The Theoretical Evaluation of Saccharin Electrochemical Detection on Cp-Based Diazonium Salts in Alkaline Media

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ABSTRACT

The possibility of saccharin electrochemical detection, based on its azo-coupling with CP-based diazonium salts in alkaline media has been evaluated from the theoretical point of view. The correspondent mathematical model has been analyzed by means of linear stability theory and bifurcation analysis. It was shown that the lightly alkaline solutions are favorable for saccharin electrochemical detection, but in strongly alkaline media, the concurrence between the electroanalytical process and hydroxylation of diazonium groups influences strongly on the system´s behavior. The possibility of oscillatory and monotonic instability has been also verified.

Keywords: Intoxication prevention; Saccharin; Conducting polymers; Electrochemical sensors; Azo-coupling: Steady-state stability
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INTRODUCTION

Saccharin is a sugar substitute, frequently used either in food industry, or in phrmaceutical formulations and even in tobacco products [1-3], as it is considered 500 times as sweet as sucrose. As it doesn´t have any energetic value, it is used in the special food for diabetic ill people or for people that keep them fit [4]. Moreover, it may be used as an antidote in the cases of heavy metal poisoning [5], as it forms stable complex compounds with them. Nevertheless, as it has a toxicophoric fragment ($CO - NH - SO_2$, or $CO - NNa - SO_2$, in its soluble form) its regular use provokes side effects [6-10], like allergic reactions and alterations of gut microbiota, the carcinogenic influence is also possible. So, the development of an efficient, cheap and rapid method of its detection is an actual problem [11-13], and the use of electrochemical methods may serve as an interesting solution for it. Various electrochemical methods have been developed for saccharin electrochemical detection, and, in its majority, they included the doping with saccharinate ion [14-18]. Another interesting strategy would be an azocoupling, yet used during the synthesis of saccharin-based colorants [19,20], inclusively in spectrophotometric saccharin determination. Azocoupling may be also used for electrochemical detection sulfanilamide drugs [21,22] in neutral, lightly acidic an lightly alkaline media.

In the coupling reaction, the neutral or lightly acidic media was used to quantify saccharin sodium salt, and lightly basic, to quantify the neutral saccharin. It let us presuppose that the reaction may be used for electrochemical determination of this compound. Nevertheless, its application to the electroanalysis may encounter some difficulties, like: the combination of the condition of the coupling reaction with that for the electrochemical reaction; the influences of the both reactions on the double electric layer (DEL), causing electrochemical instabilities [23,24]. 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 possible to 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

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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 [25-27].

SYSTEM AND ITS MODELING

The synthesis of a conducting polymer with pending diazogroups is realized according to a known methodology. In 3-aminopyrrole, the aminogroup is protected, whilst the polymerization is realized in the positions 2 and 5. When the polymerization is complete, the protection is eliminated, and then the restored aminogroups are converted into diazonium salts (Figure 1).
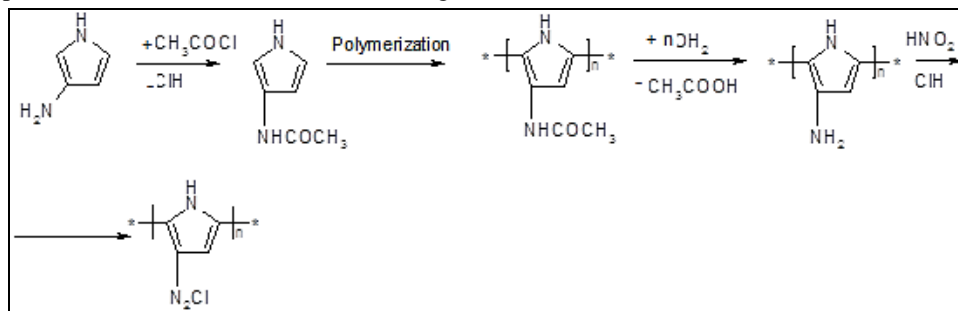

Figure 1: Synthesis and modification of specific conducting polymer

Another synthetic route to be used includes the electropolymerization of 3-nitropyrrole with the electrochemical reduction of the resulting polymer in the conditions of the electrochemical analog of Zinin reaction. The coupling in lightly alkaline media is realized as represented in Figure 2.
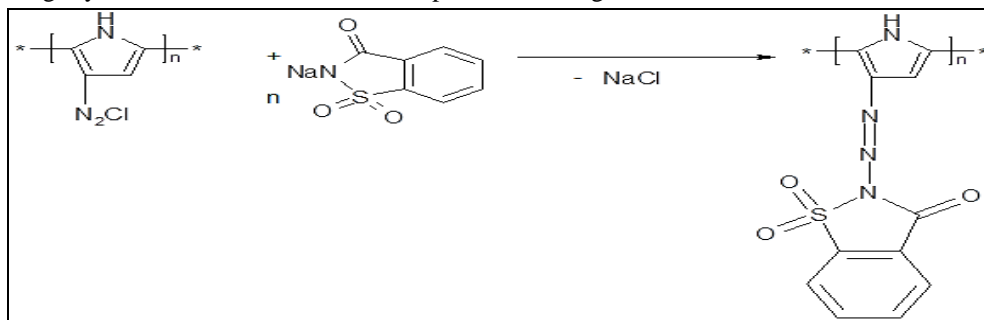

Figure 2: The coupling of the conducting polymer with saccharin

The adduct electrochemical reaction in alkaline media is realized with more negative cathodic potential applied, comparing with neutral and acidic media. Nevertheless, it may be realized, according to the reaction (Figure 3):
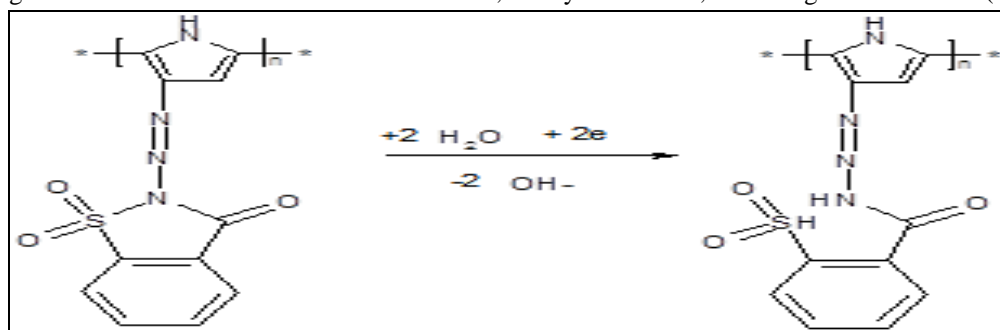

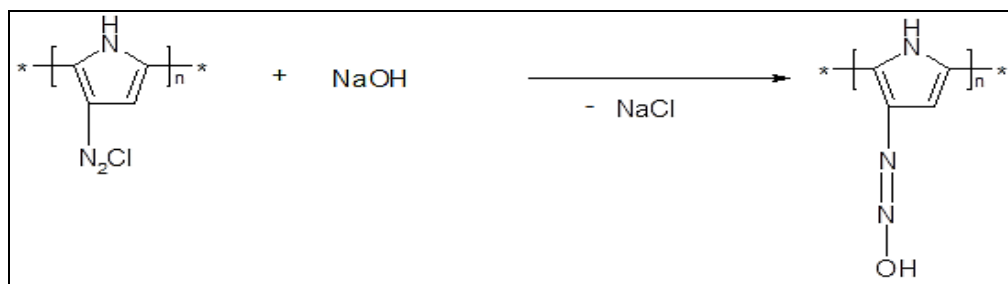**Figure 3: The adduct electrochemical reduction**

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Figure 4: The diazosalt alkaline hydrolysis

In the alkaline solutions, the diazosalt enters in the alkaline hydrolysis, by the reaction, and the hydrolysis product is unable to couple with saccharin (Figure 4). This factor has also been observed during the saccharin spectrophotometrical detection.

So, in this case, to describe the system, we introduce three variables:

s – saccharin concentration in the pre-surface layer;

θ – the modified polymer surface concentration;

a – the alkali pre-surface concentration.

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 diazosalt covers the entire electrode surface. Saccharin enters the pre-surface layer by means of its diffusion, and enters in the reaction of azo-coupling. So, its balance equation will be described as:

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

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 hydroxyl action on diazonium group. 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:

$$\frac{d\theta}{dt} = \frac{1}{G}\left(r_1 + r_a - r_2\right) \qquad (2)$$

In which G is the maximal protons' concentration, and r_2 is reduction reaction rate. The alkali enters the pre-surface layer by diffusion. It is also formed during the adduct electrochemical reduction and then modifies the polymer, hydrolyzing the diazonic fragments. So, its balance equation will be described as:

$$\frac{da}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(a_0 - a) + r_2 - r_a\right) \qquad (3)$$

The correspondent reaction rates may be described as:

$$r_1 = k_1 s(1 - \theta)\exp(\beta\theta) \qquad (4)$$

$$r_2 = k_2\theta\exp\left(-\frac{2F\gamma\theta}{RT}\right) \qquad (5)$$

$$r_a = k_a a(1 - \theta)\exp(\beta\theta) \qquad (6)$$

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 [25,26]. Their common and different features will be discussed below.

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:

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

in which:

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

$$a_{12} = \frac{2}{\delta}\left(k_1\exp(\beta\theta) - \beta k_1(1-\theta)\exp(\beta\theta)\right) \tag{9}$$

$$a_{13} = 0 \tag{10}$$

$$a_{21} = \frac{1}{G}\left(k_1(1-\theta)\exp(\beta\theta)\right) \tag{11}$$

$$a_{22} = \frac{1}{G}\begin{pmatrix} -k_1\exp(\beta\theta) + \beta k_1(1-\theta)\exp(\beta\theta) - k_a a\exp(\beta\theta) + \beta k_a a(1-\theta)\exp(\beta\theta) - \\ k_2\exp\left(-\frac{2F\gamma\theta}{RT}\right) + \gamma k_2\theta\exp\left(-\frac{2F\gamma\theta}{RT}\right) \end{pmatrix} \tag{12}$$

$$a_{23} = \frac{1}{G}\left(k_a(1-\theta)\exp(\beta\theta)\right) \tag{13}$$

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

$$a_{32} = \frac{2}{\delta}\begin{pmatrix} k_a a\exp(\beta\theta) - \beta k_a a(1-\theta)\exp(\beta\theta) + \\ k_2\exp\left(-\frac{2F\gamma\theta}{RT}\right) - \gamma k_2\theta\exp\left(-\frac{2F\gamma\theta}{RT}\right) \end{pmatrix} \tag{15}$$

$$a_{33} = \frac{2}{\delta}\left(-k_a(1-\theta)\exp(\beta\theta) - \frac{D}{\delta}\right) \tag{16}$$

Taking into account the expressions (8), (12) and (16), it is possible to observe that the *oscillatory behavior* in this case is more probable, than in the simpler cases, described in [25,26], but less probable, than during the saccharin electrochemical detection in lightly acidic media [27]. The main diagonal of the matrix contains three addendums, capable to describe the positive callback.

Three processes in this system may influence the DEL capacities, and these influences, described by the positivity of the addendums $\gamma k_2\theta\exp\left[-\frac{2F\gamma\theta}{RT}\right]$, $\beta k_1(1-\theta)\exp(\beta\theta)$ and $\beta k_a a(1-\theta)\exp(\beta\theta)$. They are correspondent to the electrochemical reduction, azo-coupling and alkaline hydrolysis of diazosalt. These influences are the cause for the oscillatory behavior in this system. In order to investigate the steady-state stability, we apply the Routh-Hurwitz criterion to the equation set (1). Avoiding the cumbersome expressions, we simplify the Jacobian analysis, so we introduce new variables, so the Jacobian determinant will be rewritten as:

$$\frac{4}{\delta^2 G}\begin{vmatrix} -\kappa_1 - \Xi & \Omega & 0 \\ \Xi & -\Omega - \Sigma - \Lambda & -P \\ 0 & \Sigma - \Omega & -P - \kappa_2 \end{vmatrix} \tag{17}$$

Opening the brackets and applying the in equation Det J<0, salient from the criterion, we obtain the steady-state stability condition, expressed as:

$$(-\kappa_1 - \Xi)(2\Sigma P + \Lambda P + \Omega\kappa_2 + \Sigma\kappa_2 + \Lambda\kappa_2) + \Xi(\Omega P + \Omega\kappa_2) < 0 \tag{18}$$

Rearranging the expression (18) with the annihilation of the elements of equal module and opposed signs, the steady-state stability requirement will be rewritten as:

$$(-\kappa_1)(2\Sigma P + \Lambda P + \Omega\kappa_2 + \Sigma\kappa_2 + \Lambda\kappa_2) - \Xi(2\Sigma P + \Lambda P + \Sigma\kappa_2 + \Lambda\kappa_2 - \Omega P) < 0 \tag{19}$$

Which is satisfied, when the parameters Ω, Σ are positive, and Λ is negative, defining the absence or fragility of DEL influences of the chemical and electrochemical reactions (P is always negative). If these conditions are satisfied, the value of the left side of the in equation (19) is more negative, so the steady-state is easy to maintain stable. Nevertheless, the electroanalytical efficiency of steady-state stability may only be achieved in lightly alkaline solutions, in which the alkaline hydrolysis rate isn't sufficient to block the active centers of the polymer azo-coupling with saccharin. In the concentrated alkaline solutions, the steady-state will remain stable, but, due to the diazosalt alkaline hydrolysis, forming compounds inert to coupling, the steady-state stability won't be electroanalytically efficient. So, it's recommended to use lightly alkaline solution. While the steady-state stability is electroanalytically efficient, it is correspondent to the linear dependence between the electrochemical parameter and concentration. The electroanalytical process is diffusion-controlled, but if the electrode is relatively small, the alkalinity is relatively high and the concentration of saccharin is relatively big, it may become kinetically controlled. 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:

$$(-\kappa_1)(2\Sigma P + \Lambda P + \Omega\kappa_2 + \Sigma\kappa_2 + \Lambda\kappa_2) - \Xi(2\Sigma P + \Lambda P + \Sigma\kappa_2 + \Lambda\kappa_2 - \Omega P) = 0 \tag{20}$$

It is correspondent to the margin between the stable steady-states and instable states, and it is caused, mostly, by DEL influences of the azocoupling and the reaction of alkali.

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The hydrogen bonding between the conducting polymer and saccharin fragment is possible, especially when the monomer used is pyrrole, an amino or acid derivative. In this case, a surface effect caused by this bonding may influence the system, and this influence will be described in our next works.

CONCLUSION

The theoretical investigation of the saccharin electrochemical detection, based on its coupling with specifically modified conducting polymers let us conclude that: the oscillatory behavior in this case is more probable, than in the usual cases of the function of CP-based electrochemical sensors, but less probable, than during the saccharin electrochemical detection in lightly acidic media; the oscillations may be caused by DEL influences of the electrochemical reaction and of the chemical reactions (azo-coupling and alkaline hydrolysis of diazosalt); the steady-state stability is installed easily. Nevertheless, the steady-state electroanalytical efficiency depends strongly on the solution pH; the process may be diffusion controlled, or reaction controlled, depending on the electrode shape and saccharin concentration; the monotonic instability in this system is possible, and it may be caused mostly by DEL influences of chemical reaction.

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