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Full Paper

The Theoretical Evaluation of Saccharin Electrochemical Detection on CP-Based Diazonium Salts

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Abstract- detection, based on its azo-coupling with conducting polymer-based diazonium salts has been evaluated theoretically. The mathematical model, describing the case, was developed and analyzed by means of linear stability theory and bifurcation analysis. It was shown, that the reaction may be realized with electroanalytical efficiency, when the pH is neutral or mildly acidic. Also it was shown, that the oscillatory behavior in this case is more probable, than for general case, due to DEL influences of diazocoupling.

Keywords- Saccharine, Electrochemical detection, Azo coupling conducting polymers, Stable steady-state

1. INTRODUCTION

The use of chemically modified electrodes has become a useful and modern tool in electrochemical analysis, being capable to provide the rapid, cheap, sensitive, precise and exact quatification of different substances [1-6], along with their affinity to the analyte.

On the other hand, the saccharin [7-9] is an artificial sweetener, widely used in food, pharmaceutical industry and even in tobacco products. It is about 500 times sweeter than

sucrose and does not possess any caloric value. It is added to many dietary products, largely consumed by humans having diabetic disease, [10-12] and may be used as an antidote in the cases of metal poisoning [13]. Nevertheless, it contains toxicophore groups, and, thus, its use is linked to side effects like gut microbiota alteration, allergic reaction, [14-20] and even with carcinogen influences [21-23]. Thus, a development of a method, capable to detect its concentration precisely and exactly, remains an actual problem [24-26].

Many electrochemical methods have been developed for saccharin [27-31] determination. In the most of cases, they were based on doping of polyelectrolytes by saccharinate ion. Another interesting technique would employ saccharine azo-coupling, yet used to obtain dyes [32-33], inclusive for its spectrometrical detection [24].

Nevertheless, its application to electrochemical saccharine detection may confront some difficulties, like:

- the combination of azo-coupling and reduction conditions;
- the influences of the reaction of two electrolytes and its product electrochemical reduction on DEL configuration, causing electrochemical instabilities, typical for the similar systems [34-38];
- the interference of the protons, present in the solution, leading to the direct electrochemical reduction of diazonium group.

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 aim of our work is to evaluate, from the mechanistical theoretical point of view, the electrochemical detection of saccharine, based on its azo-coupling with specifically modified 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 [39-41].

## 2. SYSTEM AND ITS MODELING

2.1. Electrode modification

The specifically modified conducting polymer is obtained by indirect electrochemical synthesis. The aminogroup is protected by N-acyllation during the electropolymerization, to

impede the monomer linking by aminogroup [42]. Then, the protection is removed, and the polyamine is diazotized to form the diazonium salt (See Fig 1. for the case of 3-aminopyrrole).
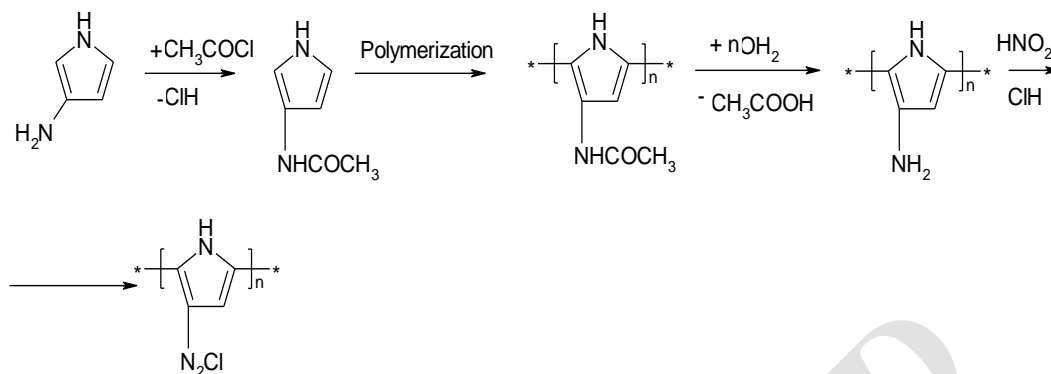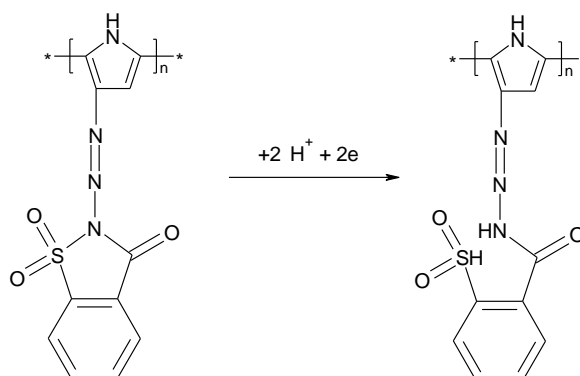
Fig. 1. The specific polymer preparation

Saccharin reacts with the specific polymer with pending diazonium groups in neutral or mightly acidic media to form an adduct (Fig. 2)
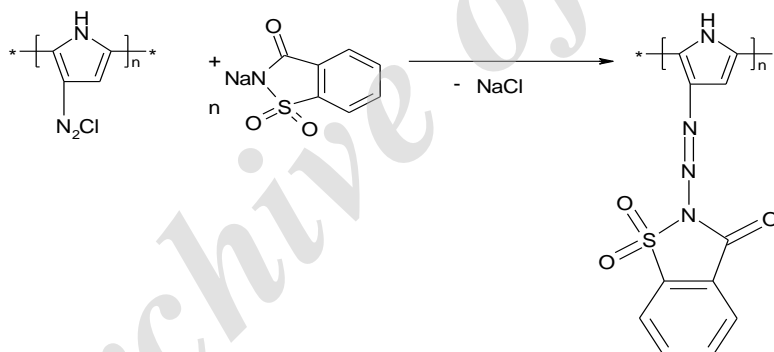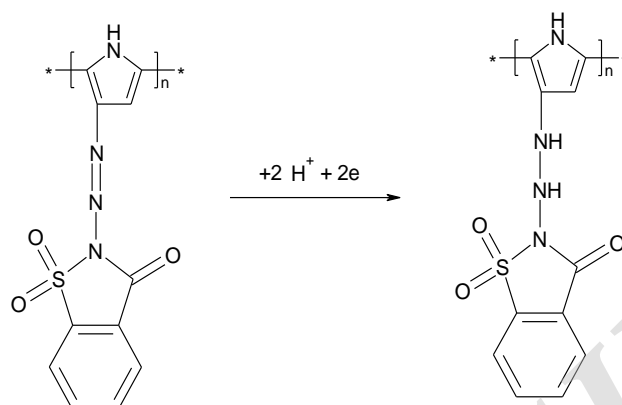
**Fig. 2.** The azo-coupling of specific polymer with saccharine

Fig. 3. The reduction of the S – N bond

In fact, this reaction may be considered as a kind of doping.

The electrochemical reduction of this adduct with dyeing properties, depending on solution conditions and cathode potential applied, may be realized either by S – N bond (Fig. 3), or by –N=N – group (Fig. 4).

Fig. 4. The reduction of the N – N bond
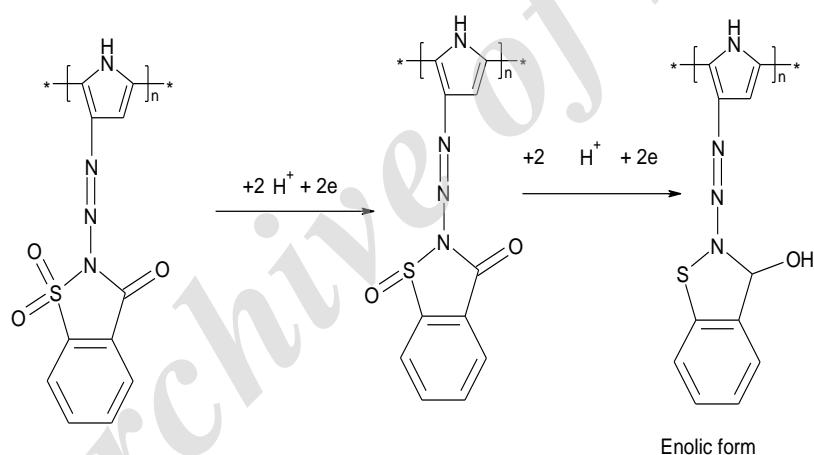
Fig. 5. Sulfogroup electrochemical reduction.

The sulfogroup is also reduced, but when lower cathodic potentials are applied and in more acidic conditions (Fig. 5).

The combination of the scenarios, described above, is possible, when strongly acidic solutions are used.

As the protons´ behavior influences much the electroanalytical process, their balance equation will be included in the model, so three variables are to be introduced:

s – Saccharin concentration in the pre-surface layer;

θ – the coverage degree of the modified polymer;

h – The protons' concentration in the pre-surface 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, and the concentration profile in it is supposed to be linear. It's also supposed that at the beginning of the reaction the initial monomer covers the entire electrode surface.

Saccharin enters the pre-surface layer by means of its diffusion, and enters in the reaction of azo-coupling. It is also capable to react with protons. So, its balance equation will be described as:

$$\frac{ds}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(s_0 - s) - r_1 - r_{H1}\right) \tag{1}$$

In which s_0 is the saccharin bulk concentration, r_1 is its coupling rate and r_{H1} is the rate of its reaction with protons.

The polymer is modified either by adduct formation by azo-coupling of saccharin with the specifically modified polymer, or by protons' action on diazonium group (Fig. 6). Then the adduct fragments are reduced by protons' participation by one of the mechanisms, mentioned in (3-5). So, the polymer's balance equation will be described as:

$$\frac{d\theta}{dt} = \frac{1}{G}(r_1 + r_{H2} - r_2) \tag{2},$$

In which G is the maximal protons' concentration, and r_2 is reduction reaction rate.
The protons enter the pre-surface layer by means of their diffusion and then attack the saccharin molecules, the azo-coupling centers of the initial polymer and participate in the adduct reduction. So, their balance equation will be described as:

$$\frac{dh}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(h_0 - h) - r_2 - r_{H1} - r_{H2}\right) \tag{3}$$

In which D is diffusion coefficient, h_0 is the protons' bulk concentration and r_{H2} is the reaction rate of the reaction of protons with active centers on polymer backbone (Fig. 6):
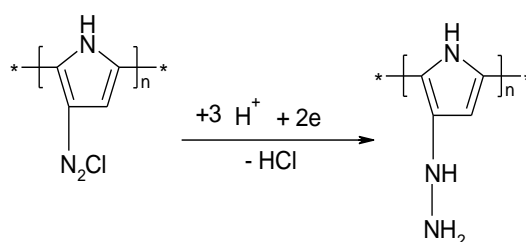
Fig. 6. The diazonium salt electrochemical reduction

The correspondent reaction rates may be calculated as:

$$r_1 = k_1 s(1-\theta)\exp(\beta\theta) \tag{4}$$

$$r_2 = k_2 \theta h^2 \exp\left(\frac{2F\gamma\theta}{RT}\right) \tag{5}$$

$$r_{H1} = k_{H1} sh \tag{6}$$

$$r_{H2} = k_{H2} h^3 (1-\theta)\exp\left(\frac{2F\gamma\theta}{RT}\right) \tag{7}$$

In which the parameters k are rate constants of the respective reactions, β and γ are parameters, describing the influences of the reactions on the surface on double electric layer (DEL) capacitances, F is Faraday number, R is universal gas constant, and T is absolute temperature.

Due to kinetic characteristics of azo coupling, the behavior of this electroanalytical system has to be more dynamic, than that characteristic for other similar systems [39-41]. Their common and different features will be discussed below.

3. RESULTS AND DISCUSSION

In order to investigate the possibility of electrochemical detection of saccharin on specifically modified conducting polymer by azo coupling, we analyze the equation set (1-3) by means of linear stability theory and bifurcation analysis. The steady-state Jacobi functional matrix elements for this system will be described as:

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

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_1(1-\theta)\exp(\beta\theta) - k_{H1}h\right) \tag{9}$$

$$a_{12} = \frac{2}{\delta}\left(k_1 s\exp(\beta\theta) - \beta k_1(1-\theta)s\exp(\beta\theta)\right) \tag{10}$$

$$a_{13} = \frac{2}{\delta}\left(-k_{H1}s\right) \tag{11}$$

$$a_{21} = \frac{1}{G}\left(k_1(1-\theta)\exp(\beta\theta)\right) \tag{12}$$

$$a_{22} = \frac{1}{G}\left(\begin{array}{l} -k_1 s\exp(\beta\theta) + \beta k_1(1-\theta)s\exp(\beta\theta) - k_{H2}h^3\exp\left(\frac{2F\gamma\theta}{RT}\right) + \gamma k_{H2}h^3(1-\theta)\exp\left(\frac{2F\gamma\theta}{RT}\right) - \\ -k_2 h^2\exp\left(\frac{2F\gamma\theta}{RT}\right) - \gamma k_2 \theta h^2\exp\left(\frac{2F\gamma\theta}{RT}\right) \end{array}\right) \tag{13}$$

$$a_{23} = \frac{1}{G}\left(3k_{H2}h^2(1-\theta)\exp\left(\frac{2F\gamma\theta}{RT}\right) - 2k_2\theta h\exp\left(\frac{2F\gamma\theta}{RT}\right)\right) \tag{14}$$

$$a_{31} = \frac{2}{\delta}\left(-k_{H1}h\right) \tag{15}$$

$$a_{32} = \frac{2}{\delta}\left(\begin{array}{l} k_{H2}h^3\exp\left(\dfrac{2F\gamma\theta}{RT}\right) - \gamma k_{H2}h^3(1-\theta)\exp\left(\dfrac{2F\gamma\theta}{RT}\right) + \\[2mm] + k_2h^2\exp\left(\dfrac{2F\gamma\theta}{RT}\right) + \gamma k_2\theta h^2\exp\left(\dfrac{2F\gamma\theta}{RT}\right) \end{array} \right) \tag{16}$$

$$a_{32} = \frac{2}{\delta}\left(-\frac{D}{\delta} - k_{H1}s + 2k_2\theta h\exp\left(\frac{2F\gamma\theta}{RT}\right) - 3k_{H2}h^2(1-\theta)\exp\left(\frac{2F\gamma\theta}{RT}\right)\right) \tag{17}$$

Observing the main diagonal elements (10), (13) and (17), it is possible to observe that *the oscillatory behavior* in this system is possible. Moreover, it is even more probable, than in the similar systems [39-41].

As in the mentioned systems, the unique factor, responsible for the oscillatory behavior in this system, are the double electric layer influences. Nevertheless, contrarily to the cases [39-41] with one process influencing the DEL, there is more than one process influencing its capacitances, and all of them may cause the oscillatory behavior.

Besides of the adduct fragments reduction, the strong influences of which are described by the positivity of the element $-\gamma k_2\theta h^2\exp\left(\frac{2F\gamma\theta}{RT}\right)$, other reactions, influencing DEL capacitances are the azo coupling, the influences of which are described by the positivity of the element $\beta k_1(1-\theta)s\exp(\beta\theta)$, and the direct reduction of diazonium salts, the influence of which are described by the positivity of the element $\gamma k_{H2}h^3(1-\theta)\exp\left(\frac{2F\gamma\theta}{RT}\right)$. Acting all the mentioned factors, the oscillation amplitude and frequency will depend directly on solution pH and on analyte concentration.

To investigate the *steady-state stability* in the system, we apply to the equation set (1-3) the Routh-Hurwitz criterion. Avoiding the appearance of cumbersome expressions, we introduce new variables, for the Jacobian determinant to be rewritten as:

$$\frac{4}{\delta^2 G}\begin{vmatrix} -\kappa_1 - \Xi - \Lambda & \Sigma & -Y \\ \Xi & -\Phi - \Sigma - \Omega & E - \Gamma \\ -\Lambda & \Phi - \Omega & -\kappa_2 - \Gamma - E - Y \end{vmatrix} \tag{18}$$

Resolving the determinant and applying the condition Det J<0, obtained from the criterion, we obtain the steady-state stability requirement, described as:

$$\begin{array}{l} (-\kappa_1 - \Xi - \Lambda)(\Phi\kappa_2 + \Phi Y + \Sigma\kappa_2 + \Sigma\Gamma + \Sigma E + \Sigma Y + \Omega\kappa_2 + \Omega E + \Omega Y + 2\Phi\Gamma) + \\[2mm] + \Xi(-\Phi\Gamma + \Omega Y + \Sigma\kappa_2 + \Sigma\Gamma + \Sigma E + \Sigma Y) - \Lambda(\Sigma E - \Sigma\Gamma - \Phi Y - \Sigma Y - \Omega Y) < 0 \end{array} \tag{19}$$

Rearranging the brackets, and eliminating the elements with equal module and opposed signs, the requirement will be described as:

$$-\kappa_1(\Phi\kappa_2+\Phi Y+\Sigma\kappa_2+\Sigma\Gamma+\Sigma E+\Sigma Y+\Omega\kappa_2+\Omega E+\Omega Y+2\Phi\Gamma)-$$
$$-\Xi(\Phi\kappa_2+\Phi Y+\Omega\kappa_2+\Omega E+\Omega Y+3\Phi\Gamma)-\Lambda(\Phi\kappa_2+\Sigma\kappa_2+\Sigma E+\Omega\kappa_2+\Omega E+2\Phi\Gamma+\Sigma E)<0 \quad (20)$$

It's possible to show, that in the case of the positivity of the parameters Φ, Σ and Ω, that is describing the fragility of the DEL influences of two electrochemical reduction processes and of the azo coupling, the steady-state will be maintained stable. Really, if the mentioned parameters are positive, (taking into account, that the rest of variables are always positive) the left side of the inequation will be driven to more negative values, describing the steady-state stability.

Nevertheless, in this concrete case, the steady-state stability may be electroanalytically inefficient. If the pH is low, the protons occupy the active sites of diazocoupling, resulting in their electrochemical reduction. Moreover, it may cause the side reaction with saccharin, making its electrochemical detection more difficult. In this case, the steady-state will be also stable, but won't be electroanalytically efficient. So, for it to be so, it is possible to use the weakly acid pH values, close to neutral.

When electroanalytically efficient, the stable steady-state is correspondent to the linearity of the dependence between electrochemical parameter and saccharin concentration. The electroanalytical process is diffusion-controlled.
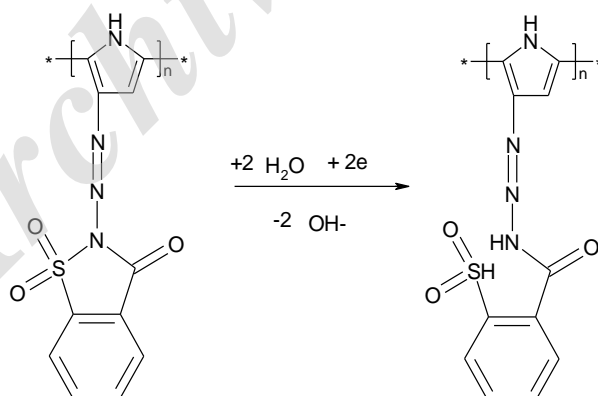
Fig. 7. The neutral media electrochemical reduction of saccharin adduct

When the impact of the destabilizing DEL influences is equal to that of the factors stabilizing the steady-state, the *monotonic instability*, correspondent to the detection limit, is realized.

Its condition for this system is:

$$- \kappa_1 (\Phi\kappa_2 + \Phi Y + \Sigma\kappa_2 + \Sigma\Gamma + \Sigma E + \Sigma Y + \Omega\kappa_2 + \Omega E + \Omega Y + 2\Phi\Gamma) -$$
$$- \Xi (\Phi\kappa_2 + \Phi Y + \Omega\kappa_2 + \Omega E + \Omega Y + 3\Phi\Gamma) - \Lambda (\Phi\kappa_2 + \Sigma\kappa_2 + \Sigma E + \Omega\kappa_2 + \Omega E + 2\Phi\Gamma + \Sigma E) = 0 \qquad (21)$$

It is correspondent to the margin between the stable steady-states and instable states, and it is caused, mostly, by DEL influences of diazonium salt and adducts reduction.

In the case of the use of *neutral pH,* the electrochemical reduction will be realized according to the Fig. 7.

As saccharin sodium salt is a system, entering in azo coupling in relatively mild conditions, neutral media won't impede this reaction. Despite of the more negative value of cathodic potential to be applied, the reaction has to be electroanalytically efficient. For this case, the variable h will leave the equation set, and the model will be two-variable. Its analysis will be made in the next stage of our investigation.

4. CONCLUSIONS

The mechanistic analysis of the possibility of saccharin electrochemical detection, based on azo-coupling, let us conclude that:

- The stable steady-state is easy to maintain. Nevertheless, its electroanalytical efficiency depends strongly on solution pH, being more expressed in neutral, or mildly acidic solutions. The electroanalytical process is diffusion-controlled;

- The oscillatory behavior, in this system, is more probable, than in similar cases, due to the presence of more than one reaction influencing the DEL capacities. The oscillations amplitude and frequency depend strongly on solution pH;

- the monotonic instability for this system is possible, and it is caused, mostly, by DEL influences of diazonium salt and adduct reduction;

- If the neutral solution is used, the electroanalytical process is more efficient, despite of the lower value of cathodic potential. The system's behavior is expected to be less complicated.

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