



The mathematical description for electrochemical determination and retention of heavy metal ions by electropolymerization of Schiff base complex

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Abstract

The possibility of the heavy metal ions determination and retention (with the example of copper ion) by a new Schiff base complex electropolymerization has been studied from the theoretical point of view. It has been shown that, despite the absence of the surface instabilities, the probability of the oscillatory instability will be more expressed than in the case of the classical assisted polymer electrochemical deposition. Nevertheless, the steady-state stability is efficient, either from electroanalytical or from electrosynthetic point of view.

Keywords: heavy metal ions, water purification, complex compounds, Schiff base, electropolymerization, stable steady-state

Introduction

Nowadays, the studies of ion-selective electrodes have become significant, due to some advantages they possess. Some of these advantages are rapidity, sensitivity, and precision [1 – 5].

On the other hand, copper is one of the most important elements – either for biotic or for abiotic processes. Taking into account their importance, dose-related action and toxicity, while in excess, [6 – 10], the development of a method of their sensitive determination is very important.

Many electrochemical methods have been developed for the quantification of copper ions, which are based on copper electrodeposition or membrane response [11 – 13]. One of these methods may include

electrode modification with Schiff bases, capable to capture copper ions with the growth of the conductivity [14 – 16].

Nonetheless, the suggestion of a principally new electrode modifier and the electroanalytical process requires a priori mechanistic theoretical analysis of the electroanalytical system. It would help us to resolve some problems like:

- The indecision in the interaction of the electrode with the analyte and on its role in the electroanalytical system;
- The evaluation of the possibility of the additional reaction of the main and side products of the electroanalytical process;
- The possibility of the appearance of electrochemical instabilities in similar systems with electrooxidation of different organic molecules [17 – 20], including electrochemical polymerization, in some cases, of organic complex compounds [19 - 20].

The priori theoretical investigation provides us the possibility to resolve the mentioned problems during the elaboration of the sensor. Such an investigation includes the development and analysis of a mathematical model, capable to describe adequately the electroanalytical system. So, the principal objective of this work is the mechanistic investigation of an electroanalytical system with copper electrochemical retention, assisted by a newly synthesized triazole Schiff base. It is realized by achieving the specific goals like:

- Suggestion of the mechanism, presented as a sequence of chemical and electrochemical transformations, leading to the appearance of the analytical signal;
- Development of a mathematical model, based on this mechanism;
- Analyze the model, obtaining the steady-state stability conditions (correspondent to the electroanalytical efficiency of the process) and of the oscillatory and monotonic instability;
- Compare the behavior of this system with that of the analogous systems [21 – 23].

System and its modeling

Materials and reagents

5-(3-fluorophenyl)-4-amino-1,2,4-triazol-3-thiole has been provided as a courtesy by Zaporizhzhya State Medical University, and 2-hydroxy-1-naphthyl aldehyde has been used from the deposit of Chernivtsi National University. Butanol, ether and DMF have been acquired from SferaSim™ (Lviv, Ukraine) and used without further purification. The ¹H NMR experiment has been carried out in Enamin (Kiev, Ukraine), by Varian Mercury 400 spectrometer (400 MHz) in DMSO-d₆. The reaction has been realized as in the Fig. 2:

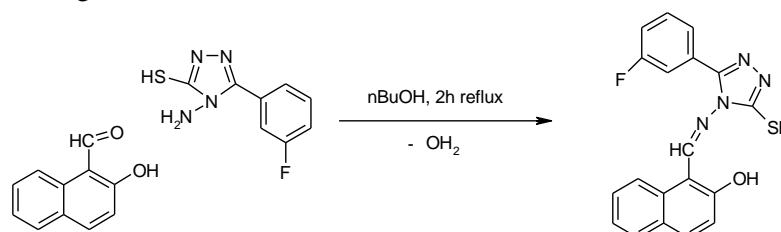


Fig.2. The synthesis of the Schiff base

Experimental

The mixture of 0,43 g (0,0025 mol) of 2-hydroxy-1-naphthyl aldehyde with 0,53 g (0,0025 mol) of 5-(3-fluorophenyl)-4-amino-1,2,4-triazolyl-3-thiole in 20 ml of butanol were refluxed during 2 hours. The reaction mixture has been kept on room temperature during 12 hours. The deposit has been filtered out and rinsed by ether, yielding 0.61 g (67 %) of the Schiff base (m. p =252 - 253⁰ C, crystallized by water from DMF). Found: C: 62.52 %, H: 3.51%; N: 15.32 %; C₁₉H₁₃FN₄OS. Calculated: C: 62.63 %, H: 3.59%; N: 15.38 %. ¹H NMR shifts of the molecule are represented on the Fig. 3:

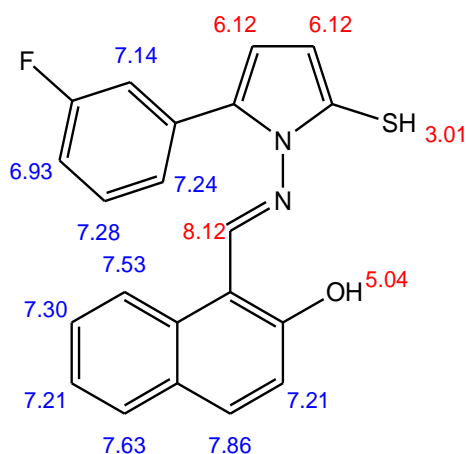


Fig.3. The ¹H NMR shifts of novel Schiff base

The metal complex with the Schiff base will be stable and, for the case of bivalent copper, will be described as:

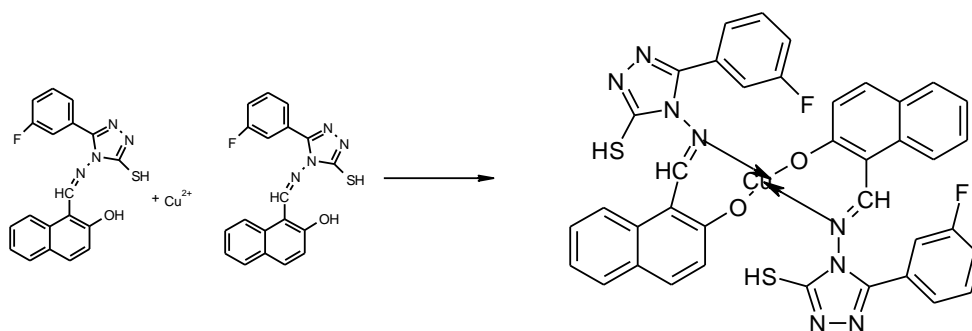


Fig.4. The complex formation with copper

Taking into account the above cited, in order to describe the behavior of this process, we introduce two variables:

m – Concentration of the metal ion in the pre-surface layer;

θ – Schiff base complex monomer coverage degree.

In order to simplify the modeling, we suppose that the reactor is intensively stirred, so we may neglect the convection flow. Also, we suppose that the background electrolyte is in excess, so we may neglect

the migration flow. It is assumed that the concentration profile of metal ions in the pre-surface layer is linear, and the layer thickness is constant, equal to δ .

It is possible to show that the system's behavior may be described by the classical bivariate equation set, described as:

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta} \left(\frac{D}{\delta} (c_0 - c) - r_c \right) \\ \frac{d\theta}{dt} = \frac{1}{G} (r_c - r_p) \end{cases} \quad (1)$$

In which D is the diffusion coefficient, c_0 , is its bulk concentration, G is the adduct maximal surface concentration, r_c , and r_p are the complex formation and polymerization rates capable to be calculated as:

$$r_c = k_c c (1 - \theta)^2 \exp(\gamma\theta) \quad (2)$$

$$r_p = k_p \theta^n \exp\left(\frac{2nF\gamma\theta}{RT}\right) \quad (3)$$

In which the parameters k are correspondent reaction rate constants, n is the number of monomer units in the complex polymer, F is the Faraday number, γ is the parameter, relating the DEL potential slope in the double, related to the zero-charge potential, with the quaternized polymer coverage degree R is the universal gas constant and T is the absolute temperature.

As both complex formation and electropolymerization influence the DEL, the oscillatory behavior in this system will be more probable than in classical assisted polymerization system. The behavioral differences of these systems will be described below.

Results and discussion

In order to describe the behavior of the system with heavy metal ions electrochemical detection and retention by new triazolic Schiff bases with the subsequent polymerization of the resulting complex compound, we analyze the equation set (1) by means of the linear stability theory. The steady-state Jacobian functional matrix elements for this system may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \quad (4)$$

$$a_{11} = \frac{2}{\delta} \left(-\frac{D}{\delta} - k_c (1 - \theta)^2 \exp(\gamma\theta) \right) \quad (5)$$

$$a_{11} = \frac{2}{\delta} (2k_c c (1 - \theta) \exp(\gamma\theta) - \gamma k_c (1 - \theta)^2 \exp(\gamma\theta)) \quad (6)$$

$$a_{21} = \frac{1}{G} (k_c (1 - \theta)^2 \exp(\gamma\theta)) \quad (7)$$

$$a_{22} = \frac{1}{G} \left(-2k_c c (1 - \theta) \exp(\gamma\theta) + \gamma k_c (1 - \theta)^2 \exp(\gamma\theta) - nk_p \theta^{n-1} \exp\left(\frac{2nF\gamma\theta}{RT}\right) - \gamma nk_p \theta^n \exp\left(\frac{2nF\gamma\theta}{RT}\right) \right) \quad (8)$$

In order to simplify the analysis of the matrix, we introduce new variables, so the matrix determinant will be described as:

$$\frac{2}{\delta G} \begin{vmatrix} -\kappa_1 - \mathcal{E} & \Omega \\ \mathcal{E} & -\Omega - \Lambda \end{vmatrix} \quad (9)$$

The main conditions for bivariate systems are described in the Table 1:

Table1. The main conditions for bivariate systems

Steady-state stability	Tr J<0, Det J>0
Oscillatory instability	Tr J=0, Det J>0
Monotonic instability	Tr J<0, Det J=0

Observing the expressions (6) and (9), it is possible to see that the *oscillatory behavior* probability in this system will be enhanced, while compared to the simplest case of the assisted conducting polymer electrodeposition and CP-based sensing [21 – 23], as there is more than one process influencing DEL. Besides of the DEL influences of the electrochemical synthesis, described by the positivity of $-\gamma nk_3 \theta^n \exp \frac{2nF\gamma\theta}{RT}$, the oscillatory behavior may be also caused by the complex formation, enhancing the conductivity of the initial Schiff base. These influences are described by the positivity of $k_1(1 - \theta)^2 \exp(\gamma\theta)$.

The *steady-state stability* condition for a two-dimensional system may be described as: Tr J<0, Det J>0. Opening the brackets with the inclusion of the variables introduced in (11 – 14), we obtain the steady-state stability condition as:

$$\begin{cases} -\kappa - \Xi - \Omega - \Lambda < 0 \\ \kappa\Omega + \kappa\Lambda + \Xi\Lambda > 0 \end{cases} \quad (10)$$

And it is warranted to be satisfied in the case of the positivity of Ω and Λ , describing the fragility of DEL influences of the electropolymerization and of the complex formation. The process is diffusion-controlled, as the complex is relatively stable, and the complex formation and polymerization are relatively rapid.

For the electroanalytical effects the steady-state stability is correspondent to the linear dependence between the electrochemical parameter and analyte concentration, or, better saying, to the electroanalytical efficiency and efficient cation retention. For the electrosynthetic effects, it is correspondent to the well-developed surface formation. It isn't compromised even by radical recombination effects if they do not provoke side reactions.

The *monotonic instability* in this system is possible, being caused by the equality between the stabilizing influences and the destabilizing ones of the electrochemical process influences on DEL. It is correspondent to the detection limit and to the N-shaped part of the polymerization voltammogram, and its condition may be described as:

$$\begin{cases} -\kappa - \Xi - \Omega - \Lambda < 0 \\ \kappa\Omega + \kappa\Lambda + \Xi\Lambda > 0 \end{cases} \quad (11)$$

In the case of the presence of the two different heavy metals, the Schiff base included in a conducting polymer two complex compound fragments are formed, being additionally polymerized. This case will be described by a trivariate equation set as following:

$$\begin{cases} \frac{dc_1}{dt} = \frac{2}{\delta} \left(\frac{A}{\delta} (c_{10} - c_1) - r_{c1} \right) \\ \frac{dc_2}{dt} = \frac{2}{\delta} \left(\frac{D}{\delta} (c_{20} - c_2) - r_{c2} \right) \\ \frac{d\theta}{dt} = \frac{1}{G} (r_{c1} + r_{c2} - r_p) \end{cases} \quad (12)$$

This interesting case will be aborded in one of our next works.

Conclusions

From the theoretical investigation of the possibility of the metal-ions electrochemical determination and retention, based on the complexation with a novel Schiff base, with the subsequent electropolymerization of the resulting complex compound, it is possible to conclude that:

- This conducting polymer may serve as an excellent modifier for sucralose quantification, immobilizing it selectively. The stable steady-state is maintained easily, and the system is electroanalytically efficient;
- Taking into account the complex stability, the process may be only diffusion controlled;
- The oscillatory behavior in this system is possible, being caused by DEL influences of the complex formation and polymerization;
- The monotonic instability in this system is also possible, being caused by the equality of the destabilizing influences in DEL to the stabilizing ones.

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