \exp\left(\frac{2F\varphi_0}{RT}\right)\right) \tag{18}$$

$$a_{31} = \frac{1}{H}(k_2 c) \tag{19}$$

$$a_{32} = \frac{1}{H}(k_2 Q) \tag{20}$$

$$a_{33} = \frac{1}{H}\left(-k_1 \exp\left(\frac{2F\varphi_0}{RT}\right) - a_2 k_1 \Theta \exp\left(\frac{2F\varphi_0}{RT}\right)\right) \tag{21}$$

In which a_1 and a_2 are coefficients, which describe the relation between the coverage degree and DEL capacitance.

To simplify the Jacobian analysis, avoiding the appearance of huge mathematical expression, we introduce new variables and the Jacobian determinant will be described as:

$$\frac{2}{\delta GH} \begin{vmatrix} -\kappa - X_1 & -\Pi_1 & 0 \\ -X_1 & -\ddot{\Omega} - \Pi_1 & \Pi_2 \\ X_1 & \Pi_1 & -\Sigma \end{vmatrix} \tag{22}$$

In which κ is a diffusion parameter, X_1 and is a Π_1 are Michael reaction parameters, Ω, Π_2 and Σ are electrochemical reactions' parameters.

3.1. Steady-state stability

Using the Routh-Hurwitz steady-state stability criterion and resolving the inequation (22)<0, we obtain the steady-state stability requisite:

$$-\kappa(\Sigma\Omega + \Sigma\Pi_1 - \Pi_1\Pi_2) < X_1\Sigma\Omega \tag{23}$$

Comparing to the inequations, described in [82–97] in this system the steady-state stability is more influenced by diffusion, which not only confirms the diffusion-controlled reaction, but also confirms that the influence of the analyte diffusion on this reaction is even stronger, than in the cases of [82–97], in which the steady-state stability expressions had less diffusion-dependent elements (despite of the diffusion-controlled reactions in the majority of the described cases). It may explain theoretically the comparation, described in the Table 2 of [81].

Moreover, the high level of X_1 and Π_1 with the negativity of Π_2 and the positivity of Σ and Ω shows that the acceleration of the Michael reaction and the absence of the influences of the electrochemical reactions (3) and (5) on DEL. In this case, the expression on the right side of the inequation will be positive and the left side will be negative and the steady-state will be stable. The zone of steady-state stability is corresponding to the linear part of the curve between electrochemical parameter and analyte concentration, so it goes in accord with the described in [81].

In the case of the equality of the influences, described above, the monotonic instability is realized and its condition is:

$$-\kappa(\Sigma\Omega + \Sigma\Pi_1 - \Pi_1\Pi_2) = X_1\Sigma\Omega \tag{24}$$

In this point the system is in the steady-state multiplicity and various unstable steady-states coexist. The system chooses one of them and it is destroyed, when the conditions are changed.

The oscillatory behavior for this system is possible in the Hopf bifurcation condition. For its realization the obligatory condition is the presence of positive elements in Jacobian main diagonal. There are two elements, capable to be positive: $-\ddot{\Omega}$, if the initial quinonic compound isn't a strong reducent and $-\Sigma$, if the Michael adduct is a strong reducent, so the oscillatory behavior, if any, will be caused by the factors of the influence of electrochemical reactions on DEL, which is the common factor for all the systems with the electroanalytical function of conducting polymers, ferrocene and other conjugated compounds, like also metal nanoparticles [82– 97].

3.2. The possible autocatalytic reaction

In general, Michael reaction isn't autocatalytic, but if the reaction between a quinonic compound does have autocatalytic properties, the autocatalysis will be one more cause for oscillatory behavior, like in [82–97].

3.3. The influence of interfering compounds

The acid and basic media in particular, like the presence of interfering compounds in general, diminish the possibility of the sensor to detect hydrazine, reacting with the analyte and all the forms of quinonic compound (especially in the acid media). Thus, the curve pH – electrochemical parameter really has to have its peak on pH=7, but it won't be symmetric. The pattern of the curve concentration of the interferent–electrochemical parameter will depend on the properties of this compound, like in [87–92].

This model may be applied not only to the concrete system [81], but for possible use of other quinonic-hydroquinonic systems, capable to enter in Michael addition, like: alizarine and its conducting polymer, which may give tips for the behavior of yet not prepared electroanalytical systems. It is very important for the investigation of electroanalytical behavior of hydrazine.

4. CONCLUSIONS

The electroanalytical behavior of hydrazine in the presence of quinonic system, entering in the Michael reaction, may be described by the mechanism of *"double respiration quinonic electroanalytical scenario"*, positively different from the common one. The steady-state stability is diffusion-controlled, and even more dependent of diffusion, than in analogous electroanalytical systems. The steady-state stability is warranted by rapid diffusion and Michael reaction, with the absence of the influences of electrochemical processes on DEL. It makes the electroanalytical system more exact, that in analogous case. The oscillatory and monotonic instabilities are possible, but only in the case of strong influences of electrochemical processes on DEL and in the case of autocatalytic reactions (if any). The described experimental system doesn't contain the last case. Other quinonic system, capable to enter in the Michael addition (like alizarine and its conducting polymer) will behave by the nearly same way, so the model is capable to predict the behavior of the non-observed sensors.

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