



The Mathematical Modeling for the Work of Electrochemical Sensors and Biosensors, Based On Conducting Polymers, In The Process Of the Common Detection of Two Sulfonic Acids

V.V. Tkach^{1,2*}, Y. G. Ivanushko¹, S. M. Lukanova¹, L.V. Romaniv¹, S.C. de Oliveira², R. Ojani³ and P.I. Yagodynets¹

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, CEP: 79074-460, Campo Grande, MS, Brasil

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

*Corresponding author: E-mail: vovovlademir@mail.ru

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Abstract

The mathematical model for the potentiostatic work of CP-based electrochemical sensors and biosensors, used for the detection of two strong organic acids with the common “acid” functional group (using the example of $-\text{SO}_3\text{H}$ group), was developed and analyzed by the using of 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: food safety, intoxication prevention, sulphoacid, conducting polymer, electrochemical sensors, electrochemical oscillations, steady-states' stability.

Introduction

The conducting polymers (CP), being one of the most studied modern class of organic compounds, attract more and more attention, because they are capable to combine the properties of plastics (corrosion resistance, light weight, tough, resiliency and versatility in shaping), flexibility in modification and metallic conductivity [1 – 10]. As they are easily modified, they are one of the “tunable” materials, or, better saying, it's possible to synthesize the CP, capable to be used in different purposes, beginning with the anti-corrosive coatings and ending with sensors and biosensors.

The sulfoacids are very important compounds in organic chemistry, biochemistry, material chemistry and also in organic analytics, because they have wide spectrum of use (Fig. 1).

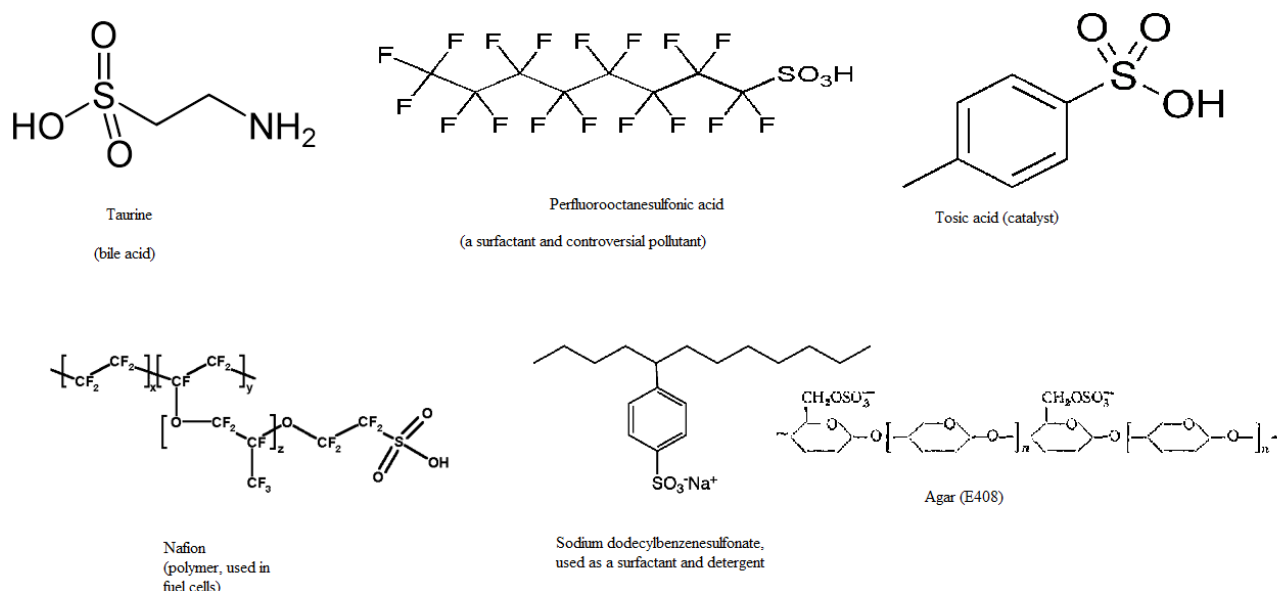


Fig.1 Some of the most important sulfoacids

It is known, for example, that the taurin concentration, forming itself in the process of cystein metabolism, could show us the concentration of sulfurorganic groups in food and also the detoxication process investigation [11 – 12]. Nafion-1-3 is a sulfoacid polymer, used as a proton conductor in fuel cells. Also, the agar (E406) used in sweets production, in bacteria quantification and electrochemical investigations [13 – 14], is in fact sulfoacid, and its concentration in sweets could be better detected by sulfogroup, than by glucopyranose fragments, because their general analysis isn't selective enough. Also, tonic acid is used as a catalyst in organic synthesis [15 – 16]. On the other hand, the sulfoacids and their derivatives, despite of their wide use, may be severely toxic (together with their combustion products), as in the case of perfluorooctanesulfoacid, a surfactant [17] with different spectrum of uses, sodium dodecylbenzene, two forms of which are toxic, while used in excess [18], and nafion, polymer, used in fuel cells [19 – 20]. So, the development of an exact, precise, rapid and efficient technique for their analysis is, without a doubt, an actual task.

As the sulfoacids are excellent electrolytes, it is possible to apply two detection strategies for them. The first is the doping of the CP, used for the sensor, with the analyzed sulfoacid with the change of their conductivity (the sulfoacids are used for the synthesis of CP as doping compounds [21, 22]). In the case of polyelectrolytes, like the mentioned agar, [23], the sulfocompounds may intercalate themselves along the CP chain. The second strategy is the modification of the CP with the functional group, capable to react specifically with sulfoacids, and then the modified CP oxidizes itself electrochemically, to finalize the electron transfer. This strategy is also used in other type of CP-based sensors [1 – 6]. By the way, chemical or electrochemical doping the CP with the sulfoacids may also be used in sensing [24]

As the sulfoacids are strong, the behavior of the electrochemical sensor, used for their detection, depends strongly of pH, which may be represented in the loss of its exactity and other electrochemical instabilities, which may make difficult the interpretation of the analytic signals. A mathematical model, capable to describe adequately the electrochemical behavior of such sensor, could serve us for better comprehension of the mechanism of the chemical and electrochemical reactions, in which its work is based. We've already made various efforts to describe mathematically the work of electrochemical CP-based sensors of different types [25 – 26]. Also the effort was made to describe mathematically electropolymerization processes [27 – 28]. So, the goal of this work is the mechanistical mathematical investigation of the possibility of sulfoacid's CP-assisted detection, realized by the development of mathematical model of the work of the possible CP-based electrochemical sensor, capable to detect 2 sulfoacids..

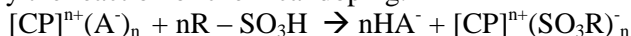
System and its model

With the objective to describe the behavior of the CP-based electrochemical sensor, detecting 2 sulfoacids in potentiostatic mode, we introduce three variables.

- C_1 – the concentration of the first sulfoacid in pre-surface layer,
- C_2 – the concentration of the second sulfoacid in pre-surface layer,
- θ – the surface concentration of the modified conducting polymer.

To simplify the modeling, we suppose that the reactor is stirred intensively, so we can neglect the convection flow. Also, we suppose that the background electrolyte is in excess and that it isn't reacting with CP, nor with both of analytes, so we can neglect the migration flow. The analytes' concentrational profiles in the pre-surface layer are supposed to be linear and the layers' thickness to be constant and equal to δ .

The analytes enter in the pre-surface layer by their diffusion and leave it by the specific reaction. They also leave it by the reaction of chemical doping:



So, the balance equations for them will be written as:

$$\frac{dC_1}{dt} = \frac{2}{\delta} \left(\frac{D}{\delta} (C_{1B} - C_1) - H_1 - r_1 \right) \quad (1)$$

$$\frac{dC_2}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (C_{2B} - C_2) - H_2 - r_2 \right) \quad (2)$$

In which, C_{1B} and C_{2B} are the analytes' bulk concentrations, δ the layer's thickness, r_1 and r_2 the specific reactions' velocities, H_1 and H_2 the undoping velocities of the analytes.

The specifically modified conducting polymer backbone is formed in specific reactions and is oxidized electrochemically. So, its balance equation will be written as:

$$\frac{d\Theta}{dt} = \frac{1}{\Gamma_{\max}} (r_1 + r_2 - r_3) \quad (3)$$

In which Γ_{\max} is the maximal surface concentration of the modified CP and r_3 the velocity of electrochemical reaction.

The reactions' rates may be calculated as:

$$r_1 = k_1 C_1 (1-\Theta); \quad r_2 = k_2 C_2 (1-\Theta); \quad r_3 = k_3 \Theta \exp(-nF\phi_0/RT) \quad (4-6)$$

$$H_1 = k_{H1} C_1 (1-\Theta); \quad H_2 = k_{H2} C_2 (1-\Theta); \quad (7-8)$$

in which, the variables "k" mean the constants of respective reactions, F, the Faraday number, ϕ_0 , the potential slope in double electric layer (DEL), referring to the non-modified and modified areas of CP coating, n the quantity of electrons transferred, R the universal gas constant, T the absolute temperature in the sensing system.

Results and discussion

We investigate the system of differential equations (1 – 3) and algebraic references (4 – 8), by using the linear stability theory. The steady-state Jacobian elements may be calculated as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (9),$$

in which.

$$a_{11} = \frac{\partial F_1}{\partial C_1} = -\frac{2}{\delta} \left(k_1 (1-\Theta) + k_{H1} (1-\Theta) - \frac{D}{\delta} \right) \quad a_{12} = \frac{\partial F_1}{\partial C_2} = 0$$

$$a_{13} = \frac{\partial F_1}{\partial \Theta} = \frac{2}{\delta} (k_1 C_1 + k_{H1} C_1)$$

$$a_{21} = \frac{\partial F_2}{\partial C_1} = 0 \quad a_{12} = \frac{\partial F_2}{\partial C_2} = -\frac{2}{\delta} \left(k_2 (1-\Theta) + k_{H2} (1-\Theta) - \frac{\Delta}{\delta} \right) \quad a_{23} = \frac{\partial F_2}{\partial \Theta} = \frac{2}{\delta} (k_1 C_1 + k_{H1} C_1)$$

$$\begin{aligned}
 a_{31} &= \frac{\partial F_3}{\partial C_1} = \frac{k_1(1-\Theta)}{\Gamma_{\max}} & a_{32} &= \frac{\partial F_3}{\partial C_2} = \frac{k_2(1-\Theta)}{\Gamma_{\max}} \\
 a_{33} &= \frac{\partial F_3}{\partial \Theta} = \frac{-k_1C_1 - k_2C_2 - k_2 \exp\left(\frac{nF}{RT}\phi_0\right) - k_2\Theta \frac{nF}{RT} \frac{\phi_0(K_0 - K_1) + K_1\phi_1}{K_1\Theta + K_0(1-\Theta)}}{\Gamma_{\max}} & & (10-18)
 \end{aligned}$$

The steady-states' stability in this system will be investigated, by using of the Routh-Hurwitz criterion. Its characteristic equation is:

$$\Phi^3 + A\Phi^2 + B\Phi + \Gamma = 0 \tag{19}$$

In which:

$$\begin{aligned}
 A &= -(a_{11} + a_{22} + a_{33}) \\
 B &= \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} + \begin{vmatrix} a_{11} & a_{32} \\ a_{31} & a_{33} \end{vmatrix} + \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} \\
 \Gamma &= -\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}
 \end{aligned} \tag{20-22}$$

The Routh-Hurwitz criterium requires, that, for a stable steady-state the principal diagonal minors of Hurwitz matrix

$$\begin{pmatrix} A & 1 & 0 \\ \Gamma & B & A \\ 0 & 0 & \Gamma \end{pmatrix} \tag{23}$$

have to be positive. The minors of the matrix's principal diagonal are:

$$\Delta_1 = A, \quad \Delta_2 = \begin{vmatrix} A & 1 \\ \Gamma & B \end{vmatrix}, \quad \Delta_3 = \begin{vmatrix} A & 1 & 0 \\ \Gamma & B & A \\ 0 & 0 & \Gamma \end{vmatrix} \tag{23-25}$$

As $\Delta_3 = \Gamma\Delta_2$, we may simplify the condition to $\Gamma > 0$.

To avoid the complicated mathematical expressions in Jacobian analysis, we introduce new variables, like:

$$\begin{aligned}
 \frac{D}{\delta} &= \kappa_1, \quad \frac{\Delta}{\delta} = \kappa_2, \quad k_1(1-\Theta) + k_{H1}(1-\Theta) = R_1, \quad k_2(1-\Theta) + k_{H2}(1-\Theta) = R_2, \quad k_1c_1 + k_{H1}c_1 = X_1, \quad k_2c_2 + k_{H1}c_1 = X_2, \\
 k_2 \exp\left(\frac{nF}{RT}\phi_0\right) &= W_1, \quad k_1c_1 = U_1, \quad k_1c_1 = U_2, \quad -U_1 - U_2 = U, \quad W_1 + W_2 = W \\
 k_2\Theta \frac{nF}{RT} \frac{\phi_0(K_0 - K_1) + K_1\phi_1}{K_1\Theta + K_0(1-\Theta)} &= W_2, \quad k_1(1-\Theta) = S_1, \quad k_2(1-\Theta) = S_2
 \end{aligned} \tag{26-39}$$

In which K_1 and K_2 are integral capacities of respective parts of DEL and ϕ_1 the potential slope in the modified part of DEL.

So, the Jacobian determinant will be represented as:

$$\frac{4D\Delta}{\delta^2\Gamma_{\max}} \begin{vmatrix} -R_1 - \kappa_1 & 0 & X_1 \\ 0 & -R_2 - \kappa_2 & X_2 \\ S_1 & S_2 & U - W \end{vmatrix} \quad (40)$$

Resolving the inequation $\Gamma > 0$ relatively to the parameter X_1 of the reactions of the first analyte, we can get the stable steady-state condition as:

$$X_1 > \frac{R_1 R_2 U + \kappa_2 R_1 U - R_1 R_2 W - \kappa_2 R_2 W - R_1 S_2 X_2}{S_1 S_2} + \frac{\kappa_1 R_2 U + \kappa_2 R_2 U - \kappa_1 R_2 W - \kappa_2 \kappa_1 W - \kappa_1 S_2 X_2}{S_1 S_2} \quad (41)$$

This means, that the steady-state will be stable (or, in analytic interpretation, the sensors' response will be clearer) if:

- The analytes' diffusion is faster, than the reaction of the second analyte (increasing of κ_2)
- The electrochemical reaction doesn't affect the DEL (the positivity of W)
- The first analyte is more active in undoping, than the second one (X_1)

The steady-state stability topological region, corresponding to the linear part of the "Electrochemical parameter – concentration" curve, is vast enough to say that such electrochemical sensor will have optimal response in more or less huge pH range. In the minimal influence of the side reactions, the work of the sensor has to be diffusion-controlled. It is possible even to join the information concerning the sensors' behavior in different modes in a table and it will resemble the shown in [25].

The monotonic instability occurs in the saddle-node bifurcation conditions ($\Gamma > 0$), in which different influences of the analytes' behavior become equivalent. It corresponds to the margin between stable steady-states and unsteady states and occurs if

$$X_1 = \frac{R_1 R_2 U + \kappa_2 R_1 U - R_1 R_2 W - \kappa_2 R_2 W - R_1 S_2 X_2}{S_1 S_2} + \frac{\kappa_1 R_2 U + \kappa_2 R_2 U - \kappa_1 R_2 W - \kappa_2 \kappa_1 W - \kappa_1 S_2 X_2}{S_1 S_2} \quad (42)$$

The oscillatory instability, the presence of which was confirmed for other systems with CP-based electrochemical sensors experimentally and theoretically, occurs in Hopf bifurcation condition. It requires, that the Jacobian principal diagonal contains positive elements. The unique element, capable to be positive in it, is "-W". The parameter W is capable to be negative in the case of the negativity of ϕ_0 , which occurs in the case of the anodic oxidation of strong reductants, that have dipole moment. As either sulfocompounds, or CP have it, the influence of electrochemical reaction on DEL will cause the oscillatory behavior. This cause is common for all the similar systems.

The difference in the reactivity of the analytes, if it is equal, may be neglected. Thus, the sulfogroup concentration will be considered the system of differential equations will be two-dimensional:

$$\begin{aligned} \frac{dC_{1+2}}{dt} &= \frac{2}{\delta} \left(\frac{D}{\delta} (C_{1+2B} - C_{1+2}) - H_{1+2} - r_{1+2} \right) = F_1 \\ \frac{d\Theta}{dt} &= \frac{1}{\Gamma_{\max}} (r_{1+2} - r_3) = F_2 \end{aligned} \quad (1')$$

Its analysis, being more simple that for tri-dimensional case, will give equal results in the case of the oscillatory instability, being more or less exact in another cases.

Autocatalysis. As the reactions of organic sulfocompounds do not tend to be autocatalytic, generally the autocatalysis on the first stage doesn't occur, but it may occur in the cause of the presence of another groups in its composition (with a specific reaction on them). For this case, the mathematical model is transformed by the way, similar to described in [25 - 28]. One more case for the oscillatory behavior will be the autocatalytic analyte transformation.

Conclusions

1. In the system of the detection of 2 sulfoacids by the CP-based electrochemical sensor, the presence of time dissipative structures, maintained by analyte diffusion and by electrochemical reaction, is confirmed.
2. The steady-state stability topological region is vast. That gives us the right to affirm, that the optimal response is maintained in the large pH-range.

3. The oscillatory instability occurs in the case of the presence of influences of anodic oxidation of strong reductants and in the case of autocatalytic analyte transformations on the first stage, if any.

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