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The Theoretical Evaluation of the Possibility of Theacrine Electrochemical Detection Over the Cubic Nanoparticles of $CoSn(OH)_6$

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ABSTRACT

The possibility of theacrine electrochemical determination, assisted by cubic nanoparticles of $CoSn(OH)_6$ has been evaluated from the theoretical point of view. The correspondent mechanism has been suggested, and the correspondent model, developed and analyzed by means of linear stability theory and bifurcation analysis. It was verified that theacrine may be electrochemically detected in neutral or lightly alkaline media over $CoSn(OH)_6$. The analytical signal has to be clear and easily interpreted. The possibility of oscillatory and monotonic instabilities has also been verified.

Keywords: Food security, Theacrine, Cobalt-tin hydroxide, Electrochemical sensor, Stable steady-state

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INTRODUCTION

Theacrine, also known as 1,3,7,9-tetramethyluric acid (Figure 1) is an alkaloid, naturally occurring in cupuaçu plant, growing in the North and the Centre-West of Brazil (mostly in the states of Pará, Amazonas, Rondônia and Acre), like also in Colombia, Peru and Bolivia [1,2]. It is also found in a Chinese tea plant, kudingcha [3].

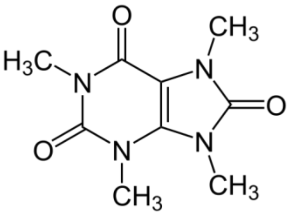


Figure 1: Theacrine

It manifests anti-inflamatory and analgesic effecs [4-7] and affects adenosine signaling by mechanism, similar to that of caffeine [8,9]. Nevertheless, although theacrine is a relatively safe drug [10,11], its effect strongly depends on the concentration [12,13]. Moreover, while used in formulations, theacrine may be confused with other uric acid derivatives. Thus, the development of a cheap, precise, exact and sensitive method of its detection and quantification remains an actual problem [14-16].

Although the electrochemical techniques have been developed and successfully applied to other uric acid derivatives (the proper uric acid, caffeine, theobromine) [17-22], none of these methods have been applied to theacrine yet. The similarity of its composition to that of the mentioned compounds makes think that theacrine may also be electrochemically detected. Moreover, the discovery of the proper theacrine has been realized recently, so this work has to be interesting also from this point of view.

On the other hand, novel cobalt-based p-type semiconducting materials gain more and more attention, especially cobalt (III) oxyhydroxide [23-25] and cobalt(II)-tin hydroxide $CoSn(OH)_6$ [26,27] gain more and more attention as catalytic, photo-, photoelectron- and electrocatalytic surfaces.

However, their electroanalytical properties´ investigation has begun only in the actual decade [28-30], which makes the scientists use them with special care.

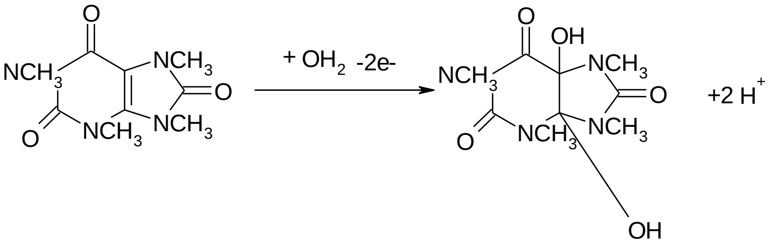
Moreover, the development of a new electroanalytical method leads the research to resolve, a priori, some problems like: The indefinition in theacrine electrochemical detection mechanism; The possibility of electrochemical instabilities, characteristic for the anodic oxidation of small organic compounds (including the electropolymerization processes) [31]; In case of use of chemically modified electrodes, the indefinition in applicability of a certain modifier.

Their resolution is impossible without development of a mathematical model, capable to describe adequately the system´s behavior. The modeling also lets us compare it with the behavior of other, similar systems.

So, the general goal of our work is the theoretical mechanistic investigation of theacrine electrochemical oxidation. It´s resolution is achieved by the realization of specific goals like: The suggestion of a mechanism of theacrine electrochemical oxidation; The development of a mathematical model, correspondent adequately to the process; The analysis of the model and steady-state stability investigation; The comparison of this system with the similar ones [32-35].

SYSTEM AND ITS MODELING

The mechanism of theacrine electrochemical oxidation in neutral solutions may be described as:



(1)

Cobalt(II)-tin(IV) hydroxide enters the reaction by:

$$\text{Thea} + 2\text{CoSnO(OH)}_5 \rightarrow \text{Thea(OH)}_2 + 2\text{CoSn (OH)}_6 \quad (2)$$
$$\text{CoSn(OH)}_6 + \text{H}_2\text{O} – \text{e}^- \rightarrow \text{CoSn O(OH)}_5 + \text{H}^+ \quad (3)$$

In which Thea stands for theacrine moiety. Taking into account that the presence of tetravalent tin stabilizes the material, we introduce two variables: c–Theacrine concentration in the pre-surface layer; θ–Surface coverage degree by $CoSn(OH)_6$; To simplify the modeling, we suppose that the reactor is intensively stirred (so we may neglect the convection flow), that the support electrolyte is in excess (so we may neglect the migration flow). Also we suppose that the concentration profile of theacrine in the pre-surface layer is linear, and its thickness is constant, equal to δ. It is possible to show that the system´s behavior may be described by a classic differential equation set (4):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_2\right) \\ \frac{d\theta}{dt} = \frac{1}{G}(r_2 - r_3) \end{cases} \quad (4)$$

In which Δ is diffusion coefficient, c_0 is the alcaloid bulk concentration, G is $CoSn(OH)_6$ surface concentration and r_2 and r_3 are the correspondent reaction rates, that may be calculated as:

$$r_2 = k_2 c(1-\theta)^2) \quad (5)$$

$$r_3 = k_3\theta \exp\left(\frac{F\gamma\theta}{RT}\right) \quad (6)$$

In which the parameters k are correspondent rate constants, F is the Faraday number, γ is the coefficient, describing the system´s behavior on double electric layer, R is the universal gas constant and T is the absolute temperature. As it may be seen, the behavior of the system may be considered analogous to yet observe [32-35], which will be discussed below.

RESULTS AND DISCUSSION

In order to investigate the behavior of the system with theacrine electrochemical detection over cobalt (III) oxyhydroxide, we analyze the differential equation set (4) by means of linear stability theory. The steady-state elements of Jacobian matrix may be described as:

:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (7)$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_2(1-\theta)^2\right) \quad (8)$$
$$a_{12} = \frac{2}{\delta}(2k_2 c(1-\theta)^2) \quad (9)$$
$$a_{21} = \frac{1}{G}(k_2(1-\theta)^2) \quad (10)$$

$$a_{22} = \frac{1}{G}\left(-2k_2c(1-\theta) - k_3\exp\left(\frac{F\gamma\theta}{RT}\right) + \gamma k_3\theta\exp\left(\frac{F\gamma\theta}{RT}\right)^2\right) \qquad (11)$$

To simplify the matrix analysis, avoiding the cumbersome expressions, we introduce new variables, and the matrix determinant will be rewritten as:

$$\frac{2}{\delta G}\begin{vmatrix} -\kappa_1 - \Xi & \Omega \\ \Xi & -\Omega - \Lambda \end{vmatrix} \qquad (12)$$

In which the new variables are defined as:

$$\kappa_1 = \frac{\Delta}{\delta} \quad (13)$$

$$\Xi = k_2(1-\theta)^2 \quad (14)$$

$$\Omega = 2k_2c(1-\theta)^2 \quad (15)$$

$$\Lambda = k_3\exp\left(\frac{F\gamma\theta}{RT}\right) - \gamma k_3\theta\exp\left(\frac{F\gamma\theta}{RT}\right) \qquad (16)$$

The principal analysis conditions for a bivariant system are:

Steady-state stability	Tr J < 0, Det J>0
Oscillatory instability (Hopf bifurcation)	Tr J=0, Det J>0
Monotonic instability (Saddle-Node bifurcation)	Tr J < 0, Det J=0

It is possible to see that, case the parameter Λ, describing the DEL influences of the electrochemical process is possible, which defines the fragility of these influences; The steady-state will be stable. Really. If the parameter $\Lambda = k_3\exp\left(\frac{F\gamma\theta}{RT}\right) - \gamma k_3\theta\exp\left(\frac{F\gamma\theta}{RT}\right) > 0$, Tr J=$a_{11}$+$a_{22}$ will be negative. Yet the Jacobian determinant will be positive, due to the positivity of the rest of the parameters composing it. Mathematically, the stability requirement will be rewritten as:

$$\begin{cases} -\kappa_1 - \Xi - \Omega - \Lambda < 0 \\ \kappa_1\Omega + \kappa_1\Lambda + \Xi\Lambda > 0 \end{cases} \qquad (17)$$

And this requirement is satisfied in a vast topological zone, or, better saying, the stable steady-state is easy to maintain. From the electroanalytical point of view it is correspondent to the linearity of the dependence between electrochemical parameter and concentration. And, taking into account the mentioned above, it is possible to conclude that $CoSn(OH)_6$ is an efficient modifier for theacrine electrochemical detection, because the electroanalytical signal is easy to interpret. The electroanalytical process will be diffusion-controlled.

As the unique element of the Jacobian main diagonal, capable to be positive is ∧, the oscillatory behavior, appearing in the case of:

$$\begin{cases} -\kappa_1 - \Xi - \Omega = \Lambda \\ \kappa_1\Omega + \kappa_1\Lambda + \Xi\Lambda > 0 \end{cases} \qquad (18)$$

In this process will be caused by the only factor of DEL rearrangement during the $CoSn(OH)_6$ electro-oxidation. This factor is characteristic to the similar systems [32-36]. The form, the frequency and the amplitude of the oscillations will be dependent of supporting electrolyte composition, but generally, the oscillations are harmonic or pseudoharmonic, frequent and of little amplitude.

Moreover, the monotonic instability, manifested by N-shaped voltammogram fragment, will also only possible, when caused by these influences. The condition of this instability, described as:

$$\begin{cases} -\kappa_1 - \Xi - \Omega - \Lambda < 0 \\ \kappa_1\Omega = -\kappa_1\Lambda - \Xi\Lambda \end{cases} \qquad (19)$$

Will be only satisfied, when the parameter Λ is negative (and the expression on the right side of the second condition of (19) will be positive). In the case of the use of lightly alkaline media, the electrochemical oxidation may be more rapid, and the electrode reversibility more efficient. This makes the lightly alkaline media a bit more efficient, than in the case of neutral media.

CONCLUSION

The theoretical investigation of the possibility of $CoSn(OH)_6$ assisted theacrine electrochemical detection let us conclude that: The steady-state stability in the electroanalytical system is easy to maintain. $CoSn(OH)_6$ is an efficient modifier for theacrine electrooxidation, as the analytical signal is easy to interpret; The electroanalytical process is diffusion-controlled; The oscillatory behavior, in this case, is possible, being caused only by DEL influences of $CoSn(OH)_6$ electrooxidation. The form, the frequency and the amplitude of the oscillations will be dependent of support electrolyte composition; The monotonic instability in this system is possible and will also be caused by the mentioned influences; The lightly alkaline media is more efficient in this system, as the reversibility of $CoSn(OH)_6$ electrode is more rapid.

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