

The Theoretical Description for CoO(OH)-Assisted Salicylic Acid Derivatives Determination in Beer

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Abstract: In this work, the possibility of the electrochemical determination of salicylic acid on conducting polymer – CoO(OH) composite has been evaluated. The electrooxidation mechanism includes the gradual phenolization of the aromatic ring carbon atoms 3 and(or) 5 with further electrooxidation to the correspondent quinone. The analysis of the correspondent mathematical model utilizing linear stability theory and bifurcation analysis confirms the conducting polymer composite efficiency in salicylic acid determination in a wide concentration range. On the other hand, the oscillatory behavior in this system is possible, but its realization and feature strongly depend on the analyte nature and background electrolyte composition.

Keywords: salicylic acid; conducting polymer; cobalt (III) oxyhydroxide; electrochemical sensor; stable steady-state.

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1. Introduction

Salicylic acid (Figure 1 to the right) [1 – 5] is one of the most widespread antioxidants. It is one of the salicylic alcohol oxidation products, the glycosides of which are found in the willow tree (from Latin *salix* – willow, see also Portuguese "salgueiro" - willow). Also, salicylic acid is found in various esters, one of which is acetylsalicylate, found in apple tree blossom, giving it a pleasant scent.

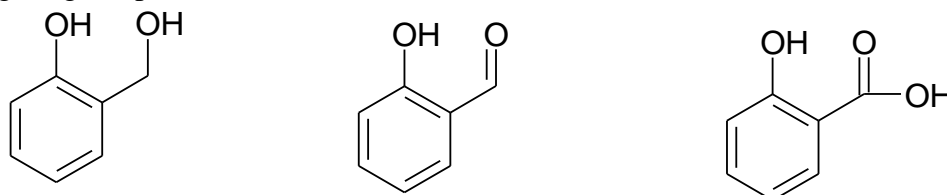


Figure 1. Salicylic alcohol, aldehyde, and acid.

Salicylic alcohol and its oxidation products are important organic and inorganic synthesis reagents. For example, the salicylic aldehyde reaction with ethyl acetoacetate with further heterocyclization is a suitable way to afford coumarin derivatives by the Knoevenagel reaction [6,7]. Yet the ester of acetic and salicylic acids has been known since 1895 as aspirin [8]. Salicylic acid occurs naturally in beer, cider, and other alcoholic drinks, and its concentration is higher in craft alcoholic drinks [9 – 10].

On the other hand, the biological action of salicylic acid derivatives strongly depends on the dose and concentration, the reason why the development of an efficient method for its quantification is really actual [11 – 14], and the electrochemical sensing is one of the most effective solutions for this task.

Salicylic acid and its derivatives are popular analytes for electrochemical sensors, due to their relatively widespread occurrence and use, low oxidation potential, and interesting oxidation mechanism, depending on the reaction conditions. Both anodic and cathodic processes may be applied to it. In the first case, due to its flexible electrochemical behavior, cobalt (III) oxyhydroxide may be a suitable electrode modifier for its quantification [14 – 18]. It may be used alone or in composite with conducting polymers, acting as mediators [19 – 25]. Besides stabilizing the metal oxyhydroxide nanoforms, the conducting polymers act as electron transfer mediators. Therefore, the function of the composite's inorganic and organic phases is well-defined.

Such hybrid materials have been used in anodic and cathodic electroanalytical processes [26 – 29].

Nevertheless, the possibility of electrochemical instabilities in the analogous electro-organic reactions has been confirmed experimentally or theoretically [29 – 33]. The theoretical and experimental data analysis confirms that the electrochemical instabilities in such systems are caused by the influence of the electrochemical and chemical reactions on the double electric layer (DEL) ionic force, capacitance, and conductivity of the electrode surface materials resistance.

Those instabilities tend to pose difficulties for analytical signal interpretation, leading to failure in electrochemical equipment. Conversely, we may detect the presence of a certain

substance (analyte or interferent) by an instability accompanying its reduction, oxidation, or catalytic effect in the system.

Therefore, a theoretical *a priori* investigation of the electroanalytical process behavior, capable of detecting the condition for the best sensor response, like the main instabilities conditions, is necessary. So, this work aims to investigate the salicylic acid electrochemical determination on CoO(OH) – conducting polymer composite-modified anode. Analyzing the correspondent mathematical model, we thereby compare the behavior of this system with that of similar systems [34 – 35].

2. System and its Modeling

Cobalt (III) oxyhydroxide is the most stable form of trivalent cobalt. It is seen as a substitute for titanium dioxide in material science, semiconductors, and sensors as an electroactive material. The oxidation state +3 for cobalt is the median. Therefore, depending on the conditions, cobalt (II) oxyhydroxide may be either oxidant, receiving electrons and losing a hydroxyl, or reductant, losing electrons and a proton. But suppose the CoO(OH)/CoO₂ redox-pair is generally used for the analytes with high oxidation potential, like some heterocyclic compounds with a pyridinic nitrogen atom. In that case, the CoO/CoO(OH) redox pair is more popularly used in electroanalytic, like also in electrosynthesis (including the initiating of the pyrrole electropolymerization [34]). Therefore, to determine salicylic acid derivatives, the use of CoO/CoO(OH) redox pair looks more reasonable.

In this work, the simplest case, in which the electropolymerization scenarios, yet described in [14], aren't counted, is evaluated. The salicylic acid electrooxidation by cobalt(III) oxyhydroxide on the first stage occurs by a mechanism similar to the aromatic electrophilic substitution. Considering the "concordant orientation" of phenolic and carboxylic groups, the second hydroxyl enters position 3 or 5, yielding an α or γ -hydroquinonic system. Furtherly it is oxidized to the correspondent quinone. Supposing, in order to simplify the model, that the ortho-product is the major product due to the ortho-effect, we will describe the electrooxidation mechanism in Figure 2:

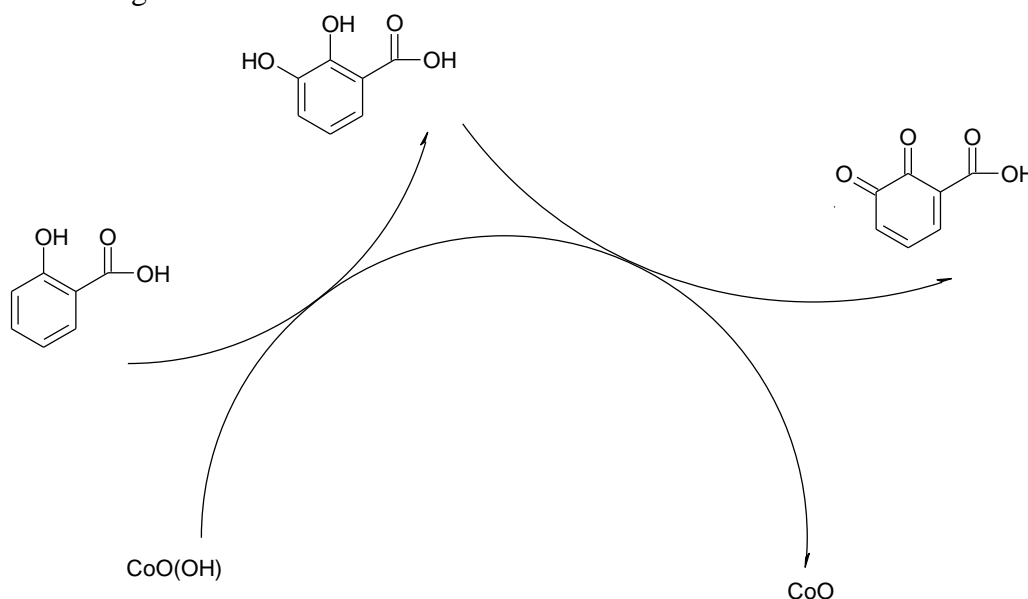


Figure 2. The mechanism for the electroanalytical process

Considering the gradual character of the electrochemical oxidation, like the similarity of the γ -hydroquinone behavior, we consider only one product in this model.

Therefore, taking some assumptions [34 – 35], we describe the behavior of this system by a trivariate balance equation-set (1):

$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (s_0 - s) - r_1 \right) \\ \frac{dp}{dt} = \frac{2}{\delta} (r_1 - r_2) \\ \frac{dc}{dt} = \frac{1}{C} (r_1 + r_2 - r_0) \end{cases} \quad (1)$$

Herein, *s* is the salicylic acid derivative concentration in the pre-surface layer, *p* is the hydroquinonic oxidation product pre-surface concentration, *c* is the cobalt (II) oxide surface coverage degree, δ is the diffusion layer thickness, Δ is the diffusion coefficient, s_0 is the salicylic acid concentration in the pre-surface layer, *C* is CoO maximal coverage degree, and the parameters *r* stand for the correspondent reaction rates:

$$r_1 = k_1 s (1 - c)^2 \exp(-as) \quad (2)$$

$$r_2 = k_2 p (1 - c)^2 \exp(-ap) \quad (3)$$

$$r_0 = k_o c \exp\left(\frac{F\varphi_0}{RT}\right) \quad (4)$$

Herein, the parameters *k* stand for the reaction rate constants, *a* is the parameter describing the influence of ionic transformations on the DEL electrophysical properties, *F* is the Faraday number, φ_0 is the zero-charge-related potential slope in DEL, *R* is the universal gas constant, and *T* is the absolute temperature.

The same process may be applied not only to the proper salicylic acid but also to its derivatives. The oscillatory behavior probability in those cases will be dependent on the nature of the salicylic acid derivative and background electrolyte composition, including pH. Either way, the electroanalytical process will be efficient, as shown below.

3. Results and Discussion

In order to investigate the electrochemical behavior for salicylic acid determination on polymer electrodes modified by cobalt (III) oxyhydroxide, we analyze by linear stability theory the equation-set (1) and express the Jacobian matrix steady-state members as:

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

Where:

$$a_{11} = \frac{2}{\delta} \left(-\frac{\Delta}{\delta} - k_1 (1 - c)^2 \exp(-as) + ak_1 s (1 - c)^2 \exp(-ac) \right) \quad (6)$$

$$a_{12} = 0 \quad (7)$$

$$a_{13} = \frac{2}{\delta} (2k_1 s (1 - c) \exp(-as)) \quad (8)$$

$$a_{21} = \frac{2}{\delta} (k_1 (1 - c)^2 \exp(-as) - ak_1 s (1 - c)^2 \exp(-ac)) \quad (9)$$

$$a_{22} = \frac{2}{\delta} (-k_2 (1 - c)^2 \exp(-ap) + ak_2 p (1 - c)^2 \exp(-ap)) \quad (10)$$

$$a_{23} = \frac{2}{\delta} (2k_2 p (1 - c) \exp(-ap)) \quad (11)$$

$$a_{31} = \frac{1}{C} (k_1 (1 - c)^2 \exp(-as) - ak_1 s (1 - c)^2 \exp(-ac)) \quad (12)$$

$$a_{32} = \frac{1}{C} (k_2 (1 - c)^2 \exp(-ap) - ak_2 p (1 - c)^2 \exp(-ap)) \quad (13)$$

$$a_{33} = \frac{1}{C} \left(-2k_1 s (1 - c) \exp(-as) - 2k_2 p (1 - c) \exp(-ap) - k_o \exp\left(\frac{F\varphi_0}{RT}\right) + jk_o c \exp\left(\frac{F\varphi_0}{RT}\right) \right) \quad (14)$$

Considering the main-diagonal elements (6), (10), and (14), we may conclude that, as this diagonal contains positive elements, a positive callback may be possible for this process. Therefore, the Hopf bifurcation and the oscillatory behavior become possible.

In this system, the oscillatory behavior will be defined by a (co)action of two factors [34 - 35].

The effect of the chemical stage on DEL ionic force and surface conductivity may lead to the oscillatory behavior, described by the positive behavior of $ak_1s(1 - c)^2 \exp(-ac)$ and $ak_2p(1 - c)^2 \exp(-ap)$. As the ionic forms are cyclically transformed during the electroanalytical process, the DEL and surface conductivity are also changed correspondently, leading to the oscillatory behavior;

It's important to mention that this factor acts only in the systems in which the carboxyl is in ionic form, capable of significantly impacting the DEL ionic force. In the case of the electroanalytical process realization in mildly acidic or neutral media, or even in the mildly basic media, in the case of less ionized derivative, in which the phenolate ionization may be neglected, the parameter a will be reset to zero, the exponential value, containing it, will be put equal to one, erasing the factor.

In strongly alkaline media, either carboxylate or phenolate is strongly ionized. Therefore, the oscillatory behavior probability enhances with increasing pH. As the beer has a lightly acidic pH, this process will be compatible with salicylic acid derivatives determination in this drink.

The main factor of the oscillatory behavior for all of the similar systems [27 – 28] is the influence of the electrochemical stage on DEL structure, ionic force, impedance, and conductivity, described by the positivity of $jk_o c \exp\left(\frac{F\varphi_0}{RT}\right)$. Considering the (co)action of two of the mentioned factors, the oscillatory behavior becomes highly probable. The frequency and amplitude depend strongly on the background electrolyte composition and analyte nature.

To investigate the steady-state stability by applying the Routh-Hurwitz criterion to the differential equation-set (1), we rewrite the Jacobian determinant as (15):

$$\frac{4}{\delta^2 C} \begin{vmatrix} -\kappa - E & 0 & A \\ E & -\Sigma & T \\ E & \Sigma & -\Lambda - T - \Omega \end{vmatrix} \quad (15),$$

And, adding the second and the third line, according to the determinant properties, as (16)

$$\frac{4}{\delta^2 C} \begin{vmatrix} -\kappa - E & 0 & A \\ E & -\Sigma & T \\ 2E & 0 & -\Lambda - \Omega \end{vmatrix} \quad (16),$$

avoiding thereby the cumbersome expressions.

Opening the straight brackets and resolving the inequation $\text{Det } J < 0$, salient from the criterion and changing the signs, we obtain the steady-state stability requirement as (17):

$$\Sigma(\kappa\Lambda - E\Lambda + \kappa\Omega + E\Omega) > 0 \quad (17)$$

This inequation described an efficient kinetically-controlled electroanalytical process.

Considering that no side reactions that compromise the analyte and(or) modifier stability are realized in this case, we conclude that the steady-state stability will correspond to the linear dependence between the salicylic derivative and current.

As for the detection limit, it is realized by the monotonic instability, delimiting the margin between the stable steady-states and unstable states. Its main condition may be expressed as $\text{Det } J=0$ or (18):

$$\Sigma(\kappa\Lambda - \varepsilon\Lambda + \kappa\Omega + \varepsilon\Omega) = 0 \quad (18)$$

The electropolymerization scenario for salicylic acid is realized at higher potentials. The low-molecular oxidation products will also participate in the electropolymerization scenario. Moreover, they will be electropolymerized at lower potentials than the salicylic acid, constituting a case of assisted monomer electrosynthesis.

This will occur if the CoO(OH)/CoO₂ redox pair is used. This system will be evaluated in one of our next works.

4. Conclusions

From the analysis of the salicylic acid and derivatives determination in beer on CP/CoO(OH) composite modified electrode, it was possible to conclude that this composite is an effective electrode modifier for salicylic acid determination. The electroanalytical process is kinetically controlled, being the analytical signal easy to interpret in a wide concentration range. As for the oscillatory behavior, its realization depends on the analyte nature and background solution composition.

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Conflicts of Interest

The authors declare no conflict of interest.

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