

The Theoretical Description of Sucralose Cathodic Electrochemical Determination Over a Poly(safranin) Modified Electrode in Acidic Media

Volodymyr V. Tkach^{1,2,*}, Nataliia M. Storoshchuk¹, Bogdan D. Storoshchuk¹, Sílvio C. de Oliveira², Yana G. Ivanushko³, Viktor V. Kryvetskyi³, Inna I. Kryvetska³, Igor V. Kryvetskyi³, Nataliia R. Yemelienenko³, Valentyn I. Narsiia³, Petro I. Yagodynets^{1,*}, Adriano O. da Silva⁴, Zoriana Z. Masna⁵, Inna M. Shevchenko⁶, Viktoriia A. Gnitsevych⁷, Anzhelika O. Medvedeva⁷, Olena O. Vasylieva⁷, Dilfuza M. Musayeva⁸, Xayriddin Kosimov⁸, Oysha Jabborova⁸, Bakhodirjon Samadov⁸, Gulandom Sagdullayeva⁸, Gulhayo Hamdanova⁸, Margaryta V. Karputina⁹, Dariia D. Khargelia⁹, Jarem R. Garcia¹⁰, Vira M. Odyntsova⁶, José Inácio Ferrão da Paiva Martins¹¹

¹ Chernivtsi National University, 58001, Kotsyubynsky Str. 2, Chernivtsi, Ukraine

² Institute of Chemistry. Federal University of Mato Grosso do Sul, 79074 – 460, Av. Sen. Felinto Müller, 1555, Vila Ipiranga, Campo Grande, MS, Brazil

³ Bukovinian State Medical University, 58001, TeatralnaSq, 9, Chernivtsi, Ukraine

⁴ Federal University of the West of Pará, Juruti Campus, 68170 – 000, Rua Veríssimo de Souza Andrade, s/n, Juruti, PA, Brazil

⁵ Danylo Halytsky Lviv National Medical University, 79010, Pekarska Str. 69, Lviv, Ukraine

⁶ Zaporizhzhia State Medical University, 69600, Mayakovsky Ave. 24, Zaporizhzhia, Ukraine

⁷ Kyiv National University of Trade and Economics, 02156, Kyoto Str. 21, Kyiv, Ukraine

⁸ Abu Ali Ibn Sino Bukhara State Medical Institute, 705018, Navoi Str., 1, Bukhara, Uzbekistan

⁹ National University of Food Technologies, Volodymyrska Str., 68, 01001, Kyiv, Ukraine

¹⁰ State University of Ponta Grossa, Uvaranas Campus, Av. Gal. Carlos Cavalcanti, 4748, 84030-900, Ponta Grossa, PR, Brazil

¹¹ Engineering Faculty of the University of Porto, 4200-465, Rua Dr. Roberto Frias, s/n, Porto, Portugal

• Correspondence: nightwatcher2401@gmail.com (V.V.T.), ved1988mid@rambler.ru (P. I.Y.);

Scopus Author ID 55758299100

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Abstract: For the first time, sucralose cathodic electrochemical determination, assisted by the safranin-modified electrode in acidic solutions, has been theoretically described. The correspondent mathematical model analysis has shown that the steady-state stability range is wider than in most systems of electrochemical determination over the pyridinic nitrogen-containing conducting polymer. Moreover, the oscillatory behavior is less probable than in similar systems in acidic media. Nevertheless, it is more probable than in neutral media. Nevertheless, poly(safranin) is an efficient electrode modifier for sucralose electrochemical determination.

Keywords: sucralose; conducting polymers; safranin; electrochemical sensors; stable steady-state.

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1. Introduction

The chemically modified electrodes (CME) constitute one of the most modern and flexible tools in electroanalytical chemistry [1–4]. Compared to the bare electrodes, they have

some advantages, including efficiency and low cost. Still, the most important of them is the affinity to the electrode, using the principle of the key and lock.

One of the interesting analytes for CME may be sucralose [5, 6], one of the most widespread sweeteners used worldwide, also known as the main constituent of splenda. Its E-code in the European Union is E955, and it is much sweeter than aspartame, saccharin, and sucrose [7–8]. Being a carbohydrate derivative, it tastes more naturally than other sugar substitutes

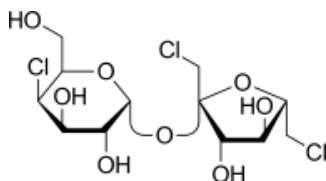


Figure 1. Sucralose structure.

It has been approved for use in most developed countries [8]. Its chemical composition is very similar to that of typical carbohydrates, but containing three chlorine atoms, it may be toxic, presenting effects of mutagenesis, carcinogenesis, obesity, and growth of glycolysis levels [7 – 12]. Moreover, it yields environmentally toxic chloroorganic compounds (mainly dioxins) if inappropriately stored [13 - 14] or decomposed during baking [15]. Therefore, developing an efficient method for sucralose detection is important for human and environmental safety [16 - 18], and electrochemical methods for it would be very interesting.

The possibility of the electrochemical sensing of sucralose by anodic oxidation of the remaining hydroxyl groups has already been foreseen by us theoretically [19 – 21], being thereby confirmed experimentally in [22]. In work [19], sucralose immobilization on an acridine derivative capable of forming a quaternary salt has been suggested. The sucralose immobilization was foreseen to be followed by the electrochemical oxidation of hydroxyl groups of the sucralose units. Another opportunity could be an electrochemical reduction of sucralose salt with the correspondent pyridinic nitrogen compound, in which safranin polymer or any other polymer with piridinic nitrogen atom or free amino group may be used as a modifier [23 – 26].

Nevertheless, the analogous processes tend to be accompanied by electrochemical instabilities, negatively impacting the sensor stability and analytical signal interpretation [27 - 28]. Taking this into account, it's necessary to theoretically evaluate this system's behavior, especially in acidic media, where the concurrence between the protons and the sucralose molecules exists, influencing the reaction mechanism by a proton attack.

So, this investigation, which also includes comparing the behavior of this system with that of similar ones, is the aim of the present study.

2. Materials and Methods

Generally, sucralose interacts with the safranin moiety follows the quaternization mechanism, yielding a quaternary salt, which will be thereby reduced, yielding a dibenzo-1,4-dihydropyrazine fragment, which becomes more basic (Fig. 2):

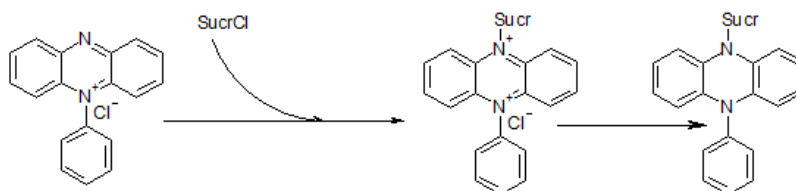


Figure 2. Sucralose interaction with safranin moiety.

In acidic media, it concurs with the proton attack (Fig. 3):

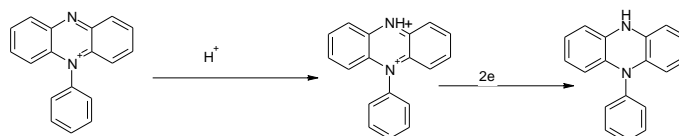


Figure 3. Proton attack of the safranin moiety.

Two possibilities of theoretical description for this system involve a bivariant and a trivariant system. In the last case, taking some assumptions, we describe the behavior of this system by a balance equation-set (1):

$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta} \left(\frac{\Sigma}{\delta} (s_0 - s) - r_s \right) \\ \frac{dh}{dt} = \frac{2}{\delta} \left(\frac{H}{\delta} (h_0 - h) - r_H \right) \\ \frac{dp}{dt} = \frac{1}{P} (r_S + r_H - r_r) \end{cases} \quad (1)$$

Herein, s , h , and p are sucralose and proton pre-surface layer concentrations and quaternized poly(safranin) coverage degree, δ is the diffusion layer thickness, Σ , and H are the sucralose and protons diffusion coefficients, s_0 and h_0 are their bulk concentrations, P is the quaternized poly(safranin) maximal surface concentration, and the parameters r are the correspondent reaction rates, calculated as:

$$r_r = k_r p^l \exp\left(-\frac{nF\varphi_0}{RT}\right) \quad (2)$$

$$r_s = k_s (1 - p) s^m \exp(-as) \quad (3)$$

$$r_h = k_h (1 - p) h^n \exp(-bh) \quad (4)$$

Herein, the parameters k are the correspondent reaction rates l , m and n are the numbers of safranin moieties capable of reacting, a and b is the parameter describing the DEL influence of the chemical stages, F is the Faraday number, φ_0 is the potential slope, related to the zero-charge potential, R is the universal gas constant and T is the solution temperature.

Compared to the neutral media, the steady-state stability zone will be narrower, and the realization of instabilities is more probable as the behavior becomes more dynamic. Nevertheless, in relation to other acidic media electroanalytical processes, this will be more stable, as shown below.

3. Results and Discussion

The steady-state Jacobian matrix members for the equation-set (1), considering the algebraic relations (2 – 4) for this system, will be described as (5):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{5}$$

Where:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Sigma}{\delta} - mk_s(1-p)s^{m-1} \exp(-as) + ak_s(1-p)s^m \exp(-as) \right) \tag{6}$$

$$a_{12} = 0 \tag{7}$$

$$a_{13} = \frac{2}{\delta} (k_s s^m \exp(-as)) \tag{8}$$

$$a_{21} = 0 \tag{9}$$

$$a_{22} = \frac{2}{\delta} \left(-\frac{H}{\delta} - nk_h(1-p)h^{n-1} \exp(-bh) + bk_h(1-p)h^n \exp(-bh) \right) \tag{10}$$

$$a_{23} = \frac{2}{\delta} (k_h h^n \exp(-bh)) \tag{11}$$

$$a_{31} = \frac{1}{p} (mk_s(1-p)s^{m-1} \exp(-as) - ak_s(1-p)s^m \exp(-as)) \tag{12}$$

$$a_{32} = \frac{1}{p} (nk_h(1-p)h^{n-1} \exp(-bh) - bk_h(1-p)h^n \exp(-bh)) \tag{13}$$

$$a_{33} = \frac{1}{p} \left(-k_s s^m \exp(-as) + k_h h^n \exp(-bh) - lk_r p^{l-1} \exp\left(-\frac{nF\phi_0}{RT}\right) + jk_r p^l \exp\left(-\frac{nF\phi_0}{RT}\right) \right) \tag{14}$$

Taking into account the main-diagonal elements (6), (10), and (14), we may observe that the main diagonal elements contain the addendums, capable of being positive, being thereby capable of describing the positive callback. They are $ak_s(1-p)s^n \exp(-as) > 0$, if $a > 0$, $bk_h(1-p)h^n \exp(-bh) > 0$, if $b > 0$ and $jk_r p^n \exp\left(-\frac{nF\phi_0}{RT}\right) > 0$, if $j > 0$, correspondent to the DEL influences of two chemical and electrochemical stages correspondently.

The positive callback is tightly related to the Hopf bifurcation, which is responsible for *the oscillatory behavior*. Its probability of the oscillatory behavior is more expressed than in the simplest cases due to the transformation of ionic forms in the polymer phases. Even though it is less manifested than in some similar systems [21], all of the mentioned elements are dependent on background electrolyte composition, and so are the amplitude and frequency of the oscillations.

Yet, if the mentioned elements are negative, the steady state will be stable, which may be shown by applying the Routh-Hurwitz criterion to the equation set (1). To simplify the analysis, we rewrite the Jacobian determinant as (15):

$$\frac{4}{\delta^2 s} \begin{vmatrix} -\kappa - \Xi & 0 & T \\ 0 & -\eta - \Sigma & \Phi \\ \Xi & \Sigma & -T - \Phi - \Omega \end{vmatrix} \tag{15}$$

avoiding cumbersome expressions.

Opening the brackets and applying the Det $J < 0$ statement, salient from the criterion and changing the signs to the opposite, we obtain the steady-state stability condition, described as (16):

$$\kappa(\eta T + \eta \Phi + \eta \Omega + \Sigma Y + \Sigma \Omega) \gg \varepsilon(2\eta T + \Sigma T + \eta \Phi + \eta \Omega + \Sigma Y + \Sigma \Omega) > 0 \quad (16)$$

Describing a stable diffusion-controlled system in which the steady-state stability topological region is a bit less wide than in the neutral media but slightly wider than in some electroanalytical and electro-converting systems [21].

As for electroanalytical efficiency, it will be strongly dependent on solution pH, as protons block the active sites for the sucralose binding to the polymer (Fig. 3). By this, in strongly acidic media, correspondent to low pH values, the electroanalytical process will be inefficient, although the electroanalytical process remains stable. By this, the electroanalytical efficiency of this system will be given in mildly acidic media, close to neutral. If this condition is satisfied, the dependence between the electrochemical parameter (current) and sucralose concentration will be linear, providing an efficient analytical signal interpretation.

The monotonic instability, correspondent to the detection limit, separates the steady stable states from unstable states. Its condition is mathematically exposed as (17):

$$\kappa(\eta T + \eta \Phi + \eta \Omega + \Sigma Y + \Sigma \Omega) \gg \varepsilon(2\eta T + \Sigma T + \eta \Phi + \eta \Omega + \Sigma Y + \Sigma \Omega) = 0 \quad (17)$$

In the case of the bivariant system, we may consider the excess of protons. By this, the variable h will be excluded from the equation set and included in the correspondent reaction rate constants.

4. Conclusions

From the theoretical description of sucralose electrochemical determination over poly(safranin), it has been possible to conclude that the polymer may serve as an excellent modifier for sucralose quantification, providing a diffusion-controlled electroanalytical efficient process. The stable, steady state is maintained easily. The process mechanism consists of the chemical and electrochemical stages, leading to the appearance of a determined, analytical signal. The electroanalytical efficiency of stable steady-state augments with the growth of pH up to neutral media due to the influences of pH on the availability of the polymer's active site. The oscillatory behavior in this system is possible, being caused by DEL influences of both chemical processes, like the electrochemical stage.

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Conflicts of Interest

The authors declare no conflict of interest.

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