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# The Theoretical Evalution of the Posiibility of OF CoO(OH)-Assisted Omeprazole Electrochemical Detection

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**Abstract**- The possibility of electrochemical oxidation of omeprazole on CoO(OH) for electrochemical analysis *in vitro* and *in vivo* has been evaluated by theoretical means. The corresponding mathematical model was analyzed by means of linear stability theory and bifurcation analysis. It was demonstrated that cobalt (III) oxy-hydroxide may be used as an electrode modifier for the electrochemical detection of omeprazole in pharmaceutical samples. The possibility for electrochemical instabilities has also been evaluated.

**Keywords**- Omeprazole, Chemically modified electrodes, Cobalt (III) oxy-hydroxide, electrochemical pharmaceutical analysis, Stable steady-state

## 1. INTRODUCTION

Nowadays, the frequency of verticular and chronic gastritis and peptic ulcers occurrences has been grown slightly [1-3], in both urban and rural areas. This may find its explanation in the strengthening of the action of exogenous factors like:

- the abundance of *Helicobacter Pilori* and other bacteria and fungi in the drinking water and in food;
- digestion disorders;
- chemical dependence and its consequences;
- the excessive and lasting use of drugs, especially, with acidic nature;
- parasite infections;
- stress;

The action of endogenous factors, which may or may not be caused by the mentioned above: endogenous intoxications, bile reflux, lack of vitamins and hormonal disorders, has also been intensified.

Gastritis and ulcers may be treated by the $H_2$-blocking molecules, detaining the proton transfer [4]. One of these molecules is omeprazole [5–7], also used in treatment of other acid-related disorders, like dyspepsia, pepticulcer disease (PUD), gastroesophageal refluxdisease (GORD/GERD), laryngopharyngeal reflux (LPR) and Zollinger–Ellison syndrome.

Its blocking effect is achieved by the formation of its sulphenamide metabolite, forming complex with both $H^+K^+ATPase^+$ and gastric mucosa carbonic anhydrase [7], inhibiting the proton transfer into the gastric lumen (Fig. 1)

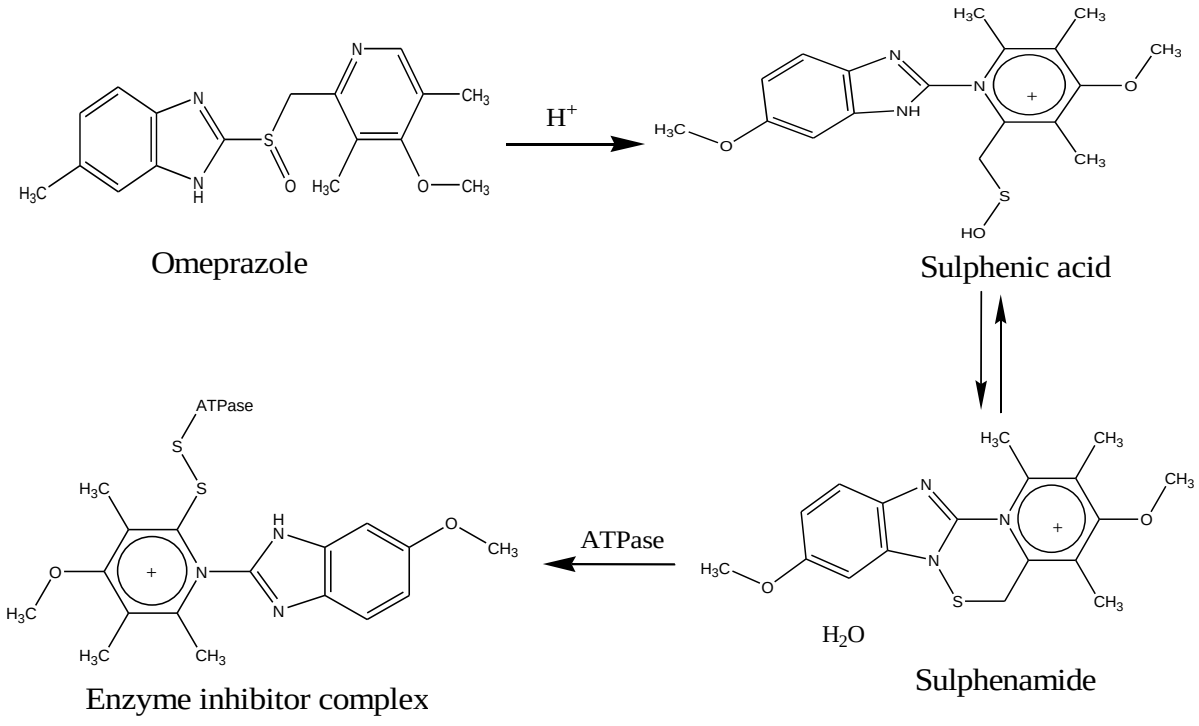



**Fig. 1.** Omeprazole mechanism of action

It´s important to mention, that this reaction is viable, due to the presence of pyridinic nitrogen atoms with basic properties, and these properties are strengthened, due to the presence of electropositive groups in the pyridinic ring (Fig. 2). On the other hand, the basic

properties of imidazolic ring may be compromised by the presence of electronegative sulfonic group, and the acidity of pyrrolic nitrogen atom, thus, may be enhanced. This makes omeprazole lightly basic compound, close to amphotericity, and the main nitrogen atom participating in the proton transfer inhibition is that of pyridinic ring. Sulfinyl functional group is also easy to be protonized. The pyrrolic nitrogen atom is also taking part in the proton-detaining mechanism (Fig. 1).

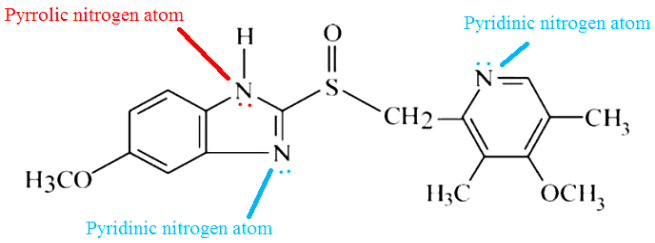



**Fig. 2.** Omeprazole structure and its nitrogen heteroatoms

The inhibition effect of omeprazole depends strongly on its concentration. Moreover, despite of being considered a relatively "secure" drug [8–10], it may present various collateral effects, like headache, vertigo, nausea, diarrhea and flatulence, which may cause discomfort. Moreover, the concentration control is also important for successful treatment of patients with liver and kidney insufficiency or older people. Thus, the seek of a precise, exact, rapid and sensitive method for its quantification is a really actual problem [11], and the use of chemically modified electrodes, yet used in the detection of the different compounds, including those with biological activity [11–20], may be an interesting solution for it.

One of the interesting compounds, capable to be used as modifiers, is cobalt (III) oxyhydroxide [21–26], a p-type semiconductor, seen by many researcher as a substitution for titanium dioxide. Although there is not any literature describing CoO(OH) as a modifier for omeprazole electrochemical oxidation, it has already been used for the oxidation of similar compounds [27–28]. Also, according to [11], the most suitable pH for the omeprazole electrochemical oxidation is neutral and lightly basic. On the other hand, CoO(OH) is also most active in neutral and slightly alkaline conditions, as shown in experimental [27–28] and theoretical [29–32] works. So, the possible use of CoO(OH) as a modifier in omeprazole oxidation is an interesting process to be evaluated by theoretical and (or) experimental means. Moreover, the close values of cyclic voltammogram oxidation peak potentials for electrooxidation of omeprazole on conducting polymer [11] and for the electrooxidation of oxalate and phenolic compounds on CoO(OH) [27–28] also reinforce the statement that CoO(OH) may be a suitable modifier for omeprazol electrochemical detection.

Nevertheless, the main problems for the development of new chemically modified electrodes are:

- the indecision in the modifier mechanism of action;
- the compatibility of the modifier with the tissue or biological object (some modifiers, used *in vitro* may be non-compatible with *in vivo* sensing);
- the presence of electrochemical instabilities, accompanying both electrochemical synthesis of cobalt (III) oxyhydroxide [33–34], and electrochemical oxidation and electrooxidative polymerization of organic molecules [35– 41].

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 any experimental essay.

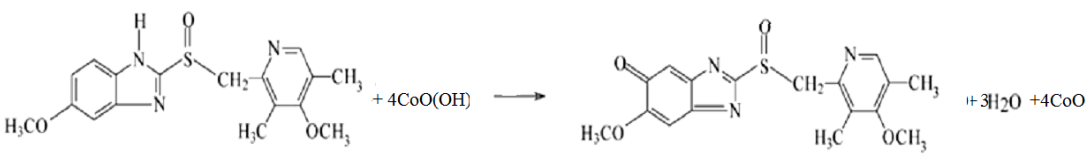
So, the goal of this work is the mechanistic theoretic analysis of the possibility of omeprazol electrochemical oxidation on CoO(OH) with possible electroanalytical use. In order to achieve it, we realize the specific objectives:

- 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 ([11], [27–32] and [42]).

This work is, in fact, a continuation of the theoretical investigation of CoO(OH) capability of assisting the electroanalytical processes

## 2. SYSTEM AND ITS MODELING

Using the data about omeprazole electrooxidation, mentioned in [11], and also the kinetic data of CoO(OH) mediating action, mentioned in [27–32], we may suggest a mechanism, by which omeprazole firstly suffers electrooxidative hydrolysis, yielding its phenolic derivative, that is oxidized by CoO(OH) to its correspondent quinonic form by:




(1)

$$CoO + OH^- - e^- \rightarrow CoO(OH) \quad (2)$$

In neutral media, the reaction will be rewritten as:

$$CoO + H_2O - e^- \rightarrow CoO(OH) + H^+ \quad (3)$$

The omeprazole electrooxidation is realized in the benzolic ring of benzoimidazolic cycle, because both imidazolic and pyridinic rings have higher oxidation potentials.

Including to the model the presence of an interfering substance, like acid or alkali, we introduce three variables:

c – omeprazole concentration in the pre-surface layer;
θ – CoO(OH) surface coverage degree;
a – interfering substance pre-surface layer 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 CoO covers the entire electrode surface.

*Omeprazole* enters the pre-surface layer by means of diffusion and participates in the CoO(OH)-assisted oxidation reaction. It is also attacked by the interfering substance. Thus, its balance equation will be written as:

$$\frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_1 - r_{a1}\right) \quad (1)$$

In which Δ is the diffusion coefficient, $c_0$ is the bulk omeprazole concentration, $r_1$ is the rate of the reaction (1) and $r_{a1}$ is the reaction rate of omeprazole with the interfering substance.

Omeprazol reacts with both acids and bases, yielding salts. Nevertheless, as it was shown, these reactions are different, so their impact will be different. It will be shown and discussed below.

*Cobalt(III)oxyhydroxide* is formed by the reaction (2) and assists the omeprazol oxidation (1). It is also capable to react with the interfering substance. Taking in account the yet mentioned statements, we describe its balance equation as:

$$\frac{d\theta}{dt} = \frac{1}{G}(r_2 - r_1 - r_{a2}) \quad (2)$$

In which G is CoO(OH) maximal surface concentration, $r_2$ is CoO(OH) reaction formation and $r_{a2}$ is the reaction rate of CoO(OH) of the interfereng substance.

*The interfering substance* (acid or base) enters in the pre-surface layer by its diffusion. It also may participate in the reaction of CoO(OH) formation (if it is a base) (2) and react with both omeprazole and CoO(OH). So, its balance equation will be rewritten as:

$$\frac{da}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(a_0 - a) - r_2 - r_{a1} - r_{a2}\right) \quad (3)$$

In which D is its diffusion coefficient and $a_0$ is its bulk concentration.
The reaction rates of correspondent reactions may be described as:

$$r_1 = k_1 c\theta^4 \quad (4)$$

$$r_2 = k_2 a(1-\theta)\exp\left(\frac{F\phi_0}{RT}\right) \quad (5)$$

$$r_{a1} = k_{a1} c a^n \quad (6)$$

$$r_{a2} = k_{a2}\theta a^m \exp(-\alpha\theta) \quad (7)$$

In which the parameters k stand for the corresponding rate constants F, for the Faraday constant $F=N_A*e$, $\varphi_0$ is the potential slope in DEL (double electric layer), relative to the zero-charge potential, R is the universal gas constant, T is the absolute temperature and α is the variable, describing the interaction between CoO(OH) particles during its dissolution.

The potential slope $\varphi_0$ depends on θ, and this dependence may be supposed as linear: $\varphi_0=\gamma\theta$.

The acid reacts with two pyridinic nitrogen atoms (Fig. 1), forming salt, despite of the partial desactivation of the pyridinic nitrogen of the imidazole fragment. Yet the alkali reacts only with pyrrolic nitrogen, and this reaction kinetically is realized only in hot solutions of the concentrated alkali. The ether groups' hydrolysis also may occur in the same alkaline solutions, yielding the corresponding enolates. So, for the case of the acid media, n=2, for the strongly alkaline media, n=1, 2 or 3, depending on the solution pH.
CoO(OH) is dissolved in acidic solutions by reaction:

$$CoO(OH) + 3H^+ + e^- \rightarrow Co^{2+} + 2H_2O \quad (4)$$

In strongly alkaline media it is dissolved by:

$$CoO(OH) + 3OH^- + H_2O \rightarrow [Co(OH)_6]^{3-} \quad (5)$$

Nonetheless, the reaction (5), for kinetic reasons, is only realized in highly concentrated hot alkaline solutions, meanwhile the reaction (4) is capable to be realized in moderately and strongly acid solutions. So, despite of the similarity of the behavior of this system to that of analogous [27–32], the system with the omeprazole CoO(OH)-assisted electrochemical oxidation shows more defined stability, which will be discussed below.

## 3. RESULTS AND DISCUSSION

To investigate the possibility of the electroanalytical use of omeprazole on CoO(OH), we investigate the equation set (1–3) by means of linear stability theory. The steady-state Jacobian functional matrix elements may be described as:

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

In which:

$$a_{11} = \frac{2}{\delta}\left( -\frac{\Delta}{\delta} - k_1\theta^4 - k_{a1}a^n \right) \quad (9)$$

$$a_{12} = \frac{2}{\delta}\left( -4k_1 c\theta^3 \right) \quad (10)$$

$$a_{13} = \frac{2}{\delta}\left( -nk_{a1}ca^{n-1} \right) \quad (11)$$

$$a_{21} = \frac{1}{G}\left( k_1\theta^4 \right) \quad (12)$$

$$a_{22} = \frac{1}{G}\left( -4k_1 c\theta^3 - k_2 a\exp\left(\frac{F\phi_0}{RT}\right) + \gamma k_2 a(1-\theta)\exp\left(\frac{F\phi_0}{RT}\right) - k_{a2}a^m\exp(-\alpha\theta) + \alpha\theta k_{a2}a^m\exp(-\alpha\theta) \right) \quad (13)$$

$$a_{23} = \frac{1}{G}\left( k_2(1-\theta)\exp\left(\frac{F\phi_0}{RT}\right) - mk_{a2}\theta a^{m-1}\exp(-\alpha\theta) \right) \quad (14)$$

$$a_{31} = \frac{2}{\delta}\left( -k_{a1}a^n \right) \quad (15)$$

$$a_{32} = \frac{2}{\delta}\left( -k_2 a\exp\left(\frac{F\phi_0}{RT}\right) - \gamma k_2 a(1-\theta)\exp\left(\frac{F\phi_0}{RT}\right) - k_{a2}a^m\exp(-\alpha\theta) + \alpha\theta k_{a2}a^m\exp(-\alpha\theta) \right) \quad (16)$$

$$a_{33} = \frac{2}{\delta}\left( -k_2(1-\theta)\exp\left(\frac{F\phi_0}{RT}\right) - mk_{a2}\theta a^{m-1}\exp(-\alpha\theta) - nk_{a1}ca^{n-1} - \frac{D}{\delta} \right) \quad (17)$$

It is possible to observe that the *oscillatory behavior* for this system is possible, because the Hopf bifurcation conditions may be satisfied. For the Hopf bifurcation to be realized, the presence of positive elements in the Jacobian main diagonal (describing the positive callback) is required.

As in the most systems envolving CoO(OH) [29–32], the oscillatory behavior is caused by surface and electrochemical instable phenomena accompanying the formation and dissolution of the mediating material. The oscillatory behavior is more probable, than in [11,42], in which the omeprazole electrooxidation was assisted by a conducting polymer, but less probable, than in [32], due to the lower probability for surface phenomena (as the number of surface-controlled processes in this case is lower).

Nevertheless, in the lightly alkaline media, in which the reaction (5) isn't realized, the surface factor doesn't cause the oscillatory behavior, so it may be caused only by DEL influences, just like in [11,42].

In the acidic media, both factors are valid, so the system's behavior will resemble that of [29–32].

To analyze the *steady-state stability*, we use the Routh-Hurwitz criterium and, in order to avoid the cumbersome expressions, introduce new variables, so Jacobian determinant now may be rewritten as:

$$\frac{4}{G\delta^2}\begin{vmatrix} -\kappa_1 - X_1 - X_{a1} & -\Lambda_1 & -\Omega_{a1} \\ -X_1 & \Lambda_2 - \Lambda_1 - \Lambda_{a2} & -\Omega_2 - \Omega_{a2} \\ -X_{a1} & -\Lambda_2 - \Lambda_{a2} & -\Omega_{a1} - \Omega_2 - \Omega_{a2} - \kappa_2 \end{vmatrix} \tag{18}$$

Opening the brackets, we may obtain the steady-state stability requirement Det J<0, expressed like:

$$\begin{aligned} &-\kappa_1(\Lambda_1\Omega_{a1} + \Lambda_1\Omega_2 + \Lambda_1\Omega_{a2} + \Lambda_1\kappa_2 + \Lambda_{\alpha 2}\Omega_{a1} + \Lambda_{\alpha 2}\kappa_2 - \Lambda_2\Omega_{a1} - 2\Lambda_2\Omega_2 - 2\Lambda_2\Omega_{a2} - \Lambda_2\kappa_{a2}) - \\ &-X_1(2\Lambda_{\alpha 2}\Omega_{a1} + \Lambda_{\alpha 2}\kappa_2 - 2\Lambda_1\Omega_2 - 2\Lambda_1\Omega_{a2} + \Lambda_1\kappa_{a2}) - \\ &-X_{a1}(2\Lambda_1\Omega_2 + 2\Lambda_1\Omega_{a2} + \Lambda_1\kappa_2 + \Lambda_{\alpha 2}\kappa_2 - 2\Lambda_2\Omega_2 - 2\Lambda_2\Omega_{a2} - \Lambda_2\kappa_{a2}) < 0 \end{aligned} \tag{19}$$

As the diffusion addendums, containing the diffusion parameters $\kappa_1$ and $\kappa_2$ form the majority, and give the greatest impact, it is possible to conclude that the process is diffusion-controlled. The same thing can be observed in [11], [27–32] and [42], in which in the majority of cases the reaction is diffusion-controlled (but in [32] the adsorption mode is very probable).

In the case of the absence of DEL influences and repulsion of adsorbed particles (if their interaction is really present), defined by the positivity of the CoO(OH) electrosynthesis parameter $\Lambda_2$ and the dissolution parameter $\Lambda_{a2}$, the inequation (19) is satisfied. So, it is possible to conclude that the steady-state stability (corresponding to the linear part of the curve electrochemical parameter–concentration) will be maintained in a vast parameter region. The sensing is more efficient in the pH range between 7 and 10. The peak of the oxidation peak current–pH curve is expected on the neutral pH with the best response expected on pH between 7 and 8, which, theoretically may be used for omeprazole remains´ quantification in some biological tissues.

As in [11], the peak current – pH curve has to be asymmetric, with the "alkaline" part more sloping. The optimal pH for the analysis may be shown on the table:

**Table 1.** The optimal pH for omeprazol CoO(OH)-assisted electronalytical detection:

| pH | CoO(OH) stability | Omeprazol stability | Electroanalytical efficiency |
|---|---|---|---|
| 0–7 | Unstable, dissolution | Unstable, salt formation, Oxidation is complicated | Inefficient |
| 7–10 | Stable | Stable | Efficient |
| 10-12 | Stable | Methoxy groups tend to hydrolyze | Conditionally efficient |
| 12-14 | Unstable, Complex formation | Hydrolysis, accompanied by salt formation | Inefficient |

When the influences, stabilizing the steady-state in the system, have equal impact to that of the surface and electrochemical instabilities, it is correspondent to the *monotonic instability*. In electroanalytical systems it may mean the system has reached the detection limit, or the conditions have been slightly changed. Its condition is:

$$\begin{aligned}&-\kappa_1(\Lambda_1\Omega_{a1}+\Lambda_1\Omega_2+\Lambda_1\Omega_{a2}+\Lambda_1\kappa_2+\Lambda_{\alpha 2}\Omega_{a1}+\Lambda_{\alpha 2}\kappa_2-\Lambda_2\Omega_{a1}-2\Lambda_2\Omega_2-2\Lambda_2\Omega_{a2}-\Lambda_2\kappa_{a2})-\\&-\mathrm{X}_1(2\Lambda_{\alpha 2}\Omega_{a1}+\Lambda_{\alpha 2}\kappa_2-2\Lambda_1\Omega_2-2\Lambda_1\Omega_{a2}+\Lambda_1\kappa_{a2})-\\&-\mathrm{X}_{a1}(2\Lambda_1\Omega_2+2\Lambda_1\Omega_{a2}+\Lambda_1\kappa_2+\Lambda_{\alpha 2}\kappa_2-2\Lambda_2\Omega_2-2\Lambda_2\Omega_{a2}-\Lambda_2\kappa_{a2})=0\end{aligned} \quad (20)$$

*The simplified model for the lightly alkaline media:* As it was described, the sensing activity is more efficient in neutral and lightly alkaline media, due to kinetic inefficiency of some of the side reactions. In this case, the general balance equations, described above, may be simplified to:

$$\frac{dc}{dt}=\frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0-c)-r_1\right) \quad (21)$$

$$\frac{d\theta}{dt}=\frac{1}{G}(r_2-r_1) \quad (22)$$

$$\frac{da}{dt}=\frac{2}{\delta}\left(\frac{D}{\delta}(a_0-a)-r_2\right) \quad (23)$$

The behavior of this system resembles that observed for the conducting polymers [42], defining, in this case, a diffusion-controlled system with the mostly stable steady-states.

*The presence of the complex-forming substance:* When an interfering substance contains ions, forming complex with cobalt (even being neither an alkali, nor an acid) the material is destroyed, and the electroanalytical system will be inefficient.

*The absence of interfering substances* is an ideal scenario for this system. In this case, the variable a leaves the equation-set, that is simplified to the bidimensional type (21–22, being $r_2$ the rate of the reaction (3)).

*The possibility of use*: the pH range of the efficient response is wide enough to provide the possibility of use this electroanalytical system not only *in vitro*, but, limitedly, *in vivo* (possibly, in micro or nanoscale). But the use of CoO(OH) *in vivo* must be realized with special care, due to the possible toxicity of the products of its reaction in the organism.

## 4. CONCLUSIONS

The theoretical evaluation of the system with the CoO(OH)-assisted omeprazole oxidation let us conclude that:

- Cobalt(III) oxyhydroxide has to be suitable electrode modifier for omeprazol electrochemical detection, due to its compatibility with the analyte;
- The best sensing efficiency is achieved in the pH range between 7 and 10, and it is maximal when the pH is neutral. The pH – peak current curve has to present asymmetry being less "inclined" to the alkaline side. The reaction may be considered diffusion-controlled. The working pH range is wide enough to provide the limited use of this system *in vivo*;
- The oscillatory behavior in this system is possible, being caused by typical factors, present in systems involving CoO(OH). It is more probable, that in the case of omeprazole electrooxidation on polyalizarine (conducting polymer), but less probable, that in the case of CoO(OH)-assisted procarbazine electrooxidation;
- In the case of the neutral or lowly alkaline media, the oscillatory behavior is less probable, than in the case of acidic or strongly alkaline solutions, being caused only by electrochemical DEL-capacitance factor;
- The monotonic instability in this system is possible, defining the detection limit. It occurs when the influences, stabilizing the steady-state in the system, have equal impact to that of the surface and electrochemical instabilities and defines the margin between stable steady-states and unstable states;
- The presence of complex-forming substances compromises the electroanalytical process, due to CoO(OH) dissolution;
- In the case of the absence of interfering substances, the ideal scenario for the electroanalytical system is formed. The model for this case is simplified to the bidimensional type.

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