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# Theoretical Description for Omeprazole Cathodical Electrochemical Determination, Assisted by Omeprazole Electrochemical Determination, Assisted by the Composite Poly(1,2,4-triazole) – VO(OH)

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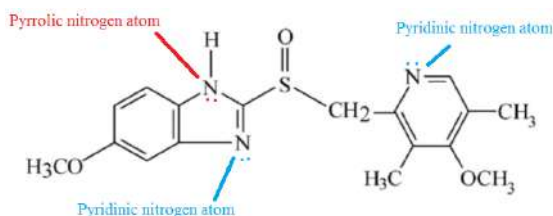
**Abstract:** In this work, we describe theoretically the possibility of omeprazole electrochemical determination, assisted by the composite containing vanadium oxyhydroxide as an active substance and the polymer of 1,2,4-triazolic derivative as a mediator. The omeprazole molecule undergoes a sulfoxide to sulfide reduction process over a trivalent vanadium compound. The vanadium oxyhydroxide, at its turn, may be oxidized to a tetravalent state, represented in two forms. The electroanalytical process behavior will be illustrated by a trivariate equation-set, analysis of which confirms the efficiency of the composite of poly(1,2,4-triazole) with VO(OH). Vanadium (III) oxyhydroxide may be efficiently used for omeprazole detection both in pharmaceutical formulations, food, and biological liquids.

**Keywords:** omeprazole; electrochemical sensors; vanadium oxyhydroxide; conducting polymers; stable steady-state.

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## 1. Introduction

Nowadays, the frequency of diverticular and chronic gastritis and gastric ulcers has grown slightly [1 - 4] all over the world. The treatment of the mentioned pathologies includes the use of proton-blocking molecules, one of them omeprazole (Figure 1):



**Figure 1.** Omeprazole molecule.

Its blocking effect is achieved by forming its sulphenamide metabolite, forming a complex with  $H^+K^+ATPase^+$  and gastric mucosa carbonic anhydrase[3,4], clogging the protons entry into the gastric lumen. This effect is based on the proton-sensitive action of pyrrolic and especially pyridinic heteroatoms in it. However, it may present various collateral effects, like headache, vertigo, nausea, diarrhea, and flatulence, which may cause discomfort [5 – 8]. Moreover, concentration control is also important for successfully treating patients with liver and kidney insufficiency or older people. Thus, searching for a precise, exact, rapid, and sensitive method for its quantification is a real problem [9 – 12].

Many electrochemical methods have been proposed for omeprazole [13 - 15] electrochemical determination, which is generally realized on the anode. As for the cathodic reduction, it is also possible, but in the presence of certain electrode modifiers, like vanadium (III) oxyhydroxide [16,17]. Its behavior is similar to that of trivalent cobalt analog (both are semiconductors) but much more likely to reduce. To enhance its sensitivity and stability, it prefers to deposit it over an organic matrix and conducting a polymer of troazolic compounds, capable of stabilizing the inorganic nanoparticles and mediating the electron transfer.

Nevertheless, the use of novel electrode modifiers with novel analytes may be impeded by: the indecision concerning the exact mechanism of electrochemical reaction, the necessity of detecting the conditions of the best sensor efficiency, and electrochemical instabilities, typical for similar systems [18,19].

The development of an adequate mathematical model is necessary for planning the cathodic omeprazole electrochemical determination. Moreover, it is also capable of comparing this system's behavior with that of similar ones without any experimental essay.

So, the goal of this work is the mechanical theoretical analysis of the omeprazole electrochemical determination, assisted by  $VO(OH) - Poly(1,2,4-triazole)$  composite. In order to realize it, we suggest the reaction mechanism, leading to the analytical signal, develop and analyze the mathematical model in terms of stability and compare the system's behavior to that of similar electroanalytical processes [20,21].

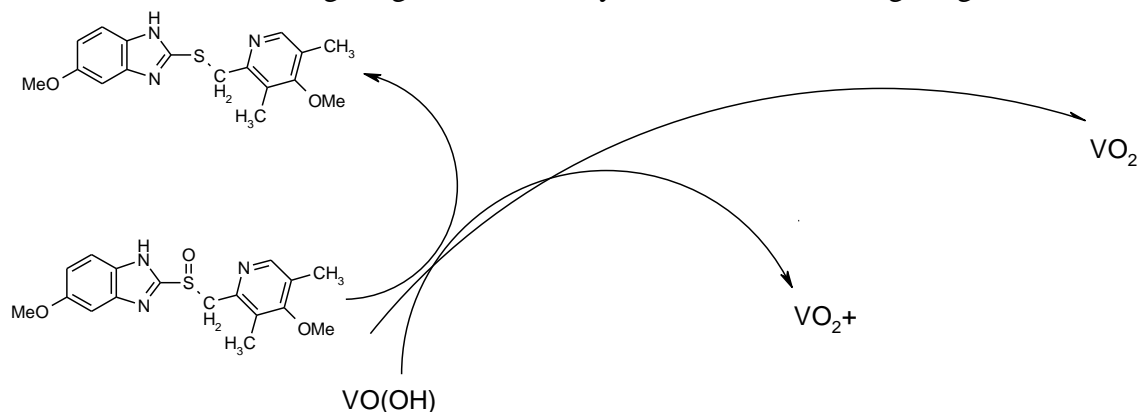
## 2. System and its Modeling

As omeprazole contains the sulfoxide group, capable of reducing, it is easily reduced by vanadium oxyhydroxide, yielding sulfide form. Yet, the tetravalent vanadium may be formed in either oxide or vanadyl-ion form. Therefore, the electroanalytical process will be shown as in Figure 2.

The vanadium (III) oxyhydroxide is, therefore, regenerated on the electrochemical stages from both forms:



In this case, in order to describe the behavior of the system with omeprazole electrochemical determination, assisted by VO(OH) – Poly(1,2,4-triazole) composite, we introduce three variables:  $c$  – omeprazole concentration in the pre-surface layer;  $v_1$  – vanadium dioxide maximal surface coverage degree;  $v_2$  – vanadyl-ion maximal coverage degree.



**Figure 2.** The scheme of the cathodic VO(OH)-assisted electrochemical detection for omeprazole.

Introducing some assumptions [20 – 21], we rewrite the correspondent equation set as (3):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left( \frac{\Delta}{\delta} (c_0 - c) - r_{11} - r_{12} \right) \\ \frac{dv_1}{dt} = \frac{1}{v_1} (r_{11} - r_{21}) \\ \frac{dv_2}{dt} = \frac{1}{v_2} (r_{21} - r_{22}) \end{cases} \quad (3)$$

Herein,  $\Delta$  is the diffusion coefficient,  $c_0$  is the omeprazole bulk concentration,  $V$  parameters are the tetravalent vanadium forms' maximal surface concentration, and the parameters  $r$  are the correspondent reaction rates, expressed as:

$$r_{11} = k_{11}c(1 - v_1 - v_2)^2 \quad (4)$$

$$r_{12} = k_{12}c(1 - v_1 - v_2)^2 \exp(\alpha v_2) \quad (5)$$

$$r_{21} = k_{21}v_1 \exp\left(-\frac{F\varphi_0}{RT}\right) \quad (6)$$

$$r_{22} = k_{22}v_2 \exp\left(-\frac{F\varphi_0}{RT}\right) \quad (7)$$

Herein, the parameters  $k$  are the correspondent rate constants,  $\alpha$  is the parameter relating the double electric layer (DEL) influences of the vanadyl-ion formation,  $F$  is the Faraday number,  $\varphi_0$  are the DEL potential slope, related to the zero-charge potential,  $R$  is the universal gas constant and  $T$  is the absolute temperature.

Herein, a hybrid scenario is realized. As one of the tetravalent vanadium forms is ionic, the system's behavior is somehow more dynamic than the simpler case. Nevertheless, the VO(OH) – Poly(1,2,4-triazole) composite is an efficient electrode modifier for omeprazole cathodic electrochemical determination, as shown below.

### 3. Results and Discussion

In order to investigate the behavior of the system with the electrochemical determination of omeprazole, assisted by poly(1,2,4-triazole) – VO(OH) composite, we

analyze the equation-set (4) by means of linear stability theory and bifurcation analysis. The steady-state functional Jacobian matrix members will be exposed as:

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

in which:

$$a_{11} = \frac{2}{\delta} \left( -\frac{A}{\delta} - k_{11}(1 - v_1 - v_2)^2 - k_{12}(1 - v_1 - v_2)^2 \exp(\alpha v_2) \right) \quad (9)$$

$$a_{12} = \frac{1}{v_1} \left( 2k_{11}c(1 - v_1 - v_2) + 2k_{12}c(1 - v_1 - v_2) \exp(\alpha v_2) \right) \quad (10)$$

$$a_{13} = \frac{1}{v_1} \left( 2k_{11}c(1 - v_1 - v_2) + 2k_{12}c(1 - v_1 - v_2) \exp(\alpha v_2) - \alpha k_{12}c(1 - v_1 - v_2)^2 \exp(\alpha v_2) \right) \quad (11)$$

$$a_{21} = \frac{1}{v_1} (k_{11}(1 - v_1 - v_2)^2) \quad (12)$$

$$a_{22} = \frac{1}{v_1} \left( -2k_{11}c(1 - v_1 - v_2) - \xi k_{21} \exp\left(-\frac{F\phi_0}{RT}\right) - \xi k_{21}v_1 \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (13)$$

$$a_{23} = \frac{1}{v_1} \left( -2k_{11}c(1 - v_1 - v_2) - \lambda k_{21}v_1 \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (14)$$

$$a_{31} = \frac{1}{v_2} (k_{12}(1 - v_1 - v_2)^2 \exp(\alpha v_2)) \quad (15)$$

$$a_{32} = \frac{1}{v_2} \left( -2k_{11}c(1 - v_1 - v_2) - \xi k_{22}v_2 \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (16)$$

$$a_{33} = \frac{1}{v_2} \left( -2k_{12}c(1 - v_1 - v_2) \exp(\alpha v_2) + \alpha k_{12}c(1 - v_1 - v_2)^2 \exp(\alpha v_2) - k_{22} \exp\left(-\frac{F\phi_0}{RT}\right) - \lambda k_{22}v_2 \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (17)$$

Taking into account the main diagonal elements (9), (13), and (17), it is possible to conclude that the *oscillatory behavior* in this system is possible. Moreover, it is more probable than in similar systems [20 – 21] due to the DEL influences of both the electrochemical and one of the chemical stages. The oscillations are expected to be frequent and of small amplitude.

For the realization of Hopf bifurcation, correspondent to the oscillatory behavior, the presence of the positive elements, correspondent to the positive callbacks, is necessary. In this system, there are three main-diagonal elements capable of being positive.

Besides the elements  $-\xi k_{21} \exp\left(-\frac{F\phi_0}{RT}\right) > 0$  if  $\xi < 0$  and  $-\lambda k_{22}v_2 \exp\left(-\frac{F\phi_0}{RT}\right) > 0$  if  $\lambda < 0$ , correspondent to the DEL influences of the electrochemical stages, typical for the similar systems [26 – 28], another element, capable of being positive, is  $\alpha k_{12}c(1 - v_1 - v_2)^2 \exp(\alpha v_2) > 0$  if  $\alpha > 0$ . This element corresponds to the DEL ionic force influence of the vanadyl-ion formation, leading to the cyclic changes of DEL conductivity. Either way, the oscillatory behavior is observed far beyond the detection limit.

In order to investigate the *steady-state stability*, we apply the Routh-Hurwitz criterion to the equation-set (4). Avoiding the cumbersome expressions, we introduce new variables, exposing the Jacobian determinant as:

$$\frac{2}{\delta V_1 V_2} \begin{vmatrix} -\kappa - \varepsilon - \Lambda & P + \Sigma & \Phi + K \\ \varepsilon & -P - B & -\Phi - \Gamma \\ \Lambda & -\Sigma - \Omega & -K - T \end{vmatrix} \quad (18)$$

and opening the brackets and applying the condition  $\text{Det } J < 0$ , salient from the criterion, we obtain the steady-state stability requirement (18):

$$-\kappa(PK + PT + BK + BT - \Sigma\Phi - \Sigma\Gamma - \Omega\Phi - \Omega\Gamma) - \varepsilon(BK + BT - \Sigma\Gamma - \Omega\Gamma - \Sigma T + \Sigma\Phi + \Sigma K + \Omega K) - \Lambda(PT + BT - \Omega\Phi - \Omega\Gamma + P\Gamma - B\Phi) < 0 \quad (19),$$

defining a dynamic kinetically-controlled electroanalytical process. It is possible to show that in the case of the absence or fragility of the DEL influences of the chemical and electrochemical stages, described by the positivity of the kinetical parameter B and electrokinetically parameters  $\Gamma$  and T, the left side of the equation (19) will be more negative.

As the insatisfaction of the mentioned conditions is hard to be often, the satisfaction of the stability requirement (19) will be observed in the vast parameter region. As no side reactions can compromise the analyte and modifier stability are observed in this system, the steady-state stability will correspond to the linear dependence between the electrochemical parameter and the concentration.

Therefore, it is possible to conclude that the composite VO(OH) – Poly(1,2,4-triazole) is an efficient electrode modifier for omeprazole electrochemical determination.

Corresponding to the detection limit, the monotonic instability is also probable if the destabilizing and stabilizing influences are equal from the electroanalytical point of view. Its conditions will be described as:

$$-\kappa(PK + PT + BK + BT - \Sigma\Phi - \Sigma\Gamma - \Omega\Phi - \Omega\Gamma) - \varepsilon(BK + BT - \Sigma\Gamma - \Omega\Gamma - \Sigma T + \Sigma\Phi + \Sigma K + \Omega K) - \Lambda(PT + BT - \Omega\Phi - \Omega\Gamma + P\Gamma - B\Phi) = 0 \quad (20)$$

If the vanadyl-ion isn't formed, the trivariate equation-set will be transformed into a bivariate. The system's behavior will be similar to the simplest case of the anodic omeprazole determination [20 – 21].

#### 4. Conclusions

From the system with the electrochemical determination of omeprazole on a VO(OH) – Poly(1,2,4-triazole) composite, it was possible to conclude that contrarily to the similar systems involving omeprazole electrochemical detection, this electroanalytical system will be kinetic controlled. The oscillatory behavior, in this case, will be more probable than for the simplest situation due to the formation of the ionic form of the tetravalent vanadium is one of the chemical stages. Also, the linear dependence between the electrochemical parameter and concentration of the omeprazole is realized in a broad topological parameter region. The composite is an efficient electrode modifier for omeprazole electrochemical determination.

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## Conflicts of Interest

The authors declare no conflict of interest.

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