The theoretical description for VO(OH)-assisted electrochemical determination for the cathodic removal of environmentally unfriendly artificial sweetener sucralose and the chemical warfare agent chloropicrin

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Abstract: An interesting electrochemical process for sucralose and chloropicrin electrochemical removal has been proposed and theoretically described. The organic halogenide ion is efficiently removed in mildly acidic media by trivalent vanadium oxyhydroxide, being the nitrogroup of chloropicrin also thereby reduced. The analysis of the mathematical model confirms that, despite of high probability of the oscillatory behavior, the electrochemical removal of chloropicrin and sucralose is really efficient.

Keywords: sucralose; chloropicrin; electrochemical removal; vanadium (III) oxyhydroxide; electrochemical oscillations; stable steady-state

1. Introduction

Chloropicrin (Fig. 1 to the left side) [1 – 4] is a toxic gas, used as antimicrobial fungicide, herbicide, insecticide and nematicide in agriculture. It is generally obtained by oxidizing picric acid by hypochlorite in acidic media. Nevertheless, it was also used as a

chemical warfare agent by Germans during World War I and by Russian troops during the Russian-Ukrainian War (2022) [4], reason why it is necessary to remove rapidly and efficiently its remains.

On the other hand, sucralose (Fig. 1 to the right) [5 – 9] is an extremely stable artificial sweetener up to 1000 times as sweet as common sugar. Its effects on human and animal organisms hasn´t been completely studied yet. Moreover, being hardly metabolized, it is accumulated in the environment. Also, the organisms capable to metabolize it transform the sucralose transform it into toxic chloroorganic derivatives like dioxines and tetrachlorodibenzofurans, reason why the sucralose removal from the environment is also actual.
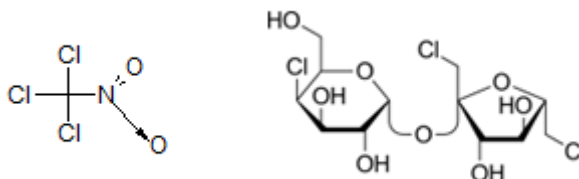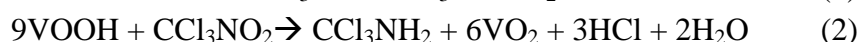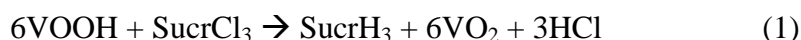

Figure 1. Chloropicrin and sucralose

Taking into account the presence of organic chlorine in both compounds, the AOP may not be compatible for their removal, due to the formation of toxic chlorine oxides. Cathodic dehalogenation is to be used instead. It leads to the chlorine substitution by hydrogen, leading to the chloride-ion formation [10 – 12]. Also, in order to impede the chloride ion passage towards the anodic electrolyte, a membrane, impeding its permeability, is posed to divide the cell into cathodic and anodic electrolyte. Vanadium (III) oxyhydroxide [13 – 14], acting as a strong reducent in neutral, basic and mildly acidic media may be potentially an interesting candidate for cathode modification for sucralose and chloropicrin removal.

In this work, the theoretical description for sucralose and chloropicrin cathodic removal is given. The mathematical model has been developed and analyzed for this system, and the stability requirements and oscillatory and monotonic instability conditions have been established. Also, the behavior of this system has been compared to that of the similar systems [15 – 21].

2. System and its modeling

Sucralose and chloropicrin are reduced cathodically in acidic media, yielding chloride ion and correspondent hydrocarbon fragments. As for chloropicrin, its nitrogroup is also reduced, yielding aminogroup:

$$6VOOH + SucrCl_3 \rightarrow SucrH_3 + 6VO_2 + 3HCl \tag{1}$$

$$9VOOH + CCl_3NO_2 \rightarrow CCl_3NH_2 + 6VO_2 + 3HCl + 2H_2O \tag{2}$$

As for vanadium (III) oxyhydroxide, it is regenerated on electrochemical stage:

$$VO_2 + H^+ + e^- \rightarrow VO(OH) \tag{3}$$

Taking this into account, in order to describe the behavior of this system, we introduce three variables:

c – chloropicrin concentration in the pre-surface layer;

s – sucralose concentration in the pre-surface layer;

v – vanadium dioxide surface coverage degree.

Accepting some assumptions [18 – 21], we describe the behavior of the system by equation-set (4):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_2\right) \\ \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(s_0 - s) - r_1\right) \\ \frac{dv}{dt} = \frac{1}{V}(r_1 + r_2 - r_3) \end{cases} \quad (4)$$

Herein Δ and D are diffusion coefficients, c_0 and s_0 are chloropicrin and sucralose bulk concentrations, V is vanadium dioxide maximal surface concentrations, and the parameters r are the correspondent reaction rates, calculated as (5 – 6):

$$r_1 = k_1 s \exp(-as)(1-v)^6 \quad r_2 = k_2 c \exp(-bc)(1-v)^9 \quad r_3 = k_3 v \exp\left(-\frac{F\varphi_0}{RT}\right) \quad (5-7)$$

In which the parameters k are the correspondent rate constants, parameters a and b define the impact of the chemical stages to DEL ionic force, F is the Faraday number, φ_0 stands for zero-charge related potential slope, R is the universal gas constant and T is the absolute temperature.

Taking into account the chloride-ion formation during the electrochemical process, changing the DEL ionic force, the oscillatory behavior occurs more probably in this system than in the similar ones. Nevertheless, the removal process is efficient for the conversion of both compounds, as shown below.

3. Results and Discussion

In order to investigate the stability of the system with chloropicrin and sucralose electrochemical conversive removal, we analyze the equation-set (4) by steady-state stability. The steady state Jacobian matrix members may be described as (8):

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

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_2 \exp(-bc)(1-v)^9 + bk_2 c \exp(-bc)(1-v)^9\right) \quad (9)$$

$$a_{12} = 0 \quad (10)$$

$$a_{13} = \frac{2}{\delta}\left(9k_2 c \exp(-bc)(1-v)^8\right) \quad (11)$$

$$a_{21} = 0 \quad (12)$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{D}{\delta}(s_0 - s) - k_1 \exp(-as)(1-v)^6 + ak_1 s \exp(-as)(1-v)^6\right) \quad (13)$$

$$a_{23} = \frac{2}{\delta}\left(6k_1 s \exp(-as)(1-v)^5\right) \tag{14}$$

$$a_{31} = \frac{1}{V}\left(k_2 \exp(-bc)(1-v)^9 - bk_2 c \exp(-bc)(1-v)^9\right) \tag{15}$$

$$a_{32} = \frac{1}{V}\left(k_1 \exp(-as)(1-v)^6 - k_1 s \exp(-as)(1-v)^6\right) \tag{16}$$

$$a_{33} = \frac{1}{V}\left(-6k_1 s \exp(-as)(1-v)^5 - 9k_2 c \exp(-bc)(1-v)^8 - k_3 \exp\left(-\frac{F\varphi_0}{RT}\right) + jk_3 v \exp\left(-\frac{F\varphi_0}{RT}\right)\right) \tag{17}$$

Taking into account the main-diagonal elements (9), (13) and (17) we conclude that the oscillatory behavior in this system is possible. Moreover, it becomes more probable than in the similar systems [18 − 21], due to the cyclic character of DEL ionic force changes during the chemical and electrochemical stages.

Besides of the element $jk_3 v \exp\left(-\frac{F\varphi_0}{RT}\right) > 0$ if j>0, describing the positive callback by DEL influences of the electrochemical stages, the positive elements responsible for this type of callback are $bk_2 c \exp(-bc)(1-v)^9 > 0$, if b>0 and $ak_1 s \exp(-as)(1-v)^6 > 0$, if a>0, both of them referent to the cyclic DEL ionic force, conductivity and impedance cyclic changes caused by chemical stages. The oscillations amplitude and frequency will be dependent on electrolyte composition. Either way, the oscillations are expected to be relatively frequent and of small amplitude.

Applying the Routh-Hurwitz stability criterion to the equation-set (1), we analyze the *steady-state stability* requirement. In order to avoid cumbersome expressions, we introduce new variables, rewriting thereby the determinant as (18):

$$\frac{4}{\delta^2 V}\begin{vmatrix} -\kappa_1 - \Xi & 0 & \Lambda \\ 0 & -\kappa_2 - \Sigma & P \\ \Xi & \Sigma & -\Lambda - P - \Omega \end{vmatrix} \tag{18}$$

Opening the brackets, applying the Det J<0 requisite, salient from the criterion and changing the signs to the opposite, we describe the stability requirement as (19):

$$\kappa_1(\kappa_2 \Lambda + \kappa_2 P + \kappa_2 \Omega + \Sigma \Lambda + \Sigma \Omega) + \Xi(\kappa_2 \Lambda + \kappa_2 P + \Sigma \Omega) > 0 \tag{19}$$

Describing an efficient diffusion-controlled process, in which the stable steady-state is easily formed. Really, the inequation (19) is warranted to be satisfied, if the kinetical parameters Ξ, Σ and Ω are positive, which occures in the majority of the cases. Being those parameters positive, the left side of the inequation (19) gains more positive values. Taking into account that sucralose and chloropicrin do not react with each other, and that the steady-state stability is easy to obtain and maintain, it is possible to conclude that this process may also serve for electroanalytical purpose, and the steady-state stability will be thereby correspondent to the linear dependence between concentration and current.

As for the *monotonic instability,* it delimits the margin for steady-state stability and, for electroanalytical effects, the detection limit. Its condition corresponds to the nulity of the determinant, or (20):

$$\kappa_1(\kappa_2 \Lambda + \kappa_2 P + \kappa_2 \Omega + \Sigma \Lambda + \Sigma \Omega) + \Xi(\kappa_2 \Lambda + \kappa_2 P + \Sigma \Omega) = 0 \tag{20}$$

If the chloroorganic compounds react with each other, or with a reagent, present in the solution, the model will be accomplished. The equation-set (4) will be thereby rewritten as (21):

$$\begin{cases} \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_2 - r_m\right) \\ \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(s_0 - s) - r_1 - r_m\right) \\ \frac{dv}{dt} = \frac{1}{V}(r_1 + r_2 - r_3) \end{cases} \quad (21)$$

And its analysis will be analyzed in one of our next works.

4. Conclusions

The analysis of the system with chloropicrin and sucralose cathodic removal let us conclude that this process is efficient diffusion-controlled system. It may also have electroanalytical function, providing the facile analytical signal interpretation, due to the easy steady-state stabilization. As for the oscillatory behavior, it is more probable than for the similar systems, due to the DEL influences of both chemical and electrochemical processes.

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Conflicts of Interest

The authors declare no conflict of interest.

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